



Surface engineering of light alloys

Aluminium, magnesium and
titanium alloys

Edited by Hanshan Dong

Surface engineering of light alloys

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Light alloys, which encompass magnesium-, aluminium- and titanium-based materials, are the materials of choice for transport applications (such as aerospace, automotive and light rail) because of their low-density and high strength-to-weight ratio. Weight reduction in transport translates directly to fuel saving and emissions deduction, thus greatly contributing to ecologically and economically sustainable development. In addition, light alloys are attractive for some specific applications due to their unique properties. For example, outstanding biocompatibility makes titanium alloys the material of choice for body implants.

On the other hand, the relatively poor surface properties of light alloys represent a serious barrier to their wider application. For example, magnesium alloys have a reputation for extremely poor corrosion resistance in most environments; therefore, corrosion protection is essential for magnesium alloys in many applications (see Chapter 1). Further, light alloys are characterised, especially in sliding situations, by poor tribological properties manifested as: low load-bearing capacity and low resistance to abrasion mainly due to low hardness; and high adhesion tendency due to relatively high ductility and reactivity (Chapters 2 and 3). Therefore, light alloys are normally restricted to applications in which tribological performance is not critical.

Currently, however, there is a growing requirement to expand the use of titanium alloys to non-aerospace tribological applications. For example, it has long been the dream of designers to substitute titanium for steel components in racing-car engines to reduce the mass of valve trains, increase top speed and increase fuel efficiency. However, titanium alloys are characterised by poor wear behaviour (Chapter 3) and therefore it is impossible to use titanium components in valve train systems without proper surface engineering. More challenging examples include: water droplet erosion in longer titanium blades for high-efficiency low-pressure turbines, and adhesive wear of telescopic-action titanium tubes for aerial refuelling systems.

Equally, while aluminium alloys and magnesium alloys have found increasing application, particularly in aerospace and automotive industries, these alloys are susceptible to surface degradation. For instance, aluminium

alloys are used in the space industry in launchers, space stations and satellites because of their lightness, adequate corrosion resistance and good cryogenic properties. However, UV degradation and cold welding (or adhesion) in vacuum are concerns for successful long-term application of aluminium alloys and their finishes in space (Chapter 18). Similarly, the poor corrosion resistance of magnesium alloys in some service environments has limited further expansion of applications (Chapter 6).

Therefore, the clear and major challenge to surface engineering researchers and engineers, from both the scientific and technological viewpoints, is how to improve the surface properties of light alloys. During the past two decades, many surface engineering technologies have been developed to combat surface related failures such as corrosion, wear and fatigue of steels. The central problem is that surface engineering of light alloys is more difficult than it is for steels.

Firstly, there is no martensitic transformation hardening in light alloys: either there is no martensitic transformation – in magnesium alloys and aluminium alloys – or martensite in titanium alloys is not hard. Consequently, light alloys cannot be effectively hardened by induction hardening and, in most cases, it is difficult to provide a hardened subsurface for thin hard coatings. For this reason, although thin hard coatings *could* provide light alloys with improved tribological properties in terms of low-friction and wear, provided the applied load is low, the plastic deformation of the substrate, resulting from high contact stresses, gives rise to collapse of the coatings – the so-called ‘thin ice effect’.

Secondly, there is always an oxide film, thin or thick, on the surface of light alloys. These oxide films confer good corrosion resistance to aluminium alloys (Al_2O_3 film) and titanium alloys (TiO_2 film). However, such oxide films may cause difficult problems for surface engineering. They can reduce the bonding strength of surface coatings (for example, varying success of Ni plating) or retard diffusion of interstitial alloying elements during thermochemical treatment.

Thirdly, light alloys are very active and have strong affinity with oxygen, and therefore high purity gases must be used to prevent surface oxidation during thermochemical treatment (e.g. plasma nitriding of aluminium alloys).

Extensive research has been conducted to develop advanced surface engineering technologies for light alloys. However, surface engineering of light alloys has not yet been covered in a single book. Therefore, the objective of this book is to present a comprehensive review of the current status of surface engineering of light alloys. It can be divided into three sections, starting with a discussion on the surface degradation of light alloys (Chapters 1 to 3), followed by a portfolio of advanced surface engineering technologies applicable to light alloys (Chapters 4 to 15) and finishing with some application case studies (Chapters 16 to 18). Among these advanced surface engineering

technologies, plasma electrolytic oxidation treatment (Chapters 5 and 6) and ceramic conversion treatment (Chapter 14) are designed for light alloys.

The editor would like to take this opportunity to thank all the contributors, who are world-leading experts in their own research areas, for their willingness to share their time and knowledge. The contributions of Woodhead Publishing Limited, Rob Sitton, Lucy Cornwell and Francis Dodds are gratefully acknowledged. Finally, I must express my special gratitude to my family for their love, encouragement and support.

H. Dong

Corrosion behavior of magnesium alloys and protection techniques

G.-L. SONG, General Motors Corporation, USA

Abstract: Magnesium alloys have low corrosion resistance and exhibit unusual corrosion behavior in aqueous environments. This chapter briefly summarizes the corrosion characteristics of Mg alloys, such as hydrogen evolution, surface alkalization, macro-galvanic damage and micro-galvanic effect, etc. It also discusses the influences of chemical composition of matrix, secondary phase, and impurities, etc. on the corrosion performance of Mg alloys. Following that, a potential strategy is presented to mitigate their corrosion.

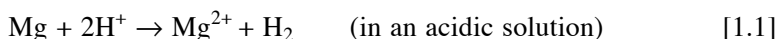
Key words: magnesium, corrosion, protection.

1.1 Introduction

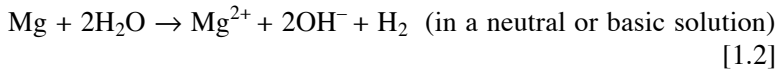
Magnesium and its alloys have a high strength/density ratio and have found many successful applications, particularly in the automotive and aerospace industries (Song, 2005b, 2006; Makar and Kruger, 1993; Aghion and Bronfin, 2000; Polmear, 1996; Bettles *et al.*, 2003a and b). However, the poor corrosion resistance of existing magnesium alloys in some service environments has limited the further expansion of their application. Existing investigations have clearly suggested that the corrosion of Mg alloys is unusual in terms of their corrosion behavior (Song, 2004a, 2005b, 2006, 2009a 2009c; Song and Atrens, 2007; Winzer *et al.*, 2005, 2007, 2008; Wan *et al.*, 2006; Wang *et al.*, 2007). For more successful application of Mg alloys, it is important to understand their characteristic corrosion phenomena. This chapter systematically summarizes the corrosion characteristics of Mg alloys in order to better understand their corrosion performance. Based on this, a potential strategy is proposed to mitigate their corrosion.

1.2 Corrosion behavior of magnesium (Mg) alloys

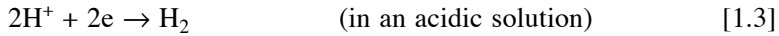
Mg alloys follow a corrosion mechanism different from other engineering metallic materials such as steel, aluminum alloys, and zinc. On pure Mg or a Mg alloy, it is well known that the overall corrosion reaction can be written as (Makar and Kruger, 1993; Song and Atrens, 1999; Song, 2005b, 2006):



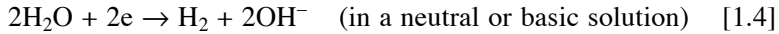
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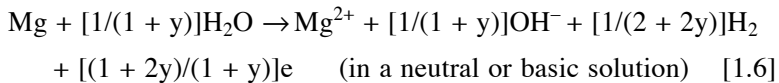
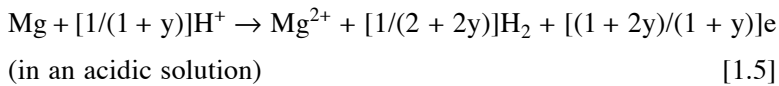
This overall corrosion can be decomposed into anodic and cathodic reactions. The cathodic process is (Song, 2005b, 2006):



or



and the anodic process (Song, 2005b, 2006):



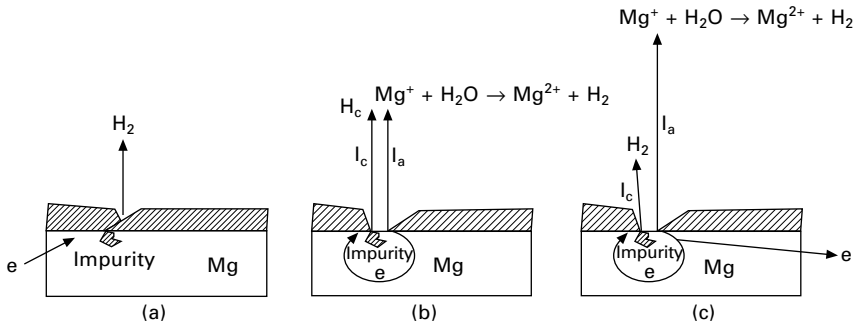
where y is the ratio of Mg^+ turning into Mg^{2+} over reacting with H_2O to produce H_2 .

The detailed anodic and cathodic reactions under a steady corrosion condition have been illustrated previously (Song *et al.*, 1997a, 1997b; Song, 2005b; Song and Atrens, 1999, 2003). In general, the anodic dissolution occurs mainly in a film-free area, while in a film covered area the anodic dissolution is negligible. The cathodic reaction, which is mainly a hydrogen evolution process, can take place in both film-free and film-covered areas, but the reaction rate in a film-free area is much faster than the rate in a film-covered area, particularly if impurity particles are present there.

If Mg is cathodically polarized to a very negative potential, Mg is fully covered by a thin film and there is no film-free area. Thus, the anodic dissolution of magnesium is very low, almost zero. However, the cathodic hydrogen evolution can still occur on the thin film surface at such a negative potential. The hydrogen evolution rate will decrease as the polarization potential becomes more positive until a critical potential E_{pt} is reached. At E_{pt} , the surface film starts to break down and both the hydrogen evolution and the Mg anodic dissolution become easier. The dissolution of Mg produces intermediate Mg^+ which subsequently leads to generation of hydrogen. In other words, there are two mechanisms of hydrogen evolution; one is a normal cathodic hydrogen evolution process driven by negative polarization potentials, and the other is a magnesium dissolution induced reaction. The process is schematically illustrated in Fig. 1.1.

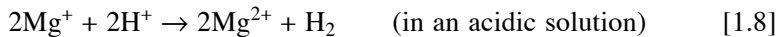
The reactions involved in the process are as follows:



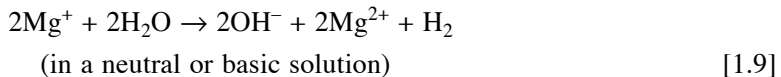


1.1 Electrochemical corrosion and negative difference effect on the magnesium surface (Song, 2005a): (a) at a very negative cathodic potential; (b) at the critical potential E_{pt} ; (c) at a potential more positive than E_{pt} .

then:



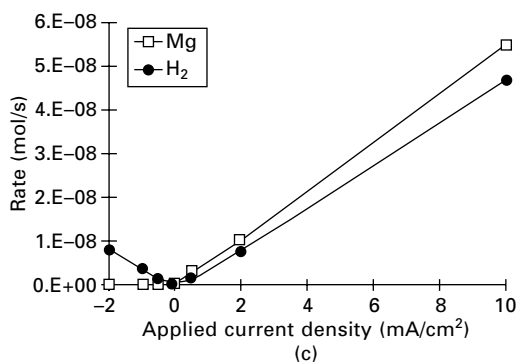
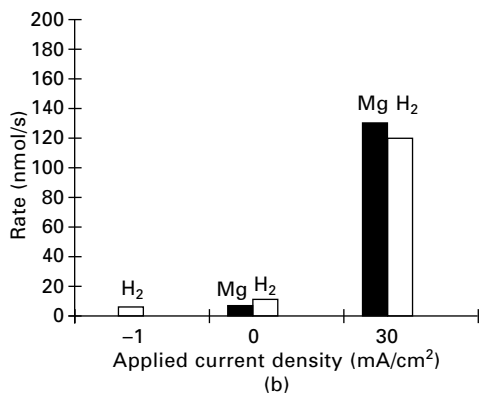
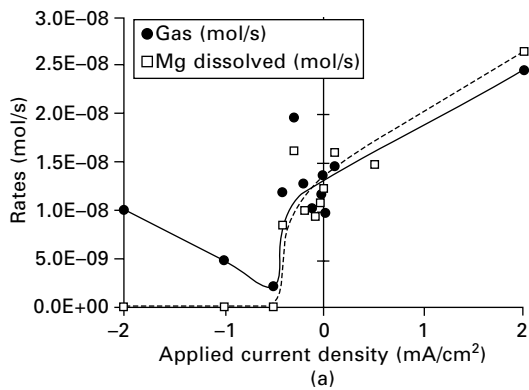
or



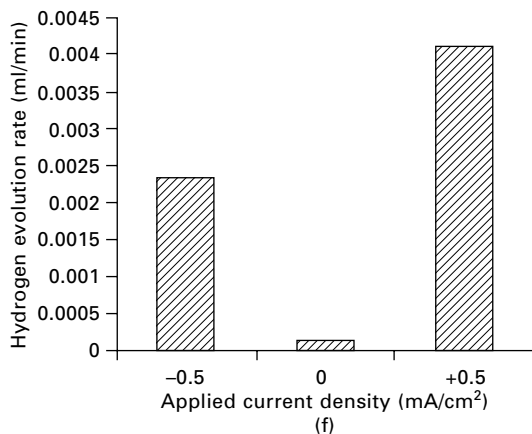
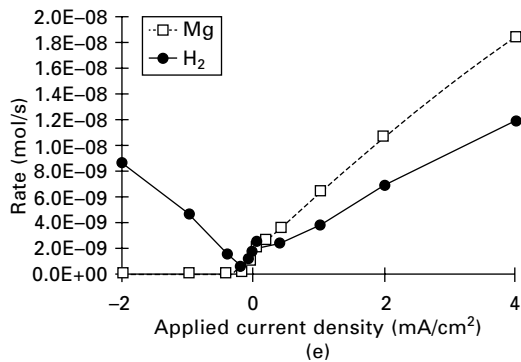
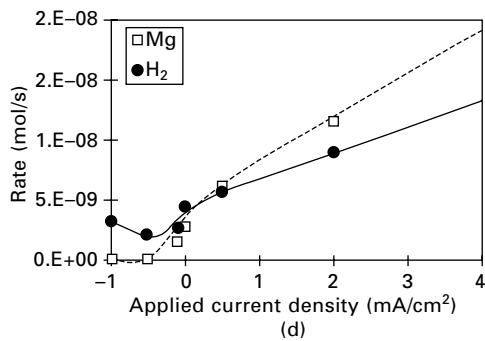
The anodic dissolution rate of Mg (Eq. 1.7) increases as the polarization potential or current becomes more positive. This produces additional hydrogen at a more positive potential via the reactions in Equations 1.8 or 1.9. The hydrogen evolution occurring in a corroding (film-free) area is termed ‘anodic hydrogen evolution’ (AHE), because it is closely associated with the anodic dissolution process. One important aspect is that it becomes faster as the anodic polarization potential becomes more positive, as if it were an anodic process (see Fig. 1.2). This differs from the normal cathodic hydrogen evolution (CHE) in that hydrogen evolution can occur on either the film-free or the film-covered areas, and decreases with positively shifting polarization potential in the cathodic region (see Fig. 1.2).

1.2.1 Hydrogen evolution

The overall corrosion Equations 1.1. or 1.2 suggest that the dissolution of Mg is always accompanied by hydrogen evolution. This corrosion-related hydrogen evolution is also applicable to Mg alloys in aqueous solutions (Song *et al.*, 1998, 2001, 2005a; Song and Atrons, 1998, 2003; Song and St John, 2002), including engine coolants (Song and St John, 2004, 2005) and simulated body fluids (SBF) (Song and Song, 2006, 2007; Song, 2007b). In a severe corrosion process, Mg particle undermining (Mg particles falling into solution due to the surrounding material being completely corroded) may take place.



1.2 Hydrogen evolution and Mg dissolution rates: (a) Mg in 1N NaCl (pH 11) (Song *et al.*, 1997b); (b) Mg in 1N Na₂SO₄ (pH 11) (Song *et al.*, 1997a); (c) AZ21 (matrix phase) in 1N NaCl (pH 11) (Song, 2005b); (d) AZ91 ingot in 1N NaCl (pH 11) (Song, 2005b); (e) diecast AZ91 in 1N NaCl (pH 11) (Song, 2005b); (f) sand cast MEZ in 5wt% NaCl (Song, 2005b).



1.2 Continued

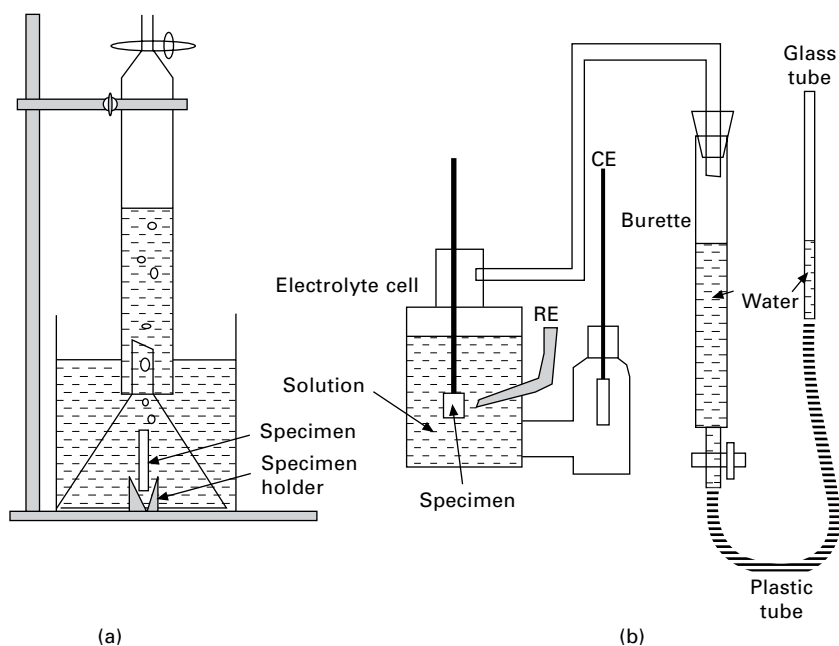
However, this process has been shown to have no influence upon either of the reactions in Equations 1.1 or 1.2 (Song *et al.*, 1997b). Therefore, for Mg and Mg alloys in an aqueous solution, the hydrogen evolution phenomenon, which includes cathodic hydrogen evolution (CHE) and ‘anodic hydrogen evolution’ (ACE), is one of the most important features.

Having realized that the hydrogen evolution is closely associated with the

corrosion of Mg and its alloys, a simple hydrogen evolution measurement technique was first employed by Song *et al.* (1997b) to estimate the corrosion rate of Mg. After further illustration of the theory and analysis of possible errors inherent to this method (Song, 2005b, 2006; Song *et al.*, 2001), it has also been widely used on many Mg alloys (Song, 2005a; Song and St John, 2002; Hallopeau *et al.*, 1999; Bonora *et al.*, 2000; Eliezer *et al.*, 2000; Mathieu *et al.*, 2000).

According to Equations 1.1 and 1.2, dissolution of one Mg atom always corresponds to the generation of one hydrogen gas molecule. In other words, if there is one mole of hydrogen evolved, then there must be one mole of magnesium dissolved (Song *et al.*, 2001; Song, 2005b, 2006). Measuring the volume of hydrogen evolved is equivalent to measuring the weight-loss of a corroding Mg alloy, and the measured hydrogen evolution rate is equal to the weight-loss rate if they are both converted into the same unit (e.g. mole per minute).

The experimental set-up for measuring hydrogen evolution is straightforward (Song *et al.*, 2001) and can simply consist of a burette, a funnel and a beaker (see Fig. 1.3a). This set-up can also be combined into an electrolytic cell



1.3 Schematic illustration of the set-up used to measure the volume of hydrogen evolved. (a) Simple set-up for short-term corrosion measurements (Song *et al.*, 1997b); (b) Combination of hydrogen evolution and electrochemical measurements (Song and St John, 2002).

for electrochemical measurements (see Fig. 1.3b) (Song and St John, 2002). The overall theoretical error of this technique is less than 10% (Song *et al.*, 2001). In practice, the corrosion rates of various Mg alloy specimens measured by the hydrogen evolution method have been found to be in very good agreement with those measured by weight loss (Song *et al.*, 2001). Furthermore, the hydrogen evolution measurement has several advantages over the traditional weight-loss measurement (Song 2005b, 2006):

- (i) smaller theoretical and experimental errors;
- (ii) easy to set up and operate;
- (iii) suitable for corrosion monitoring of magnesium and its alloys; and
- (iv) no need to remove corrosion products.

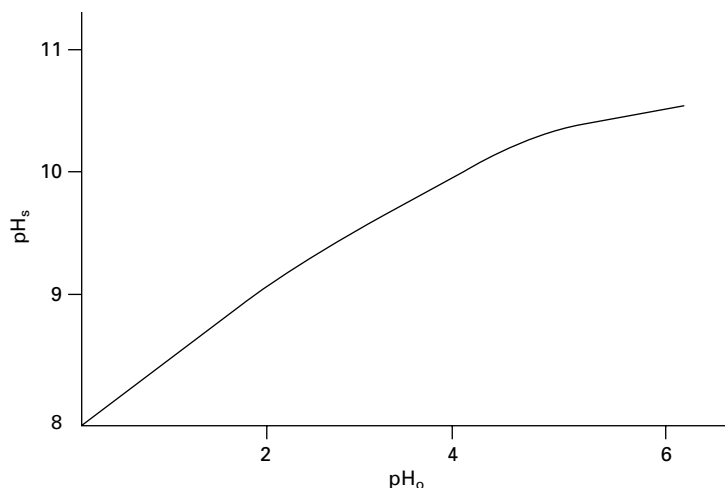
1.2.2 Alkalization

A relationship between the dissolution of Mg and the generation of OH^- or consumption of H^+ during the corrosion of Mg alloys is also given by either Equation 1.1 or 1.2. Similar to hydrogen evolution, the production of OH^- or consumption of H^+ always accompanies the corrosion of Mg and its alloys, which can result in an increased pH value for the solution. However, the pH increase levels-out at ~ 10.5 , even though the corrosion will continue at this pH value. This is a result of the deposition of $\text{Mg}(\text{OH})_2$ at this pH (Song, 2005b, 2006). The additional hydroxyls generated at this pH level are consumed by dissolved Mg^{2+} through deposition of $\text{Mg}(\text{OH})_2$, which stabilizes the pH value of the solution at approximately 10.5.

The surface of a corroding Mg alloy always experiences an alkalization process because either hydroxyls are generated or protons are consumed directly in the corroding area. It has been estimated that the local pH value of the solution adjacent to a Mg surface can be around 10.5 even if the bulk solution is acidic (Song, 2005b, 2006; Nazarov and Mikhailovskii, 1990) (see Fig. 1.4).

The alkalization effect can change according to the ratio of the surface area of the Mg alloy over the volume of the solution it is exposed to. A more significant alkalization effect is likely with a larger Mg alloy specimen in a smaller volume of solution. For example, under an atmospheric corrosion condition, only a thin aqueous film stays on the surface of a Mg alloy. This is a case of a large specimen with a small volume of solution, which can easily result in a strong alkalization effect. Hence, the corrosion of a Mg alloy in an atmospheric environment is normally less severe than under an immersion condition (Song *et al.*, 2004b, 2006b; Wan *et al.*, 2006).

The alkalization effect has also been utilized to monitor the corrosion rate of a Mg alloy. For example, Bo-Young Hur *et al.* (1996) and Weiss *et al.* (1997) tried to measure the change in pH value or concentration of H^+ of the solution in order to monitor the corrosion process of a Mg alloy. The



1.4 Estimated alkalinity (pH_s) of solution adjacent to Mg surface vs bulk solution pH_o (Song, 2006).

pH method may be convenient in monitoring the corrosion of Mg alloys in a neutral solution in the initial stage. However, it is not as reliable as the hydrogen evolution technique. Firstly, the alkalization is dependent on the volume of the testing solution, which can vary in different experiments and it is difficult to compare corrosion rates measured at different ratios of surface/volume. Secondly, in the later stages of corrosion, as considerable Mg has been dissolved and the solution has become $Mg(OH)_2$ saturated, the pH value of the testing solution will be stable at 10.5 and will not increase further, even though the corrosion rate may still be high. Thirdly, the dissolution of carbon dioxide from air could influence the pH value of the testing solution and result in a faulty corrosion indication. Lastly, in a strong acidic or basic solution the variation of the pH value is not sufficiently sensitive to reflect the change of proton or hydroxyl concentration.

1.2.3 Macro-galvanic corrosion

Mg has the highest chemical activity of the engineering metals. Because the standard equilibrium potential of Mg/Mg^{2+} is as negative at $-2.4V_{-NHE}$ (Song, 2005b; Perrault, 1978), Mg and its alloys normally have a very negative open-circuit (or corrosion) potential (around $-1.5V_{-NHE}$) in a neutral aqueous environment). This means that Mg alloys are always the anode if they are in contact with other engineering metals.

Macro-galvanic corrosion is an anodic dissolution process of an anode accelerated by the cathodic reactions on a cathode that is in electrical contact

with the anode. In theory, the galvanic corrosion rate (i_g) is determined by (Song *et al.*, 2004b):

$$i_g = (E_c - E_a) / (R_a + R_c + R_s + R_m) \quad [1.10]$$

where E_c and E_a are the open-circuit (corrosion) potentials of cathode and anode respectively in a given electrolyte; R_c and R_a are the cathode and anode polarization resistances; and R_s and R_m are the solution and electronic resistances between the anode and cathode, respectively.

The corrosion potential difference ($E_c - E_a$) between the anode and cathode is the first critical variable determining the galvanic corrosion rate i_g . As presented in Table 1.1, the corrosion potential of Mg in a NaCl solution is the least noble among the engineering metals and in fact, is over 600 mV more negative than zinc, which is second in the galvanic series. Based on corrosion potentials, engineering metals exposed to seawater can be ranked in a galvanic series from active (negative) to passive (noble) (Hack, 1995):

Magnesium → magnesium alloys → zinc → galvanized steel → aluminum 1100 → aluminum 6053 → Al clad → cadmium → aluminum 2024 → mild steel → wrought iron → cast iron → 13% Cr stainless steel, type 410 (active) → 18-8 stainless steel, type 304 (active) → 18-12-3 stainless steel, type 316 (active) → lead–tin solders → lead → tin → muntz metal → manganese bronze → naval brass → nickel (active) → 76Ni-6Cr-7Fe alloy (active) → 60Ni-30Mo-6Fe-1Mn → yellow brass → admiralty brass → aluminum brass → red brass → copper → silicon bronze → 70:30

Table 1.1 Corrosion potentials for common metals and alloys in wt. 3–6% NaCl solutions (Song, 2007a)

Metal	Corrosion potential (V_{-NHE})
Mg	–1.73
Mg alloys	–1.67
Mild steel, Zn-plated	–1.14
Zn	–1.05
Mild steel, Cd-plated	–0.86
Al (99.99%)	–0.85
Al alloy (12%Si)	–0.83
Mild steel	–0.78
Cast iron	–0.73
Pb	–0.55
Sn	–0.50
Stainless steel 316, active	–0.43
Brass (60/40)	–0.33
Cu	–0.22
Ni	–0.14
Stainless steel, passive	–0.13
Ag	–0.05
Au	0.18

cupro nickel $\rightarrow$ G-Bronze $\rightarrow$ Silver solder $\rightarrow$ Nickel (passive) $\rightarrow$ 76Ni-16Cr-7Fe alloy (passive) $\rightarrow$ 13% Cr stainless steel, type 410 (passive) $\rightarrow$ titanium $\rightarrow$ 18-8 stainless steel, type 304 (passive) $\rightarrow$ 18-12-3 stainless steel, type 316 (passive) $\rightarrow$ silver $\rightarrow$ graphite $\rightarrow$ gold $\rightarrow$ platinum

Mg and its alloys are at the most active end in this series, and thus they always act as the anode if in contact with other engineering metals. Because of the large difference between their corrosion potentials ($E_c - E_a$), the galvanic corrosion tendency is always significant between a Mg alloy and another engineering metal.

Equation 1.10 also suggests that the galvanic corrosion is determined by the anodic and cathodic polarization resistances (R_a and R_c). Mg and its alloys normally have a low anodic polarization resistance (Song, 2004b, 2009b Song, *et al.*, 1997a, 1997b, 2004a) while the cathodic polarization resistance of other metals in a neutral solution resulting from diffusion controlled oxygen reduction is relatively large. For a specific Mg alloy in a given solution whose corrosion potential and anodic resistances are fixed, the corrosion potential and the cathodic polarization resistance of a cathode metal will have a decisive influence on the galvanic corrosion of the Mg alloy (Song *et al.*, 2004b). A metal with a noble potential and relatively low cathodic polarization resistance will severely accelerate the corrosion of the

Table 1.2 Standard equilibrium potentials of typical metals in aqueous solution (Bard and Faulkner, 1980)

Reactions	Standard equilibrium potential (V_{-NHE})
$Au^+ + e = Au$	1.68
$Pt^{2+} + 2e = Pt$	~ 1.2
$Pd^{2+} + 2e = Pd$	0.83
$Ag^+ + e = Ag$	0.7996
$PtCl_4^{2-} + 2e = Pt + 4Cl^-$	0.73
$Cu^+ + e = Cu$	0.522
$Ag_2O + H_2O + 2e = 2 Ag + 2OH^-$	0.342
$Cu^{2+} + 2e = Cu$	0.3402
$Pb^{2+} + 2e = Pb$	-0.1263
$Sn^{2+} + 2e = Sn$	-0.1364
$Ni^{2+} + 2e = Ni$	-0.23
$Co^{2+} + 2e = Co$	-0.28
$PbSO_4 + 2e = Pb + SO_4^{2-}$	-0.356
$Cd^{2+} + 2e = Cd$	-0.4026
$Fe^{2+} + 2e = Fe$	-0.409
$Cr^{2+} + 2e = Cr$	-0.557
$Ni(OH)_2 + 2e = Ni + 2OH^-$	-0.66
$Zn^{2+} + 2e = Zn$	-0.7628
$Mn^{2+} + 2e = Mn$	-1.029
$ZnO_2^{2-} + 2H_2O + 2e = Zn + 4OH^-$	-1.216
$Al^{3+} + 3e = Al$ (0.1M NaOH)	-1.706
$Mg + 2e = Mg^{2+}$	-2.4

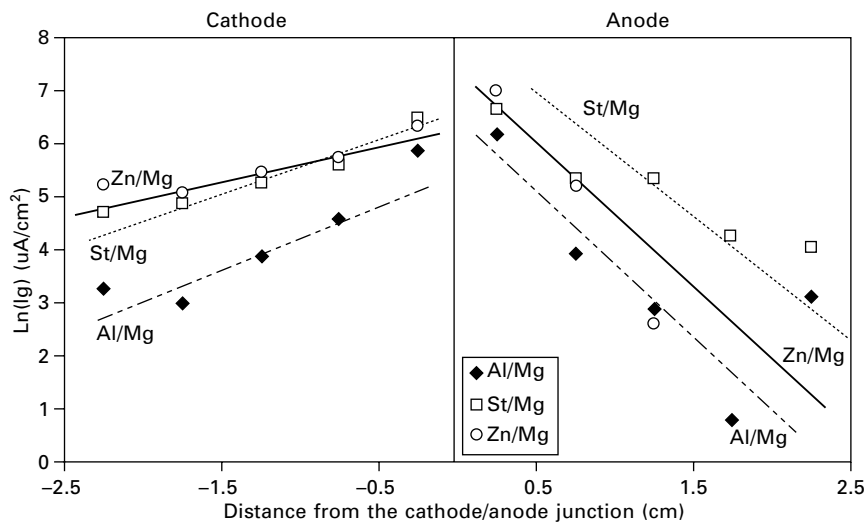
Mg alloy. It is well known that Fe, Co, Ni, Cu, W, Ag and Au metals are much nobler than Mg alloys in an aqueous solution (Tables 1.1 and 1.2) and have relatively low hydrogen evolution over-potentials (lower than 500mV, i.e. low cathodic polarization resistance). Thus, these metals in contact with a Mg alloy can form galvanic corrosion couples and result in serious galvanic corrosion damage to the Mg alloy. This type of galvanic couple should be avoided. Unfortunately, aluminum, steel and galvanized steel are widely used engineering materials and are quite often used together with Mg alloys. In this case, steel is the most detrimental and Al the least harmful to Mg alloys (Avedesian and Baker, 1999; Song *et al.*, 2004b).

In Equation 1.10, R_m can also significantly affect the galvanic corrosion current. If it is large enough (for example, in the case where the anode and cathode are separated by an insulator), then the galvanic corrosion will stop. Unfortunately, the anode and cathode are normally electrically connected and thus $R_m = 0$ in practice. Therefore, R_m is not seriously considered in many galvanic corrosion studies.

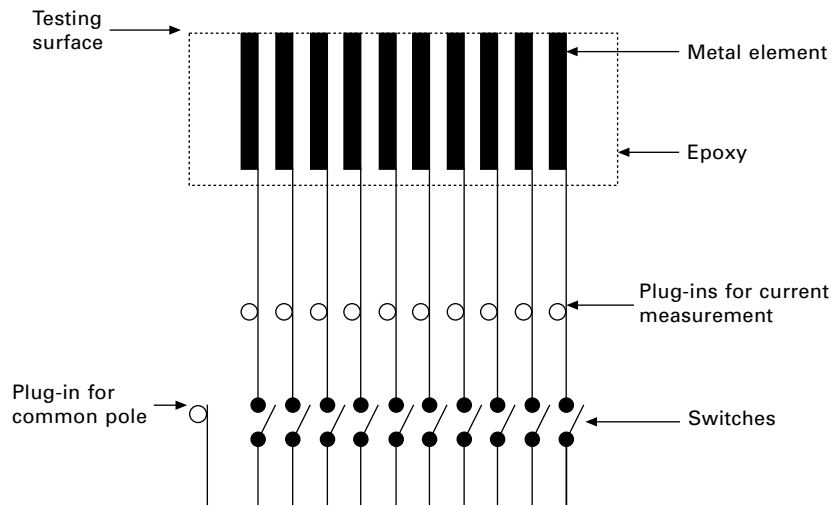
The parameters involved in Equation 1.10 can determine the overall galvanic corrosion current, i_g , which represents the overall galvanic corrosion of an anode (Song, 2009d). As long as all the parameters of Equation 1.10 are measured, the overall galvanic corrosion damage can be estimated. Many applied studies have tried to estimate the compatibility of various materials (including fasteners) with Mg alloy parts, using this equation (Starostin *et al.*, 2000; Gao *et al.*, 2000; Hawke, 1987; Senf *et al.*, 2000; Skar, 1999; Boese *et al.*, 2001).

However, in many practical applications, the distribution of galvanic current density, I_g , over a Mg alloy component surface is of greater concern as it cannot simply be predicted by Equation 1.10. The distribution of galvanic current density is closely associated with the parameter R_s , which is dependent on the geometric configuration of the solution path for the galvanic current between the anode and cathode. For a simple, one-dimensional galvanic couple consisting of a Mg alloy and another metal, an analytical prediction of the galvanic current density distribution is possible (Waber and Rosenbluth, 1955; Kennard and Waber, 1970; Gal-Or *et al.*, 1973; McCafferty, 1976, 1977; Melville, 1979, 1980). It has been reported that the galvanic current density has an exponential distribution (Song *et al.*, 2004b; Song, 2009d). This can be confirmed experimentally (refer to Fig. 1.5) by direct measurement of the distribution of galvanic current density of a Mg alloy in contact with another metal under a standard salt spray condition (Song *et al.*, 2004b).

A specially designed ‘sandwich’-like galvanic probe (See Fig. 1.6) (Song *et al.*, 2004b; Song, 2009d) can be used for these measurements. The measured galvanic current density exponentially decreases with the thickness of an insulating spacer, which implies that the galvanic corrosion can still be significant even when the thickness of the insulating spacer between a Mg



1.5 The dependence of $\ln(I_g)$ on the distance from the 'anode/cathode' junction (Song *et al.*, 2006b).



1.6 Configuration of a 'sandwich' like probe used to measure the galvanic current (Song *et al.*, 2006b).

alloy and steel is as large as 9 cm under a salt spray condition (Song, 2005b, 2006; Song *et al.*, 2004b). It seems that insertion of an insulating spacer may reduce but cannot eliminate galvanic corrosion. The reason is that the insulating spacer does not completely block the ionic current path.

When the geometry of a galvanic couple becomes complicated, experimental measurement of the galvanic corrosion rate using the above 'sandwich'

galvanic probe will be difficult. In this case, computer modeling is an option (Klingert *et al.*, 1964; Doig and Flewitt, 1979; Fu, 1982; Sautebin *et al.*, 1980; Helle *et al.*, 1981; Kasper and April, 1983; Munn, 1982; Munn and Devereux, 1991a, 1991b; Miyaska *et al.*, 1990; Aoki and Kishimoto, 1991; Hack, 1997). There are already a few successful studies of the galvanic corrosion of Mg alloys by computer modeling (Jia *et al.*, 2004, 2005a, 2005b, 2006, 2007). Nevertheless, experimental measurement of the polarization curves of the coupling metals is still important in numerical analysis and computer modeling. Polarization curves are required as boundary conditions in computer modeling. Due to the negative difference effect, alkalization effect, 'poisoning' effect, and 'short-circuit' effect, etc. (Song, 2005b, 2006; Song *et al.*, 2004b), current computer modeling techniques cannot, at this time, comprehensively simulate a practical macro-galvanic process and quite often there are significant deviations between computer-modeled data and measured galvanic corrosion results.

1.2.4 Micro-galvanic effect

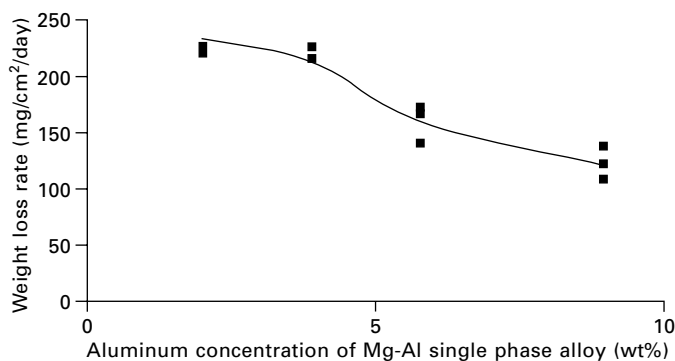
The surface of Mg or a Mg alloy cannot be perfectly uniform and, as such, it is impossible for anodic and cathodic reactions to occur uniformly throughout the entire surface. Due to this non-uniformity in terms of the composition, microstructure and even crystal orientation, galvanic couples can be formed within a Mg alloy. These micro-galvanic cells dominate the corrosion of the alloy. Within the Mg alloy, the Mg matrix always acts as a micro-anode and is preferentially corroded (Song, 2005b, 2006, 2007a). For the micro-cathode, it could be:

- (i) areas with significantly different solid solution concentrations of alloying elements within the matrix phase;
- (ii) secondary phases along grain boundaries; and/or
- (iii) impurity-containing particles.

1.2.5 Corrosion of matrix phase

In a magnesium alloy, the matrix phase is a major constituent and its corrosion performance is responsible for the corrosion behavior of the alloy. Therefore, the corrosion of a magnesium alloy is actually a problem of the matrix phase.

In the matrix, which is a solid solution, its solute has an important influence on its corrosion behavior. For an Al-containing Mg alloy, the matrix phase is a Mg-Al single phase which becomes less active as the Al content increases (Song, 2005a Song, *et al.*, 1998, 1999, 2004a). Figure 1.7 shows that the corrosion rate of the matrix decreases as the Al content increases.



1.7 Average corrosion rates of Mg-Al single phases in 5wt% NaCl for 3 hours (Song *et al.*, 2004a).

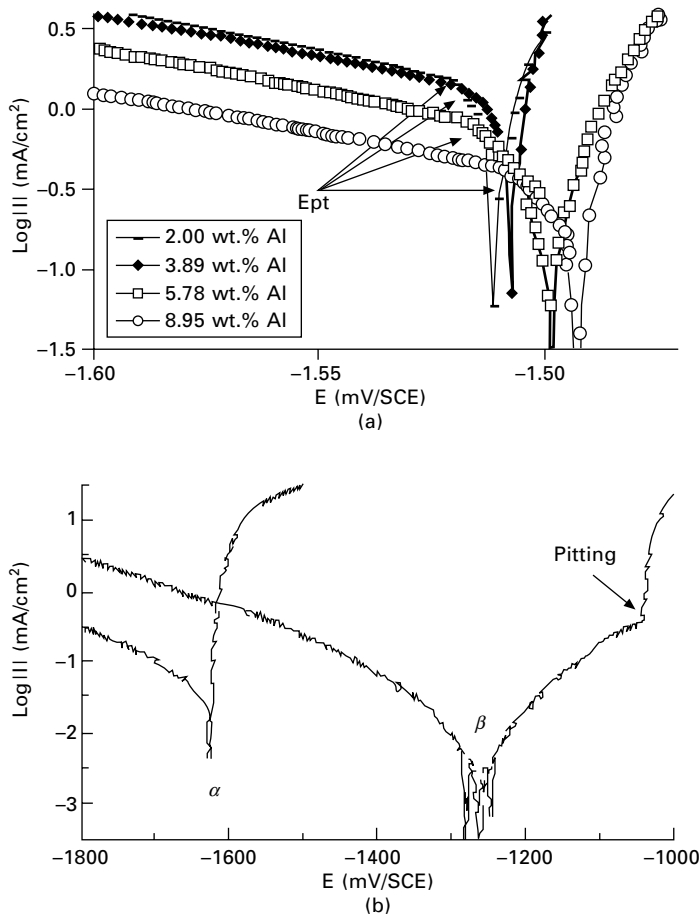
More importantly, the difference in solid solution concentration can result in differences in corrosion potential and anodic/cathodic activity, as shown in Fig. 1.8a.

These differences can lead to the formation of a micro-galvanic cell within a grain because the Al content is higher along the grain boundary than the grain interior for a cast Mg-Al alloy. The Al content in the solid solution can vary from 1.5wt % in the grain center to about 12wt % along the grain boundary (Dargusch *et al.*, 1998). Therefore, the difference in electrochemical activity and corrosion resistance can be significant, even within the same grain of a Mg-Al alloy. Experimental evidence for the differences between the grain center and boundary is the corrosion morphology of an AZ91E alloy as presented in Fig. 1.9 (Song, 2005a). The corrosion occurs mainly in the interior areas of α grains and the grain boundary areas are much less corroded.

In the group of non-Al containing alloys, the matrix typically contains Zr as a grain refiner. The role of Zr in corrosion is remarkable and is as important as Al is for the Al-containing alloys. An example is presented in Fig. 1.10 to demonstrate the relationship between Zr addition and corrosion resistance. It can be seen that the central areas of many grains remain uncorroded while the grain boundaries have been severely corroded, which is converse to the corrosion morphology of Al-containing Mg alloys (refer to Fig. 1.9 and Fig. 1.10). It was found (Song, 2005a; Song and St John, 2002) that the distribution of Zr in the grain is not uniform. The grain center is rich in Zr, which is thought to be the reason for its higher corrosion resistance.

These results suggest that a typical Mg alloy cannot be uniform because of the non-uniformly distributed solid solution within the matrix phase. This non-uniformity can generate micro-galvanic cells. Therefore, before the alloy is homogenization-treated, localized corrosion attack in some particular areas is inevitable.

In high purity Mg (in which there is no micro-galvanic effect caused

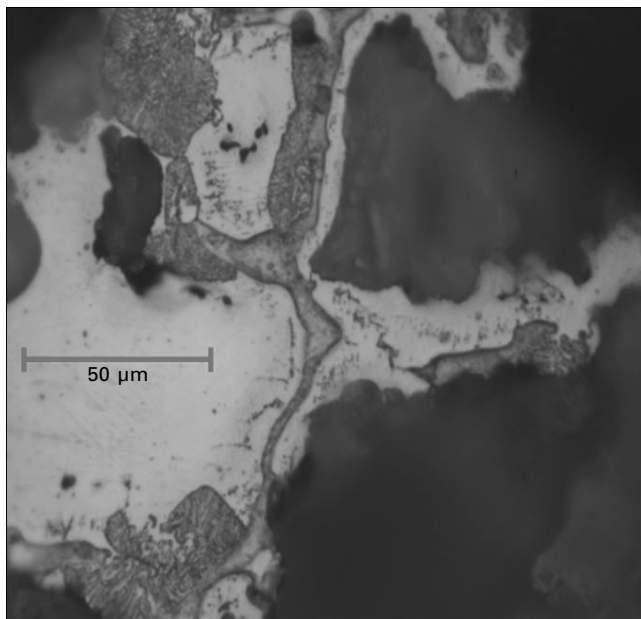


1.8 Polarization curves of Mg and Mg alloys in corrosive solutions: (a) Diecast AZ91 and sand cast MEZ alloys in 5wt% NaCl (pH 11) (Song *et al.*, 2004a), (b) Mg-Al matrix phase and secondary phase in NaCl at pH 11 (Song *et al.*, 1998).

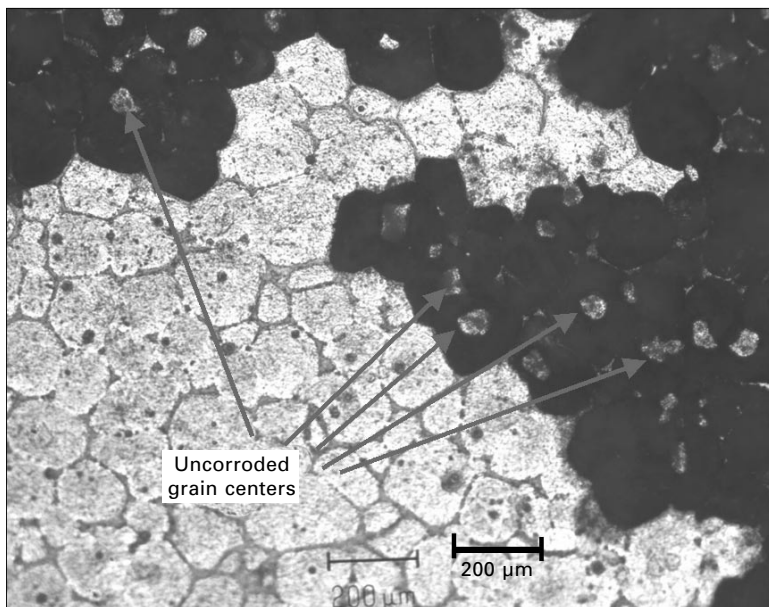
by impurities or different solid solution concentrations), different exposed crystal planes, i.e. different crystal orientations, can still produce different electrochemical activities. Figure 1.11 shows a few pure Mg grains having different depths of corrosion after immersion in an acidic solution (Liu *et al.*, 2008). The corrosion depths of different crystal planes were compared and it was found that the corrosion rates on the three lowest index planes follows the following increasing order (Liu *et al.*, 2008):

$$(0001) < (11\bar{2}0) < (01\bar{1}0)$$

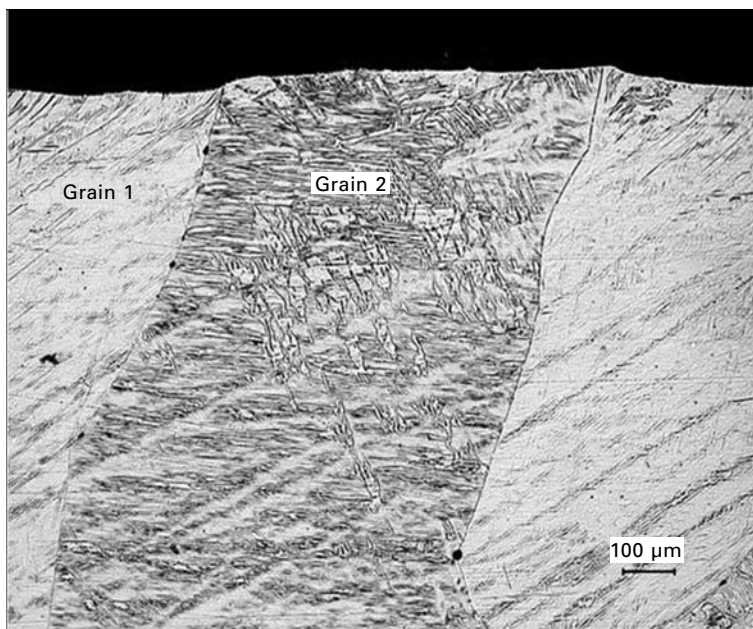
The different corrosion rates of individual grains can be ascribed to their



1.9 Corrosion morphologies of AZ91E after a four hour immersion in 5% NaCl (Song 2005a).



1.10 Optical micrograph of the surface of a Mg-RE-Zr alloy after immersion in 5% NaCl for three hours (Song and St John, 2002).



1.11 Typical cross-sections after corrosion of pure Mg in 0.1 N HCl solution for 15 h (Liu *et al.*, 2008).

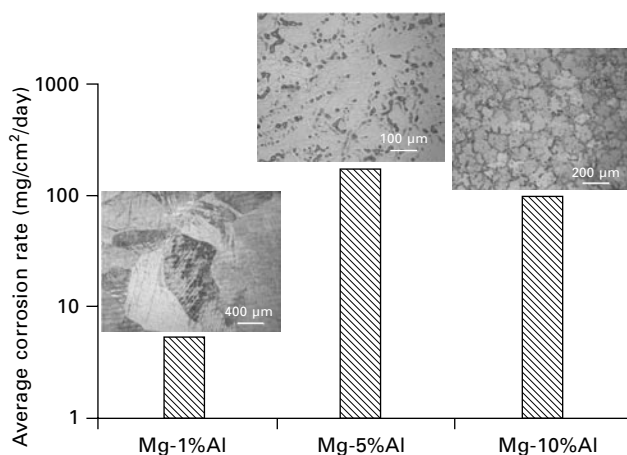
unique orientation or the unique crystal plane exposed to the corrosive solution. The corrosion rate of a metal can, to some extent, be correlated to its surface energy (Ashton and Hepworth, 1968; Abayarathna *et al.*, 1991; Buck and Henry, 1957; Weininger and Breiter, 1963; König and Davepon, 2001) which, in turn, is associated with its atomic density. It is well known that pure Mg has a hexagonal crystallographic cell with axes: $a = b = 0.3202$ nm, $c = 0.5200$ nm and angles: $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic densities of the three lowest index planes can be calculated (König and Davepon, 2001) to be 1.13×10^{15} , 6.94×10^{14} and 5.99×10^{14} , respectively. Different crystal planes have different electrochemical activities when they are exposed to an aqueous solution. The atoms in the lower surface energy planes are more difficult to dissolve or corrode away. Therefore, the lowest index plane (0001) has the lowest energy and should be dissolved slower than the other surfaces. This has been evidenced by a dependence of the corrosion resistance of a crystal plane on its atomic density (Liu *et al.*, 2008).

1.2.6 Influence of secondary phase

Almost all the Mg intermetallic phases are nobler than the magnesium matrix itself and many of them exist in commercial magnesium alloys as secondary phases (Song *et al.*, 1998, 1999; Song and St John, 2002; Nisancioglu *et al.*,

1990). These phases are cathodic to the matrix phase and can act as micro-galvanic cathodes to accelerate the corrosion of the matrix. For example, in Fig. 1.8b, the β phase has not only a corrosion potential about 400 mV more positive but also a cathodic current density much larger than the α matrix phase, suggesting that the β phase is an active cathode to the matrix phase. Therefore, in a magnesium alloy, the matrix can be subjected to micro-galvanic corrosion attack caused by the β phase.

It is well known that the galvanic corrosion current density of a galvanic couple increases when the cathode electrode surface area increases. Due to the galvanic effect of the secondary phase, a Mg alloy is expected to be subjected to increasingly severe corrosion with an increasing amount of the secondary phase in the alloy. This has been verified by some experimental results. It was found (see Fig. 1.12) (Song, 2005b, 2006; Shi *et al.*, 2005) that the corrosion rate of a Mg-Al alloy first increased and then decreased as the amount of the secondary phase β increased. The increasing corrosion rate with the amount of the β phase before the maximum corrosion rate suggests that the micro-galvanic effect was dominating the corrosion of the alloy. However, it has also been widely reported (Nisancioglu *et al.*, 1990; Lunder *et al.*, 1993, 1995, 1989; Ambat *et al.*, 2000; Uzan *et al.*, 2000; Yim and Shin, 2001) that the corrosion rate of a Mg alloy can decrease as the volume fraction of the β phase increases. Even within the same alloy sample, some areas having a large amount of the secondary phase can display higher corrosion resistance than other areas having only a small amount of the secondary phase. For example, a cold-chamber die-cast AZ91D has different microstructures in its interior and surface layer. The surface layer has a larger amount of the finely and continuously distributed β -phase than the interior,



1.12 Salt spray corrosion rates of Mg-Al alloys and their microstructures (Song 2005b; Shi *et al.*, 2005).

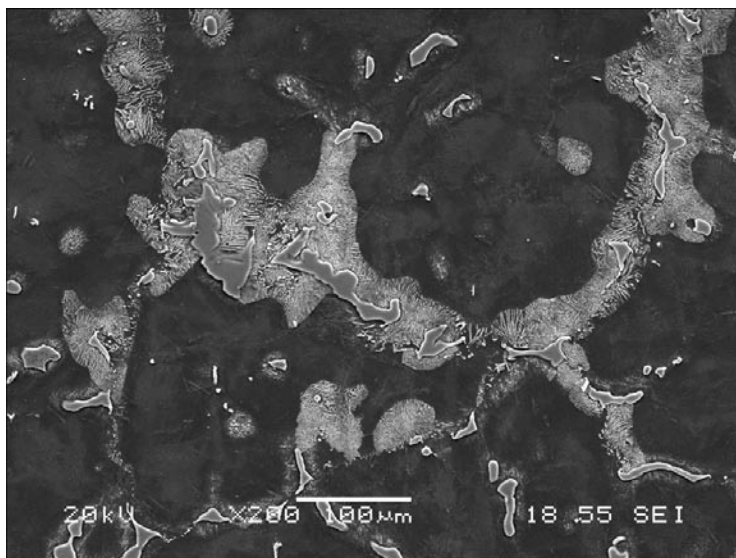
and the corrosion rate of the surface layer is about ten times lower than the interior under the same salt solution (Song, 2005b; Song and Atrens, 1998; Song *et al.*, 1999). In this case, the galvanic effect of the secondary phase does not appear to be responsible for the corrosion behavior.

In fact, the secondary phase can also play another important role within a Mg alloy as a barrier against corrosion. It has been found that the secondary phase in Mg alloys is much more stable than the magnesium matrix (Song *et al.*, 1998, 2007; Song and Atrens, 2003). In AZ alloys, the β -phase is normally not corroded if they are exposed to a NaCl solution (Song *et al.*, 1998; Zhao *et al.*, 2008a, 2008c) and in the corroded areas where the matrix phase has been severely corroded, the β -phase is still intact (see Fig. 1.13).

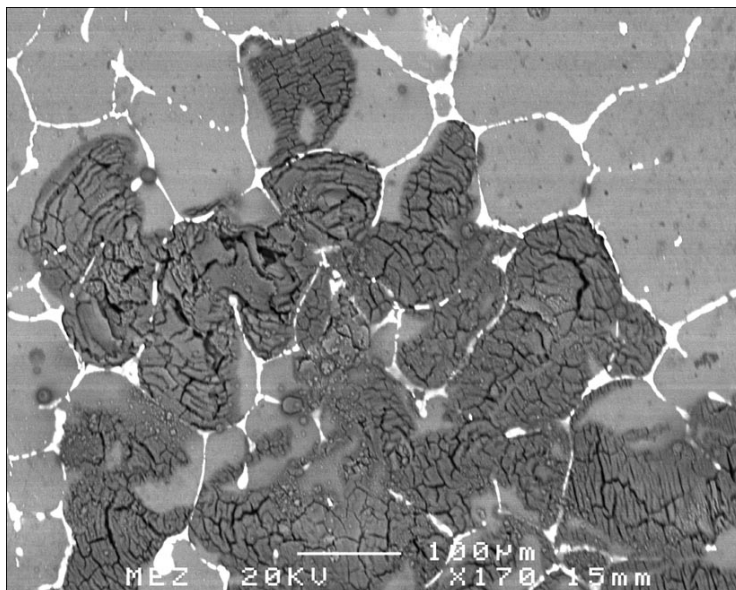
Similarly, the secondary phase in a Mg-RE alloy is also superior to the matrix in terms of the corrosion resistance. Figure 1.14 shows that the secondary phase is still intact in corroded areas.

The high corrosion resistance of the secondary phase in a Mg alloy can retard the corrosion of the alloy through a barrier mechanism. A piece of direct evidence is that the corrosion within the matrix phase stops upon reaching the β phase in an AZ Mg alloy (see Fig. 1.15) (Song, 2005a). The same barrier effect from the secondary phase of a non-aluminum containing alloy has also been found in a Mg-RE-Zr (Fig. 1.10) (Song and St John, 2002).

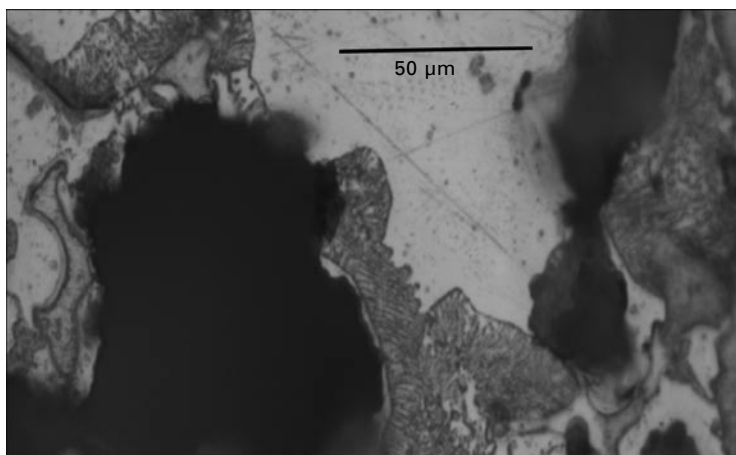
The barrier effect and the micro-galvanic effect are two different aspects of the role that the secondary phase plays in corrosion. In other words, the



1.13 Microstructure of AZ91 after immersion in 1 M NaCl solution at room temperature for 18 h (Zhao *et al.*, 2008a).



1.14 A Mg-RE alloy after immersion in 5% NaCl for three hours. The white contrast is the secondary phase and the black contrasts are corroded areas (Song and St John, 2002).



1.15 Corrosion morphology of AZ91E after a four hour immersion in 5% NaCl (Song, 2005a).

secondary phase has a dual-role in the corrosion (Song, 2005b; Song *et al.*, 1999, 2004a; Song and Atrens, 1998, 2003). Whether the barrier effect or the galvanic effect of the secondary phase dominates the corrosion of a Mg alloy depends on the continuity and amount of the secondary phase. If the

amount of the secondary phase is small and the distribution is discontinuous, then the galvanic effect will govern the corrosion of the alloy. Conversely, if the secondary phase effectively separates the grains and thus acts as a barrier, it will retard the corrosion development from grain to grain (Song, 2005b; Song and Atrens, 1999; Song *et al.*, 1999; Song and St John, 2000, 2002). This dual-role can explain many corrosion phenomena of Mg alloys. For example, in Fig. 1.12, the higher corrosion rate of Mg-5%Al can be attributed to the galvanic effect of the β phase in a discontinuous distribution, whereas for Mg-10%Al, there is sufficient β phase continuously distributed along the grain boundaries to stop corrosion from progressing across grain boundaries, and hence its corrosion rate is lower than that of Mg-5%Al.

1.2.7 Detrimental effect of impurities

A very small amount of Fe, Ni, Co, or Cu addition can dramatically increase the corrosion rate of Mg through a micro-galvanic effect (Hanawalt *et al.*, 1942; Nisancioglu *et al.*, 1990; Lunder *et al.*, 1995). Currently, Fe, Cu and Ni, which are likely to be contained in Mg alloys, are defined as Mg alloy impurities.

It is well known that the over-voltages for hydrogen evolution on Fe, Co, Ni, Cu, etc. are less than 0.7 V. This means that Fe, Co, Ni and Cu are very active under cathodic polarization and that hydrogen evolution from them is easy and fast. Moreover, they are cathodic to Mg in most aqueous solutions. If these impurities are present in Mg alloys as separate phases, they will be effective micro-galvanic cathodes and can significantly accelerate the corrosion of the matrix phase.

As stated, a very small amount of impurity present in Mg or its alloys can result in strikingly deteriorated corrosion performance. For each impurity in Mg and its alloys, there is a critical concentration, also known as the impurity tolerance limit, above which the corrosion rate increases significantly. Corrosion rates are considerably high and can be accelerated by a factor of 10 to 100 when the concentrations of the impurities Fe, Ni and Cu are increased above their tolerance limits (Hillis and Murray, 1987). If the impurity levels are lower than their tolerance limits, the corrosion rates are low and the impurities have an insignificant influence on the corrosion rates. A higher level of the impurity can lead to lower corrosion resistance for Mg and most Mg alloys (Emley, 1966; Avedesian and Baker, 1999; Busk, 1987; Hillis, 1983). Studies (Hillis, 1983; Frey and Albright, 1984; Aune, 1983) have shown that dramatic improvement of corrosion resistance can be realized through controlling impurity levels in a Mg alloy. For this reason, Dow has recommended that the following specific impurity tolerance limits should be used to ensure optimum salt water corrosion performance for AZ91: Fe < 50ppm, Ni < 5ppm, Cu < 300ppm (Hillis, 1983).

It seems that the impurity tolerance limit is associated with its solubility in Mg alloys. When these impurities are below their tolerance limits, they are present in the form of solutes in the Mg solid solution. No micro-galvanic cells between the impurities and the Mg matrix are formed. Only after the contents of the impurities reach their solubility limits in a Mg alloy, can they precipitate as separate phases in the Mg alloy and act as galvanic cathodes to accelerate the corrosion. It is calculated by Liu *et al.* (2009) that the Fe tolerant limit in Mg corresponds well to the solubility of Fe in Mg. The Mg-Fe system has a eutectic temperature of $\sim 650^{\circ}\text{C}$ and a eutectic Fe concentration of 180 ppm. For a content of 180 ppm Fe in the Mg system, the liquid Mg undergoes eutectic solidification at 650°C and forms α -Mg containing about 10 ppm iron in solid solution. However, the region of (Mg + α -Mg) is extremely narrow, such that both the pre-eutectic and eutectic reactions would be suppressed in practical ingot or casting production. Thus, commercial Mg containing less than 180 ppm Fe would solidify to a single α -Mg phase with a super-saturation of Fe in Mg solid solution. Consequently, Mg can have up to 180 ppm of Fe dissolved in the Mg solid solution. At a concentration higher than 180 ppm, Fe will precipitate out via eutectic reaction. The value of 180 ppm Fe corresponds well to the Fe tolerance level of 170 ppm (Song *et al.*, 2004a; Song and Shi, 2006) or 150 ppm (Song and St John, 2004) noted for pure Mg.

Other alloying elements present in Mg can shift the eutectic point and thereby alter the impurity tolerance limits (Emley, 1966). For example, when a few percent of Al is added to Mg, the tolerance limit of iron decreases from 170 ppm to a few ppm. It is calculated (Liu *et al.*, 2008) that the eutectic point is shifted to a lower Fe content after Al is added and thus the Fe tolerance limit decreases rapidly with increasing Al content. With a higher addition of Al in Mg, Fe and Al can form Fe-Al phase (i.e. FeAl_3) particles which precipitate out in Mg-Al alloys and potentially act as galvanic cathodes (Hawke, 1975; Loose, 1946; Linder *et al.*, 1989). This is why a Mg alloy with 7% Al can tolerate about 5 ppm Fe, while the tolerance limit becomes too low to be determined when Al concentration is increased to 10 wt% (Loose, 1946). Therefore, it is also understandable that different Mg alloys have different impurity tolerance limits (Song, 2007a; Albright, 1988).

The solubility-related critical concentration can be extended to some other elements. There is a rough correspondence between the critical concentrations and the solubility of some elements in Mg alloys (Roberts, 1960). Only after the element concentration levels are greater than their solubility in the Mg matrix (which is a solid solution), do they start to form separate phases in the Mg alloy, and is the subsequent corrosion of the alloy dramatically accelerated. Moreover, the various cathodic activities of these elements are responsible for the different levels of their corrosion acceleration after their concentrations exceed their solubility.

It should be noted that Mn and Zr are two special elements in terms of their beneficial influence on the impurity tolerance limits. They cannot improve the corrosion resistance of a Mg alloy by themselves and in the case that their additions exceed their solubility in a Mg alloy, they may even deteriorate the corrosion performance of a high purity Mg alloy due to the galvanic effect of their precipitates (Song, 2005b, 2006). However, they can effectively reduce the detrimental effect of impurities in low purity Mg alloys. It is now well known that the iron tolerance limit in a Mg-Al alloy depends on the Mn concentration. A small addition (0.2%) of Mn can reduce the detrimental effect of impurities when their tolerance limits are exceeded (Hillis, 1983), resulting in increased corrosion resistance of the Mg alloy (Makar and Kruger, 1993; Polmear, 1992). Mn increases the iron tolerance limit to 20 ppm for Mg-Al alloys (Emley, 1966). It can also increase the Ni tolerance limit (Makar and Kruger, 1993). Similarly, Zr additions can also lead to a higher purity Mg by causing impurities to settle out and hence give a more corrosion resistant Mg alloy.

Since the iron tolerance limit is dependent upon the Mn content in a Mg alloy, it is understandable that the Fe/Mn ratio is a critical factor determining the impurity tolerance limits (Hillis and Shook, 1989; Zamin, 1981). A nearly direct proportionality has been observed between the Fe/Mn ratio and the corrosion rate (Nisancioglu *et al.*, 1990). It is assumed that Mn reduces the corrosion rate by the following two mechanisms: First, Mn combines with Fe in the molten Mg alloy during melting and forms intermetallic compounds which settle to the melt bottom, thereby lowering the iron content of the alloy. Second, Mn encapsulates the iron particles that remain in the metal during solidification, thereby making them less active as micro-galvanic cathodes. The beneficial effect of Zr is also associated with the reaction of Zr with impurities to form heavier intermetallic particles which quickly settle out due to their high density in the molten Mg. Therefore, the addition of Zr can purify Mg alloys or increase impurity tolerance limits.

1.3 Corrosion mitigation strategy

The purpose of a comprehensive understanding of corrosion is to effectively mitigate the corrosion damage of metals, which means development of suitable approaches to retard the corrosion. A successful corrosion mitigation strategy needs effective approaches, and in each approach the key is selection and development of corrosion protection/prevention techniques. There are no fundamental differences in the corrosion protection principles for Mg alloys versus other conventional metals. However, due to the unique corrosion characteristics and behavior of Mg alloys, the detailed corrosion prevention techniques will have some unusual requirements.

1.3.1 Typical approaches and possible techniques

Numerous corrosion prevention/protection techniques have been, and are being, developed for Mg alloys in various applications. In this section, the fine details of those possible corrosion prevention techniques will not be covered; however, the advantages and disadvantages of a few typical approaches will be briefly compared.

Reasonable design

An ideal design can ensure that a Mg alloy in a given service environment has the lowest thermodynamic possibility for, and the highest kinetic resistance to, corrosion. A successful corrosion protection design is one of the most cost-effective corrosion mitigation approaches. A simple modification in design may lead to huge savings in subsequent corrosion protection. There are many factors to consider in design although, because there are a large number of limitations in practical service, a perfect design is unlikely to be achieved. However, a reasonable one can be pursued if the following two basic aspects are considered: (i) alloy selection and (ii) component geometry.

Cathodic protection

Cathodic protection of a metal normally requires the applied cathodic protection potential to be more negative than the equilibrium potential of the metal to be protected. Mg has a very negative equilibrium potential (~ -2.7 V). An existing engineering metal cannot act as a sacrificial anode to offer cathodic protection for a Mg alloy, as it is unlikely to have a potential more negative than this value. Nevertheless, cathodic protection can theoretically still be provided by an imposed cathodic current. Certainly, this requires a very high cathodic current density which can lead to intensive hydrogen evolution and low current efficiency, and may not be acceptable in practical applications. Moreover, the cathodic protection may charge hydrogen into a Mg alloy (Mg can store a certain amount of hydrogen at room temperature), which could lead to an embrittlement problem. Therefore, traditional cathodic protection is not a practical approach for Mg alloys. It is, at least, not recommended for use currently. However, according to Fig. 1.2a, the Mg dissolution can become nearly zero while the hydrogen evolution rate reaches the minimum at a potential between its corrosion and equilibrium potentials. This means that there is the possibility that an effective cathodic protection of Mg alloys can be achieved at a less negative potential than that theoretically required. This would make cathodic protection possible for Mg alloys in practice. Certainly, to make it practical, several issues should be addressed first. For example, is there always such a minimum hydrogen evolution point for Mg

alloys in any corrosive environment? Is this point stable in practice? How is its long-term effectiveness?

Development of corrosion resistant alloys

Improving the corrosion resistance of Mg alloys through a change in their chemical composition, phase constituent and distribution, and/or other micro-structural characteristics is the most reliable and trouble-free corrosion mitigation approach. However, it is difficult and will be a long-term goal.

The critical part of a Mg alloy is its matrix, which is a weak region preferentially suffering from corrosion attack according to the analysis in previous sections. Therefore, the key to this approach is transforming the matrix phase into an inert or passive state.

From a thermodynamic point of view, there may be a theoretical possibility of reducing the tendency of oxidation or dissolution of Mg through alloying with inert elements. However, due to the high chemical activity of Mg, the addition of alloying elements needs to be in large amounts, which will significantly change the physical properties of Mg. To date, it is known that the elements lighter than Mg are more active than Mg, thus making it impossible for Mg to become inert through alloying. Even though an inert Mg alloy is achievable in theory (by alloying with heavy noble metals), the alloy will be quite heavy and will have lost the advantage of low density.

From a kinetic point of view, corrosion-resistant Mg alloys may be achievable through alloying with highly passive elements. This idea of significantly improving the passivity of Mg alloys appears to be more practical than the proposal of an inert Mg alloy, but it is far from easy. All the known highly passive elements (such as Ti, Al, Cr, and Ni) have a limited solid solubility in the Mg matrix phase. None of them, even with an addition up to its solid solubility limit, can really make Mg passive in a corrosive solution, e.g. 5wt% NaCl. Nevertheless, there is still a possibility that some highly passive alloying elements form a super-saturated solid solution with Mg in the matrix phase, thereby making the matrix passive. Certainly, such a super-saturated passive alloy is difficult to obtain through traditional alloying production methods. Some innovative techniques should be considered, including new casting processes (e.g. semi-solid casting, rapid solidification, vapor deposition (CVD and PVD), sputtering and cold spray).

Alloy modification

Alloy modification is different from the approach of developing corrosion resistant alloys. It only slightly modifies an existing alloy, without significantly changing its basic composition and phase constituent. This can be realized

through several techniques, such as: (i) purification, (ii) passivation of impurity, (iii) modification of composition and phase distributions. Generally speaking, the improvement of corrosion resistance by this approach is not dramatic, but the approach is attractive for its compatibility with Mg alloy production and processing. For example, heat-treatment is a common practice for some Mg alloys and it has been found that the corrosion resistance of some Mg alloys can be improved through carefully designed heat-treatments (Song *et al.*, 2004a; Zhao *et al.*, 2008a, 2008b, 2008c). A disadvantage of this approach is that some mechanical properties of Mg alloys may also be changed after alloy modification, which could be undesirable in some cases.

Surface modification and treatment

Sometimes, it is difficult to improve the corrosion resistance without sacrificing the mechanical performance of an alloy. In this case, surface modification or treatment is a favorable option, because surface modification or treatment occurs only on the surface layer of a Mg alloy and the bulk alloy is left unchanged.

Surface modification and treatment can lead to enhancement of anodic and/or cathodic polarization resistance, isolation of anodic or cathodic phase, or elimination or reduction of electrochemical differences between anodic and cathodic phases. These effects can be achieved by various methods, such as: (i) surface cleaning, (ii) ion implantation, (iii) laser treatment, (iv) hot diffusion, (v) surface conversion and (vi) anodizing. It should be stressed that hot diffusion is relatively inexpensive and is suitable for a large surface area (Zhu and Song, 2006; Zhu *et al.*, 2005) compared with ion implantation or laser treatment; and anodizing is more corrosion resistant (Shi *et al.*, 2001, 2005, 2006a, 2006b, 2006c; Blawert *et al.*, 2006) than surface conversion.

Coating

A protective coating for a Mg alloy refers to an independent layer applied on the Mg alloy. It is different from the surface modification or treatment, as Mg alloy surfaces normally do not participate in a reaction or experience a significant change under the coating. The coating can: (i) effectively separate the Mg alloy substrate from the corrosive environment and/or (ii) considerably increase the polarization resistance of the alloy substrate and hence dramatically retard its corrosion.

Coatings can be obtained by many methods for Mg alloys and they can be metallic, oxide/hydroxide, organic, etc. Deposition on a Mg surface in a normal aqueous plating bath is difficult due to the intensive hydrogen evolution and the rapid oxide or hydroxide formation. In addition, a modern electro- or electroless-plating technique must be cost-effective, non-toxic

and environmental friendly. This makes the development of a new plating technique for Mg alloys more difficult. Pinholes are common defects in a plating layer and, in many cases, a plating layer with pinholes can even worsen the corrosion performance of a Mg alloy due to micro-galvanic corrosion in the pinholes. The most attractive feature of a plated coating for an Mg alloy is its metallic characteristics, which are important in some practical applications. CVD and PVD techniques can also deposit metallic coatings on Mg alloys. Recently, hot-spray, cold spray and magnetic sputtering techniques have been tried to form a corrosion resistant coating for Mg alloys. They are all capable of producing a metallic coating on Mg alloys, but at a relatively high cost.

Organic coating can be a cost effective method to separate a Mg alloy from its corrosive environment and hence protect it from corrosion attack. Many organic coatings can be applied to Mg alloys, such as normal paints, E-coatings, sol-gel coats, and electro-polymerized coats. However, due to the high surface alkalinity of Mg, which is not favorable to many organics, Mg alloys normally need to be surface-treated prior to the application of an organic coating. Organic coating is a mature corrosion protection technique and there are many organic coating brands available for Mg alloys. As long as Mg alloys are properly surface-treated, these coatings can be applied in the same manner as they are used for conventional metals.

Environmental modification

Environmental parameters to corrosion are as important as the composition and microstructure of an alloy. A change in environment can significantly alter the corrosion rate of a Mg alloy. Hence, modification of the environment can be a strategic method for corrosion prevention of a Mg alloy.

It is difficult to modify an open environment. If a Mg alloy is in a closed service environment, modification of the environment is possible. It is also possible to modify a local environment after an open system is partially isolated. Basically, modification of the environment includes increasing the pH value, reducing the concentration of aggressive species, and adding passivators or inhibitors (Song, 2007a; Song and Song, 2007). Under atmospheric conditions, keeping the air dry is also a very effective method for controlling the corrosion of Mg alloys (Song *et al.*, 2006b). Environmental modification, if achievable, is relatively cost-effective compared with other approaches. However, environmental impact and health hazards are major concerns.

1.3.2 Selection of corrosion protection techniques

Mitigating the corrosion of a Mg alloy is not done to simply reduce the corrosion rate. Many issues other than corrosion performance need to be

considered as well, as there may be conflicts between improving corrosion resistance and other key properties. Some basic principles should be followed in selecting a corrosion protection approach.

Enhancement of corrosion resistance

Any considered approach or technique should first be able, to the greatest degree, reduce the corrosion damage of Mg alloys. Mg alloy corrosion mechanisms differ from those of conventional metals and thus it is quite possible that some corrosion prevention measures suitable for conventional metals may not be so effective for Mg alloys. An inappropriate corrosion protection technique may even accelerate corrosion damage. It is dangerous to estimate the effectiveness of existing corrosion mitigation techniques, which were originally developed for conventional metals, on Mg alloys simply based on previous experience.

Compatibility with other properties

Corrosion resistance is only one of the important properties of Mg alloys. It is quite common that designers, engineers, or users, are more concerned about the mechanical performance of a Mg alloy rather than corrosion performance. Usually, only after the mechanical properties of a Mg alloy have met application requirements, is the alloy tested and improved for its corrosion performance. In this case, the improvement of corrosion resistance should not deteriorate the mechanical or other properties that have met the design requirements. Moreover, low density is one of the most attractive features of Mg alloys for which they have found many applications. Improving the corrosion performance of a Mg alloy should not compromise this advantage. There are still other unique properties of Mg alloys which make them irreplaceable in some applications. These should be preserved when corrosion protection measures are taken.

Combination of various corrosion mitigation approaches

In applications, there are usually many practical requirements for corrosion protection. Meeting all these requirements is difficult with one corrosion mitigation technique alone. However, it is possible that some of the requirements are met by one corrosion mitigation method and others by a different corrosion protection technique. Hence, all the requirements may be met through a combination of several corrosion prevention techniques together. Each corrosion mitigation technique has its own advantages and disadvantages. When various corrosion mitigation methods are combined, they may strengthen the advantages and offset the drawbacks of each other.

Cost, toxicity and environment impact

Direct economic cost can include immediate investment and ongoing expenses, and is always a critical issue when selecting corrosion prevention techniques. Mg alloys are in a position to compete against Al alloys in many cases. If the overall economic cost of a corrosion mitigation scheme for a Mg alloy is higher than the benefits gained from its mass savings over an Al alloy, the corrosion mitigation method is unlikely to be adopted, unless the Mg alloy has some unique properties so important that Al alloys or other materials in the application cannot meet. Apart from the direct economic cost, there are significant indirect social costs, such as health and environmental impacts. It is pity that some very effective corrosion prevention techniques are toxic to human or hazardous to the environment.

1.4 Future trends

As a result of their unique properties, Mg alloys have a variety of potential applications, particularly in the automotive and aerospace industries. There is no doubt that the corrosion problem of Mg alloys is becoming a significant issue, especially as the demand for lighter engineering metals increases and the cost of corrosion prevention for Mg alloys becomes relatively low compared to the increasing energy cost of using other materials. Therefore, some topics will become ‘hot’ in the field of Mg corrosion and protection:

1.4.1 Innovative surface conversion/treatment and coating techniques

Surface conversion/treatment and coating techniques are the most cost-effective approaches of immediately improving the corrosion performance of Mg alloys in some applications. Currently, it is already a ‘hot’ topic in corrosion and protection of Mg alloys. In theory, all the surface engineering approaches used for conventional metals may be applicable to Mg alloys. However, due to the unique surface properties of Mg alloys, further developments of innovative technical details are still required. In fact, new surface conversion/treatment and coating techniques are urgently needed for Mg alloys in many applications and the relevant research should be prioritized.

1.4.2 Corrosion database for Mg alloys in typical environments

As a relatively new material, there is a lack of understanding of the corrosion behavior of Mg alloys in given service environments. The application of Mg alloys requires this information, particularly the long-term corrosion

behavior. Unfortunately, Mg alloys are only recently increasingly considered for various applications. It is impossible to estimate or predict their long-term corrosion behavior, based on the existing experience of other conventional metals or some short-term lab corrosion results of the Mg alloy. Therefore, a collection of long-term corrosion exposure results will be an essential task in the field of Mg alloy corrosion and protection.

1.4.3 Estimation and prediction of corrosion damage for Mg alloys in service

It is impossible to measure the long-term corrosion performance of Mg alloys in all possible service environments. Therefore, estimation or prediction of the corrosion behavior of Mg alloys in various corrosion environments based on their existing long-term corrosion results under a few typical corrosion environments is important and essential. This work includes establishment of lab and field corrosion testing methods, planning of *in-situ* long-term corrosion exposure of specimens, analysis of corroded components from real service environments, development of the relationship between experimental results and real component corrosion damage, etc. This is a challenging area in the corrosion and protection of Mg.

1.4.4 Fundamental understanding of corrosion mechanisms

To reasonably estimate or predict the corrosion of Mg alloys, their corrosion mechanisms should be understood. Using a corrosion mechanism to predict the corrosion performance of a Mg alloy that is actually governed by a different mechanism can generate a misleading result. Moreover, only after the corrosion mechanism of a Mg alloy in its service environment is known, can the most effective mitigation approach be developed. Furthermore, with both new Mg alloys and applications being developed, the corrosion mechanisms and behaviors of the new alloys and applications should also be investigated. Therefore, a fundamental study of the corrosion mechanism and behavior will be an area of great significance in the corrosion and protection of Mg alloys.

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1.6 References

- Abayarathna D., Hale E. B., O'Keefe T. J., Wang Y. M., Radovic D. (1991), *Corrosion Science*, 32, 755.
- Aghion E., Bronfin B. (2000), 'Magnesium Alloys Development Towards the 21st Century', *Materials Science Forum*, 350–351: 19–28.
- Albright D. L. (1988), 'Relationship of Microstructure and Corrosion Behavior in Magnesium Alloy Ingots and Castings', Edited by H.G. Paris and W.H. Hunt, *Advances in Magnesium Alloys and Composites*, International Magnesium Association and the Non-Ferrous Metals Committee, The Minerals, Metals, and Materials Society, Phoenix, Arizona, January 26, pp 57–75.
- Ambat R., Aung N. N., Zhou W. (2000), 'Evaluation of microstructural effects on corrosion behaviour of AZ91D magnesium alloy', *Corrosion Science*, 42, 1433–1455.
- Aoki S., Kishimoto K. (1991), *Mathematical and Computer Modelling*, 15, 11.
- Ashton R. F., Hepworth M. T. (1968), *Corrosion*, 24, 50.
- Aune T. K. (1983), 'Minimizing Base Metal Corrosion on Magnesium Products. The Effect of Element Distribution (Structure) on Corrosion Behavior', *Proceedings of the 40th World Magnesium Conference*, Toronto, June.
- Avedesian M. M., Baker H. (1999), 'ASM Specialty Handbook, Magnesium and Magnesium Alloys', Chapter 'Cleaning and Finishing' pp 138–162, Chapter 'Corrosion Behaviour' pp 194–210, Chapter 'Stress Corrosion' pp 210–215, Chapter 'Fatigue and Fracture Resistance' pp 173–176, ASM.
- Bard A. J., Faulkner L. R. (1980), *Electrochemical Methods, Fundamentals and Applications*, John Wiley and Sons, Inc.
- Bettles C. J., Forwood C. T., St John D. *et al.* (2003a), 'AMC-SC1: An elevated temperature magnesium alloy suitable for precision sand casting of powertrain components', in H Kaplan (ed.), *Magnesium Technology*, TMS, San Diego, pp 223–226.
- Bettles C. J., Forwood C. T., Griffiths J. R. *et al.* (2003b), 'AMC-SC1: New magnesium alloy suitable for powertrain applications', SAE Technical paper# 2003-01-1365, *SAE World Congress*, Detroit, Mich.
- Blawert C., Dietzel W., Ghali E., Song G. (2006), 'Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments – a critical review', *Advanced Engineering Materials*, Vol. 8(7): 511–533.
- Boese E., Gollner J., Heyn A., Strunz J. (2001), *Materials and Corrosion*, 52, 247.
- Bonora P. L., Andrei M., Eliezer A., Gutman E. (2000), 'Corrosion Behaviour of Stressed Magnesium Alloys', E. Aghion and D. Eliezer, ed., *Magnesium 2000, Proceedings of the Second Israeli International Conference on Magnesium Science and Technology*, (Dead Sea, Israel), 410–416.
- Buck I. W. R., Henry L. (1957), *Journal of The Electrochemical Society*, 104, 474.
- Busk R. S. (1987), *Magnesium Products Design*, International Magnesium Association.
- Dargusch M. S., Dunlop G. L., Pettersen K. (1998). in *Magnesium Alloys and Their Applications*, Wolfsburg, Germany: Werkstoff-Informationen GmbH, pp. 277–282.

- Doig P., Flewitt P. E. J. (1979), *Journal of The Electrochemical Society*, 126, 2057.
- Eliezer A. *et al.* (2000), 'Dynamic and Static Corrosion Fatigue of Magnesium Alloys in Electrolytic Environment', E. Aghion and D. Eliezer, ed., *Magnesium 2000, Proceedings of the Second Israeli International Conference on Magnesium Science and Technology*, (Dead Sea, Israel), 356–362.
- Emley E. F. (1966), '*Principles of Magnesium Technology*', Chapter XX, Pergamon Press.
- Frey D., Albright L. L. (1984), 'Development of a Magnesium Alloy Structural Truck Component', *Proceedings of the 41st World Magnesium Conference*, London, June.
- Froats A., Aune T. K., Hawke D. 'Corrosion of Magnesium and Magnesium Alloys', A.S.M., *Metals Handbook*, 740–754.
- Fu J. W. (1982), *Corrosion*, 38, 295.
- Gal-Or L., Raz Y., Yahalon J. (1973), *Journal of the Electrochemical Society*, 120, 598.
- Gao G., Cole G., Richetts M., Balzer J., Frantzeskakis P. (2000), 'Effects of fastener surface on galvanic corrosion of automotive magnesium components', in: E. Aghion and D. Eliezer (ed.), *Magnesium 2000, Proc. of the Second Israeli International Conference on Magnesium Science and Technology*, Dead Sea, Israel, pp 321–338.
- Hack H. P. (1995), Chapter 20 'Galvanic', in Robert Baboian (ed.), *Corrosion tests and standards: Application and interpretation* ASTM, pp 186–196.
- Hack H. P. (1997), *Corrosion Review*, 15, 195.
- Hallopeau X., Beldjoudi T., Fiaud C., Robbiola L. (1999), 'Electrochemical Behaviour and Surface Characterisation of Mg and AZ91E Alloy in Aqueous Electrolyte Solutions Containing XOyn-inhibiting Ions', G.W. Lorimer, ed., *Proceedings of the Third International Magnesium Conference*, The Institute of Materials, London, 1997, 713–724.
- Hanawalt J. D., Nelson C. E., Peloubet J. A. (1942), 'Corrosion Studies of Magnesium and its Alloys', *Trans. Am. Inst. Mining Met. Eng.*, 147, 273.
- Hawke D. (1975), 'Corrosion and Wear Resistance of Magnesium Die Castings', *SYCE 8th International Die Casting Exposition and Congress*, Detroit, Paper No. G-T75–114.
- Hawke D. L. (1987), 'Galvanic corrosion of magnesium', *SDCE 14th International Die Casting Congress and Exposition*, Toronto, Canada, May, Paper No. G–T87–004.
- Helle H. P. E., Beck G. H. M., Ligtelijin J. T. (1981), *Corrosion*, 37, 522.
- Hillis J. E. (1983), 'The Effects of Heavy Metal Contamination on Magnesium Corrosion Performance', *SAE Technical Paper # 830523*, Detroit.
- Hillis J. E., Murray R. W. (1987), 'Finishing Alternatives for High Purity Magnesium Alloys', *SDCE 14th International Die Casting Congress and Exposition*, Toronto, Paper No. G–T87–003.
- Hillis J. E., Shook S. O. (1989), 'Composition and Performance of an Improved Magnesium AS41 Alloy', *SAE Technical Paper Series # 890205*, Detroit.
- Hur B.-Y., Kin K.-W., Ahn H.-J., Kim K.-H. (1996), 'A new method for evaluation of pitting corrosion resistance of Mg alloys', in G.W. Lorimer (ed.), *Proceedings of the Third International Magnesium Conference*, Manchester, 1996, pp 557–564.
- Jia J., Song G., Atrens A., St John D., Baynham J., Chandler G. (2004), 'Evolution of the BEASY Program using linear and piecewise linear approaches for the boundary conditions', *Materials and Corrosion*, 55: 845–852.

- Jia J., Song G., Atrens A. (2005a), 'Boundary element method predictions of the influence of the electrolyte on the galvanic corrosion of AZ91D coupled to steel', *Materials and Corrosion*, 56(4): 259–270.
- Jia J., Atrens A., Song G. *et al.* (2005b), 'Simulation of galvanic corrosion of magnesium coupled to a steel fastener in NaCl', *Materials and Corrosion*, 56(7): 468–474.
- Jia J., Song G., Atrens A. (2006), 'The influence of the geometry on the galvanic corrosion of AZ91D coupled to steel', *Corrosion Science*, 48: 2133–2153.
- Jia J., Song G., Atrens A. (2007), 'Experimental measurement and computer simulation of galvanic corrosion of magnesium coupled to steel', *Advanced Engineering Materials*, 9(1–2): 65–74.
- Kasper R. G., April M. G. (1983), *Corrosion*, 39, 181.
- Kennard E., Waber J. (1970), *Journal of the Electrochemical Society*, 117, 880.
- Klingert J. A., Lynne S., Tobias C. W. (1964), *Electrochimica Acta*, 9, 297.
- König U., Davepon B. (2001), *Electrochimica Acta*, 47, 149.
- Linder O., Lein J. E., Aune T. K. *et al.* (1989), *Corrosion*, 45(9): 741–747.
- Liu M., Qiu D., Zhao M., Song G., Atrens A. (2008), 'The effect of crystallographic orientation on the active corrosion of pure magnesium', *Scripta Materialia*, 58: 421–42.
- Liu M., Ungowitz P. J., Nagasekhar A. V., Schmutz P., Easton M., Song G., Atrens A. (2009), 'Calculated phase diagrams and the corrosion of die-cast Mg-Al alloys', *Corrosion Science*, 51: 602–619.
- Loose W. S. (1946), 'Corrosion and Protection of Magnesium', in L. M. Pidgeon, J. C. Mathes, N. E. Woldman, J. V. Winkler, W. S. Loos (eds), *Magnesium*, A series of five educational lectures on magnesium presented to members of the ASM during the Twenty-seventh National Metal Congress and Exposition, Cleveland, February, 4–8, American Society for Metals, pp 173–260.
- Lunder O., Lein J. E., Aune T. K., Nisancioglu K. (1989), 'The role of Mg₁₇Al₁₂ phase in the corrosion of Mg alloy AZ91', *Corrosion*, 45(9), 741–748.
- Lunder O., Nisancioglu K., Hansen R. S. (1993), 'Corrosion of Diecast Magnesium–Aluminium Alloys', *SAE Technical Paper Series #930755*, Detroit.
- Lunder O., Videm M., Nisancioglu K. (1995), 'Corrosion Resistant Magnesium Alloys', *SAE 1995 Transactions, Journal of Materials and Manufacturing*, Section 5-Volume 104: pp 352–357, Paper#950428.
- Makar G. L., Kruger J. (1993), 'Corrosion of Magnesium', *International Materials Reviews*, 38(3): 138–153.
- Mathieu S., Hazan J., Rapin C., Steinmetz P. (2000), 'Corrosion Behaviour of Die Cast and Thixocast AZ91D Alloys – The Use of Sodium Linear Carboxylates as Corrosion Inhibitors', E. Aghion and D. Eliezer, ed., *Magnesium 2000, Proceedings of the Second Israeli International Conference on Magnesium Science and Technology*, (Dead Sea, Israel), 339–346.
- McCafferty E. (1976), *Corrosion Science*, 16, 183.
- McCafferty E. (1977), *Journal of the Electrochemical Society*, 124, 1869.
- Melville P. H. (1979), *Journal of the Electrochemical Society*, 126, 2081.
- Melville P. H. (1980), *Journal of the Electrochemical Society*, 127, 864.
- Miyasaka M., Hashimoto K., Kishimoto K., Aoki S. (1990), *Corrosion Science*, 30, 299.
- Munn R. S. (1982), *Materials Performance*, August, 29.
- Munn R. S., Devereux O. F. (1991a), *Corrosion*, 47, 612.
- Munn R. S., Devereux O. F. (1991b), *Corrosion*, 47, 618.

- Nazarrov A. P., Mikhailovskii Y. N. (1990), *Protection of Metals*, 26(1): 9–14.
- Nisancioglu K., Lunder O., Aune T. (1990), ‘Corrosion Mechanism of AZ91 magnesium alloy’ presented at *47th World Magnesium Conference*, Cannes, France.
- Perrault G. G. (1978), Chapter VIII-4 ‘Magnesium’, in A.J. Bard (ed.): *Encyclopedia of Electrochemistry of the Elements*, Marcel Dekker, New York, pp 263–319.
- Polmear I. J. (1996), *Metallurgy of Light Alloys*, Halsted Press, NY, 362.
- Polmear I. J. (1992), *Physical Metallurgy of Magnesium Alloys*, DGM Informationsgesellschaft, Oberursel, Germany; p 201.
- Roberts C. S. (1960), Chapter ‘Magnesium alloy systems’ in *Magnesium and its Alloys*, John Wiley & Sons, pp 42–80.
- Sautebin R., Froidewaux H., Landolt D. (1980), *Journal of the Electrochemical Society*, 127, 1096.
- Senf J., Broszeit E., Gugau M., Berger C. (2000), ‘Corrosion and Galvanic corrosion of die cast magnesium alloys’, in: H.I. Kaplan, J. Hryn, and B. Clow (eds), *Magnesium Technology 2000*, TMS, Nashville, March, pp 137–142.
- Shi Z., Song G., St John D. (2001), ‘A method for evaluating the corrosion resistance of anodised magnesium alloys’, *Corrosion and Prevention 2001*, ACA, Newcastle, Australia, Paper # 058.
- Shi Z., Song G., Atrens A. (2005), ‘Influence of the β phase on the corrosion performance of anodised coatings on magnesium–aluminum alloys’, *Corrosion Science*, 47: 2760–2777.
- Shi Z., Song G., Atrens A. (2006a), ‘Corrosion resistance of anodized single-phase Mg alloy’, *Surface & Coatings Technology*, 201: 492–503.
- Shi Z., Song G., Atrens A. (2006b), ‘Influence of anodizing current on the corrosion resistance of anodized AZ91D magnesium alloy’, *Corrosion Science*, 48: 1939–1959.
- Shi Z., Song, G., Atrens A. (2006c), ‘The corrosion performance of anodized magnesium alloys’, *Corrosion Science*, 48: 3531–3546.
- Skar J. I. (1999), *Materials and Corrosion*, 50, 2.
- Song G. (2004a) (CAST Research Center), ‘Environment-friendly, Non-toxic and Corrosion Resistant Magnesium Anodisation’, Australian Patent 2004904949.
- Song G. (2004b), ‘Investigation on corrosion of magnesium and its alloys’, *The Journal of Corrosion Science and Engineering* (JCSE), Volume 6, Paper C104.
- Song G. (2005a), ‘Corrosion and protection of magnesium alloys: An overview of research undertaken by CAST’, *Materials Science Forum*, Vol. 488–489: 649–652.
- Song G. (2005b), ‘Recent progress in corrosion and protection of Mg alloys’, *Advanced Engineering Materials*, 7(7), 563–586.
- Song G. (2006), *Corrosion and Protection of Magnesium Alloys*, Chemical Industry Press, (in Chinese).
- Song G. (2007a), ‘Control of biodegradation of biocompatible magnesium alloys’, *Corrosion Science*, 49: 1696–1701.
- Song G. (2007b), ‘Control of degradation of biocompatible magnesium in a pseudo-physiological environment by a ceramic-like anodized coating’, *Advanced Materials Research*, 9(4): 1–5.
- Song G. (2009a), ‘An irreversible dipping sealing technique for anodized ZE41 Mg alloy’, *Surface & Coatings Technology*, 203: 3618–3625.
- Song G. (2009b), ‘Effect of tin modification on corrosion of AM70 magnesium alloy’, *Corrosion Science*, 51: 2063–2070.
- Song G. (2009c), ‘Electroless E-coating: An innovative surface treatment for magnesium alloys’, *Electrochemical and Solid-state Letters*, 12: D77–D79.

- Song G. (2009d), 'Potential and current distributions of one-dimensional galvanic corrosion systems', *Corrosion Science*, doi:10.1016/j.corsci.2009.10.003
- Song G., Atrens A. (1998), 'Corrosion Behaviour of Skin Layer and Interior of Diecast AZ91D', *International Conference on Magnesium Alloys and Their Applications*, pp 415–419, Wolfsburg.
- Song G., Atrens A. (1999), 'Corrosion Mechanisms of Magnesium Alloys', *Advanced Engineering Materials*, 1(1): 11–33.
- Song G., Atrens A. (2003), 'Understanding Magnesium Corrosion, a Framework for Improved Alloy Performance', *Advanced Engineering Materials*, 5(12): 837–857.
- Song G., Atrens A. (2007), 'Recent insights into the mechanism of magnesium corrosion and research suggestions', *Advanced Engineering Materials*, 9(3): 177–183.
- Song G., Shi Z. (2006), 'Characterization of anodized coatings on a magnesium alloy', in M.O. Pekguleryuz and L.W.F. Mackenzie (eds), *Magnesium Technology in the Global Age, 45th Annual Conference of Metallurgists of CIM*, Montreal, Quebec, Oct. 2006, pp 385–395.
- Song G., Song S. (2006), 'Corrosion Behaviour of Pure Magnesium in a Simulated Body Fluid', *Acta Physico Chimica Sinica*, 22(10): 1222–1226.
- Song G., Song S. (2007), 'A possible biodegradable magnesium implant material', *Advanced Engineering Materials*, 9(4): 298–302.
- Song G., St John D. (2000), 'Corrosion Performance of Magnesium Alloys MEZ and AZ91', *International Journal of Cast Metals Research*, 12, 327–334.
- Song G., St John D. (2002), 'The effect of zirconium grain refinement on the corrosion behaviour of magnesium–rare earth alloy MEZ', *Journal of Light Metals*, 2, 1–16.
- Song G., St John D. (2004), 'Corrosion behaviour of magnesium in ethylene glycol', *Corrosion Science*, 46: 1381–1399.
- Song G., St John D. (2005), 'Corrosion of magnesium alloys in commercial engine coolant', *Materials and Corrosion*, 56(1): 15–23.
- Song G., Atrens A., St John D. H., Wu X., Nairn J. (1997a), 'Anodic dissolution of magnesium in chloride and sulphate solutions', *Corrosion Science*, 39(10–11): 1981.
- Song G., Atrens A., St John S., Nairn J., Li Y. (1997b), 'The Electrochemical Corrosion of Pure Magnesium in 1N NaCl', *Corrosion Science*, 39 (5): 855–857.
- Song G., Atrens A., Wu X., Zhang B. (1998), 'Corrosion Behaviour of AZ21, AZ501 and AZ91 in Sodium Chloride', *Corrosion Science*, 40 (10): 1769–1791.
- Song G., Atrens A., Dargusch M. (1999), 'Influence of microstructure on the corrosion of diecast AZ91D', *Corrosion Science*, 41: 249–273.
- Song G., Atrens A., St John D. (2001), 'A Hydrogen Evolution Method for the Estimation of the Corrosion Rate of Magnesium Alloys', in J. Hryn (ed), *Magnesium Technology 2001*, TMS, New Orleans, 2001, pp 255–262.
- Song G., Bowles A. L., St John D. H. (2004a), 'Corrosion resistance of aged die cast magnesium alloy AZ91D', *Materials Science and Engineering*, A366: 74–86.
- Song G., Johannesson B., Hapugoda S., St John D. H. (2004b), 'Galvanic corrosion of magnesium alloy AZ91D in contact with an aluminum alloy, steel and zinc', *Corrosion Science*, 46, 955–977.
- Song G., St John D., Abbott T. (2005a), 'Corrosion behaviour of a pressure diecast magnesium alloy', *International Journal of Cast Metals Research*, 18(3): 174–180.
- Song G., St John D., Bettles C., Dunlop G. (2005b), 'Corrosion performance of magnesium alloy AM-SC1 in automotive engine block applications', *JOM*, 57(5): 54–56.

- Song G., Shi Z., Hinton B., McAdam G., Talevski J., Gerrard D. (2006a), 'Electrochemical evaluation of the corrosion performance of anodized magnesium alloys', *14th Asian-Pacific Corrosion Control Conference*, Oct., Shanghai, Paper# Keynote-11.
- Song G., Hapugoda S., St John D. (2006b), 'Degradation of the surface appearance of magnesium and its alloys in simulated atmospheric environments', *Corrosion Science*, 49: 1245–1265.
- Song G., Song S., Li Z. (2007), 'Corrosion Control of Magnesium as an Implant Biomaterial in Simulated Body Fluid', *Ultralight2007 – 2nd International Symposium on Ultralight Materials and Structures*, Beijing, Sept.
- Starostin M., Smorodin A., Cohen Y., Gal-Or L., Tamir S. (2000), 'Galvanic corrosion of magnesium alloys', in: E. Aghion and D. Eliezer (ed.), *Magnesium 2000, Proc. of the Second Israeli International Conference on Magnesium Science and Technology*, Dead Sea, Israel, pp 363–370.
- Teeple H. O. (1956), 'Atmospheric galvanic corrosion of magnesium coupled to other metals', *ASTM, STP 175*, pp 89–115.
- Uzan P., Frumin N., Eliezer D., Aghion E. (2000), 'The Role of Composition and Second Phases on the Corrosion Behaviour of AZ Alloys', in E. Aghion and D. Eliezer (eds), *Magnesium 2000, Proc. of the 2nd Israeli International Conference on Magnesium Science and Technology*, Dead Sea, pp 185–191.
- Waber J. T., Rosenbluth M. (1955), *Journal of the Electrochemical Society*, 102, 344.
- Wan Y., Tan J., Song G., Yan C. (2006), 'Corrosion Morphology of AZ91D exposed in a simulated atmospheric environment', *Metallurgical and Materials Transactions*, 37A(7): 2313–2316.
- Wang H., Estrin Y., Fu H. M., Song G., Zúberová Z. (2007), 'The effect of pre-processing and grain structure on the bio-corrosion and fatigue resistance of magnesium alloy AZ31', *Advanced Engineering Materials*, 9(11): 967–972.
- Weininger J. L., Breiter M. W. (1963), *Journal of The Electrochemical Society*, 110, 484.
- Weiss D., Bronfin B., Golub G., Aghion E. (1997), 'Corrosion resistance evaluation of magnesium and magnesium alloys by an ion selective electrode', in E. Aghion and D. Eliezer (eds) *Magnesium 97, Proceedings of the First Israeli International Conference on Magnesium Science and Technology*, Dead Sea, pp 208–213.
- Winzer N., Atrens A., Song G., Ghali E., Dietzel W., Kainer K. U., Hort N., Blawert C. (2005), 'A critical review of the stress corrosion cracking (SCC) of magnesium alloys', *Advanced Engineering Materials*, 7(8): 659–693.
- Winzer N., Atrens A., Dietzel W., Song G., Kainer K. U. (2007), 'Stress corrosion cracking of magnesium alloys', *JOM*, August: 49.
- Winzer N., Atrens A., Dietzel W., Song G., Kainer K. (2008), 'Stress corrosion cracking (SCC) in Mg-Al alloys studied using compact specimens', *Advanced Engineering Materials*, 10(5): 453–458.
- Yim C., Shin E. K. (2001), 'Effect of Heat Treatment on Corrosion Behaviour of an AZ91HP Magnesium Alloy', in *Proc. of the 12th Asia Pacific Corrosion Control Conference 2001*, Seoul, Vol. 2, pp 1306–7.
- Zamin M. (1981), *Corrosion*, 37(11): 627.
- Zhao M., Liu M., Song G., Atrens A. (2008a), 'Influence of Homogenization Annealing of AZ91 on Mechanical Properties and Corrosion Behavior', *Advanced Engineering Materials*, 10, No. 1–2, 93–103.
- Zhao M., Liu M., Song G., Atrens A. (2008b), 'Influence of pH and chloride ion concentration on the corrosion of Mg alloy ZE41', *Corrosion Science*, 10 (1–2): 104–111.

- Zhao M., Liu M., Song G., Atrens A. (2008c), 'Influence of the beta phase morphology on the corrosion of the Mg alloy AZ91', *Corrosion Science*, 50: 1939–1953.
- Zhu L., Liu H., Li W., Song G. (2005), 'Zinc alloyed coating on AZ91D magnesium alloys', *Journal of Beijing University of Aeronautics and Astronautics*, 31(1): 8–12.
- Zhu L., Song G. (2006), 'Improved corrosion resistance of AZ91D magnesium alloy by an aluminum-alloy coating', *Surface and Coatings Technology*, 200(8): 2834–2840.

Wear properties of aluminium-based alloys

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Abstract: Aluminium is one of the light-weight elements that form several engineering alloys and composites because of its unusual blend of properties such as low density, high strength, corrosion resistance, non-magnetic properties and low cost. In this chapter, a brief background on aluminium is described, followed by an introduction to wear and its various types. Wear behaviour of aluminium alloys is complex and can vary under different application conditions. Under sliding wear conditions, the wear rate of aluminium is affected by applied load, sliding speed, type of counterface material, etc. The influence of alloying elements on the wear behaviour is highlighted. The concept of wear mechanism mapping is described.

Key words: aluminium, wear, abrasion, sliding, friction, alloys, composites, metal matrix composite (MMC), wear map, counterface, wear rate, microstructure, casting, alloying, silicon, copper, nickel, precipitation hardening, strengthening, wear mechanism.

2.1 Introduction

Aluminium (or aluminum) is an element with symbol Al and atomic number 13. It is the third most abundant element occurring in the earth's crust after silicon and oxygen. As it has very high affinity towards oxygen, aluminium occurs as oxide or silicate compounds. The most common ore is bauxite, which contains aluminium oxide from which metallic aluminium is extracted.

Ancient Greeks and Romans used aluminium in salt form before Humphry Davy identified the existence of a metallic form of aluminium. Before the discovery of the Hall–Heroult electrolytic process, aluminium was very difficult to extract from its ore. It was considered more valuable than gold. Napoleon was known to provide gold spoons to his army generals and other lower ranking officials, reserving aluminium cutlery for the visiting royals!

Bauxite, the main ore of aluminium, is converted to aluminium oxide (alumina) via the Bayer Process. The alumina is then converted to aluminium metal using electrolytic cells and the Hall–Heroult process. Since the Hall–Heroult electrolytic process requires an enormous amount of energy, most of the aluminium extraction plants are located where energy is cheaper. Aluminium and its alloys are used in many different applications ranging from kitchen utensils through automotive parts to aerospace components. The automotive industry has been spearheading the use of light-weight materials to reduce the total vehicle weight in order to produce fuel efficient vehicles.

Table 2.1 shows the cast aluminium–silicon alloys used in automotive applications.

The important factors in selecting aluminium and its alloys are their high strength-to-weight ratio, good corrosion resistance, high thermal and electrical conductivity, appearance, and good fabrication characteristics. These properties make aluminium a very important material in applications in the aircraft, automotive, construction, packaging and electrical machinery industries.

Various elements are mixed with aluminium to form different types of alloys. Some of the alloying elements form solid solutions while others contribute to strengthening/hardening through precipitation effects. The extent of solid solution of an individual element in aluminium depends on its solid solubility limits, which can be determined from the phase diagrams. Precipitation hardening is a two-stage heat treatment process applicable to certain alloy types.

Another method of strengthening is through cold working. This is widely used with certain aluminium alloys by subjecting them to cold rolling or some other mechanical process. The plastic deformation resulting from the mechanical work creates new dislocations. The strength of the alloy increases because of the hindrance to the dislocation movement through the complex interactions of dislocations.

Metal matrix composite (MMC) materials based on aluminium are now commercially available. The MMC route is yet another way of making aluminium alloys stronger and more wear resistant. There are several types of second-phase particulates or fibres that can be incorporated through a liquid or powder metallurgy route. MMC products are stronger, stiffer and harder than their matrix alloys. Soft second-phase particles such as graphite can also be added for improved frictional and wear properties.

2.2 Classification of aluminium alloys

Wrought aluminium alloys are identified in the US by a four digit system. (This American classification system has an equivalent one in the ISO

Table 2.1 Aluminium–silicon alloys used in automotive applications

SAE alloy	Application
319.0	General purpose alloy
332.0	Compressor pistons
333.0	General purpose
336.0	Piston alloy (low expansion)
339.0	Piston alloy
355.0	Pump bodies, cylinder heads
390.0	Cylinder blocks, transmission pump and air compressor housings, small engine crankcase, air conditioner pistons

system.) The first digit indicates the alloy group according to the major alloying element:

- 1xxx Aluminium 99.0% minimum
- 2xxx Copper (1.9 – 6.8%)
- 3xxx Manganese (0.3 – 1.5%)
- 4xxx Silicon (3.6 – 13.5%)
- 5xxx Magnesium (0.5 – 5.5%)
- 6xxx Magnesium and Silicon (Mg 0.4 – 1.5%; Si 0.2 – 1.7%)
- 7xxx Zinc (1 – 8.2%)
- 8xxx Other elements
- 9xxx Unused series

A range of heat treatments can be applied to aluminium alloys. Homogenization is the removal of the segregation of alloying elements by heating after casting. Annealing is used after cold working to soften work-hardening alloys (1xxx, 3xxx and 5xxx). Hardening treatment involves solution heat treatment followed by the ageing of precipitation hardenable alloys (2xxx, 6xxx and 7xxx).

After heat treatment, a suffix is added to the designation numbers:

O means annealed wrought products.

T means that it has been heat treated.

W means the material has been solution heat treated.

H refers to non-heat treatable alloys that are cold worked or strain hardened.

The non-heat-treatable alloys are those in the 3xxx, 4xxx and 5xxx groups.

Cast aluminium alloys are designated by a four-digit number with a decimal point separating the third and the fourth digits. The first digit indicates the alloy group based on the major alloying element:

- 1xx.x Aluminium 99.0% minimum
- 2xx.x Copper (4 – 4.6%)
- 3xx.x Silicon (5 – 17%) with added copper and/or magnesium
- 4xx.x Silicon (5 – 12%)
- 5xx.x Magnesium (4 – 10%)
- 7xx.x Zinc (6.2 – 7.5%)
- 8xx.x Tin
- 9xx.x Others
- 6xx.x Unused series

The second and third digits indicate the alloy purity or identify the alloy type. In the alloys of the 1xx.x series, the second and third digits indicate the level of purity of the alloy – they are the same as the two digits to the right of

the decimal point in the minimum concentration of aluminium (in percents). For example, Alloy 150.0 indicates a minimum of 99.50% aluminium in the alloy whereas Alloy 120.1 indicates a minimum of 99.20% aluminium in the material. In all other groups of aluminium alloys (2xx.x through 9xx.x) the second and third digits signify different alloys in the group.

The last digit indicates the product form – casting (designated by ‘0’) or ingot (designated by ‘1’ or ‘2’ depending on chemical composition limits).

2.3 Composites

Metal matrix composite (MMC) products based on aluminium alloys are increasingly being used for commercial applications in the automotive, aerospace and electronic industries. Aluminium-based composites contain a second phase in the form of particulates, continuous fibres or discontinuous/short fibres, or whiskers. The process of incorporation of these reinforcements can range from liquid to powder metallurgy to spray deposition technologies. Particulate reinforcements are predominant in aluminium matrix composites. The key issues in the adoption of MMC products are the high manufacturing cost, machining and competition from other materials.

Aluminium alloys such as the 2000, 5000, 6000 and 7000 alloy series, are most commonly utilized as matrix materials in the fabrication of MMCs for aerospace applications. In the cast alloy series, aluminium–silicon alloys such as A356 are widely used. Alumina, zirconia or silicon carbide particles are widely used as reinforcing materials for automotive applications.

2.4 Introduction to wear

Wear can be defined as ‘progressive loss of material from surfaces which are in relative motion under load’ (Suh, 1986). Over 6% of US GDP has been estimated to be lost due to wear (Rabinowicz, 1984). By adapting the current technologies, some of these losses can be reduced. Wear reduction technologies can be developed by understanding the behaviour of materials under different conditions. There are many different classifications of wear described in the literature – sliding, abrasive, erosive, corrosive and fatigue wear. A brief overview of each wear type is given below.

- *Sliding wear.* This type of wear occurs when a solid rubs against another solid. It has been popularly known as adhesive wear. The word ‘adhesive’ assumes that there is adhesion between contacting surfaces ignoring other possible mechanisms. Rigney (1988) has advocated the use of the term sliding wear instead of adhesive wear. This type of wear, is also described as metal-on-metal wear, as sliding occurs often between two

metallic surfaces. However, a metal alloy sliding on a non-metal such as a ceramic or a plastic can also be considered as a sliding wear couple. The sliding interface can be unlubricated (dry), partially lubricated, or fully lubricated, depending on the application. The surfaces of the contacting parts are generally smooth.

- *Abrasive wear.* Abrasive wear (or abrasion) occurs when a hard particle or protuberance on the surface of a body interacts with the surface of the component, tool or machinery. Abrasion can be two or three body, depending on the number of components involved in the system. For example, when a rough, hard surface is sliding on a softer surface, it is called two-body abrasion. On the other hand, when loose abrasive particles are present between sliding surfaces, it is termed three-body abrasion.

Abrasive wear can also be termed mild or severe, depending on the wear rate. In very extreme cases, it is called gouging wear, where large chunks of metal are removed at a fast rate.

The mechanisms by which wear occurs can also be used to further classify abrasive wear. For example, ploughing, cutting, cracking and fatigue are commonly found as micro mechanisms.

Factors influencing abrasion include applied load, speed, angle of attack, abrasive particle size, shape and hardness, fracture toughness and lubrication.

- *Erosive wear.* Erosive wear (or erosion) occurs when hard particles carried in a stream of fluid (gas or liquid) impinge on the surface of components. If the particles are hard and sharp, they accelerate erosive wear rate. The angle of impact and the strength and toughness of the substrate material are important factors in determining the erosion rate. Other key factors that influence erosion are velocity, temperature, particle hardness, size, shape, volume fraction, microstructure and surface hardness.
- *Corrosive wear.* Corrosive wear occurs when there is mechanical action (wear) combined with chemical action (corrosion). Generally, there is a synergy between corrosion and wear, meaning that the rate of material loss is more than the sum of material losses due to corrosion or wear alone. When a surface is exposed to a corrosive atmosphere, the surface reacts with the environment and forms a thermodynamically more stable compound such as oxide. If this surface layer is disturbed by a mechanical process such as wear, the virgin material gets exposed, forming more oxide. Thus the corrosion is accelerated due to mechanical action. Further, the environment product may also accelerate wear as its hardness is often higher than the substrate material and thus it also causes abrasion.
- *Contact fatigue wear.* The repeated application of contact stress to a component can result in crack initiation and growth, leading to spallation

of material from the surface. For example, contact fatigue occurs in rail/wheel contact situations, where the surface material is loaded and unloaded as the wheel moves on the rail. These repetitive loading and unloading cycles lead to fatigue. The subsurface material gets deformed and a crack gets initiated at a second phase particle or a defect, leading to the removal of a large debris particle. This leaves a crater on the surface. Other examples where contact fatigue is observed are in gears and bearings.

2.5 Sliding wear of aluminium alloys

As the majority of the tribological applications involving aluminium alloys are related to sliding wear or metal-to-metal contact, the focus in this chapter will be on dry sliding wear (The effect of lubrication is important in sliding wear situations but it will not be covered here. However, knowledge obtained under dry sliding conditions is useful in understanding lubricated wear conditions. It should be pointed out that even under lubricated conditions wear occurs whenever there is a breakdown of lubricant film.) The dry sliding wear behaviour of aluminium alloys is influenced by a number of factors including material factors such as chemical composition, microstructure and hardness, and system factors such as counterface and temperature.

2.5.1 Chemical composition

The aluminium alloys used in wear applications contain silicon, copper, magnesium, zinc and nickel as their alloying elements, along with other elements such as modifiers, grain refiners and impurities.

No element is completely soluble in aluminium in the solid state. Only five elements have a maximum solubility of more than 5 at.% and at room temperature and only a few elements have a solid solubility of more than 0.5 at.%. Therefore the extent of solid solution strengthening in aluminium is limited.

Silicon is a very important alloying element for aluminium. There is very little solid solubility of silicon in aluminium, or *vice versa*. Aluminium and silicon form a eutectic at around 12.5 wt.%. The aluminium alloys used in wear applications generally contain silicon as the major alloying element. The hard silicon crystals offer strength and wear resistance. The key factors of silicon that control wear are amount, size, shape and distribution.

Copper, with maximum solubility limits of 5.7 wt.%, is an important alloying element. Its solubility decreases as the temperature decreases to room temperature, making this alloy amenable for precipitation hardening. In fact, the first age hardening effect was observed in an aluminium–copper alloy with very fine CuAl_2 precipitates. As the hardness of aluminium alloys

increases due to precipitation, their wear resistance increases to a maximum around peak hardness (Subramanian, 1985).

The addition of copper up to 4 wt.% to Al–Si alloys has reportedly increased their wear resistance (Eyre and Beesley, 1976). The beneficial effects of copper in aluminium–silicon alloys have also been studied by others (Yamada and Tanaka, 1987; Sukimoto, *et al.*, 1986; Rohatgi and Pai, 1974). It should be noted that the addition of copper beyond its solid solubility limit forms second phase particles which have been reported to have an adverse effect on wear (Eyre and Beesley, 1976).

Manganese forms solution up to 1.4 wt.% and it increases the hardness and tensile strength of aluminium. The amount of manganese is limited to 0.7 wt.% in aluminium–silicon alloys.

Although it has higher solid solubility limits, the amount of magnesium used in aluminium–silicon alloys is generally around 1 wt.%, because of poor mechanical properties at higher amounts due to the formation of brittle, acicular shaped intermetallic compounds. The improvement in wear behaviour of aluminium–silicon alloys containing magnesium is through solid solution hardening.

Zinc, along with Mg, forms an important group of the aluminium alloy family that are age hardenable. Although it has higher solubility, the amount of zinc added to aluminium–silicon alloys is limited to less than 1 wt.%. A systematic study of the addition of zinc on wear behaviour has shown that higher amounts of zinc degrade the wear behaviour of aluminium alloys due to poor high-temperature mechanical properties (Eyre and Beasley, 1976).

Nickel, though not used very much due to high cost, reacts with aluminium to form Ni_3Al precipitates that increase hardness and temperature resistance. Its solubility is less than 0.5 wt.%, although aluminium alloys containing up to 4 wt.% have been studied (Rooy, 1972). Nickel additions in aluminium–silicon alloys can vary from 1 to 3 wt.% with associated improvement in wear resistance.

Iron, if present alone, forms an intermetallic compound with aluminium at grain boundaries and impairs mechanical properties. When elements such as manganese, chromium, cobalt and molybdenum are present, iron forms intermetallic compounds that are less harmful to mechanical properties.

Other elements usually added to aluminium alloys include tantalum, titanium and zirconium (grain refiners), sodium and strontium (eutectic silicon modifiers) and phosphorus (primary silicon modifier). The influence of refiners and modifiers on the wear behaviour is not straightforward, but they can change the morphologies of both eutectic and primary silicon and thus may affect the wear behaviour of aluminium alloys.

The limits of equilibrium solid solubility in the ingot alloys can be overcome by rapid solidification and powder metallurgy (including mechanical alloying) methods. The abrasive wear resistance has been shown to be better in a

rapidly solidified alloy than in conventional ingot alloys (Rao and Sekhar, 1986).

2.5.2 Microstructure

In the previous section, we have seen the role of varying alloying elements. Silicon and other second phases present in the aluminium matrix control the mechanical properties including the wear behaviour of aluminium–silicon alloys. Often, the role of microstructure in wear is not fully understood because of varying operating conditions.

There are reports that state there is no effect of silicon on wear behaviour of aluminium–silicon alloys, whereas others have found a definitive advantage of using eutectic alloy with around 12.5 wt.% silicon. Yet another group has advocated a hypereutectic alloy's better wear resistance. It has been speculated that uncontrolled composition and varying test conditions are to be blamed for this confusion (Subramanian, 1989). For example, Vandelli (1968) found that aluminium-17 wt.% silicon alloy has better wear resistance than alloys containing 14.5 or 25 wt.% silicon, but other alloying elements such as copper and nickel were not held constant. The alloy that had higher wear resistance had higher hardness, presumably due to solid solution strengthening by the presence of copper. Pramila Bai and Biswas (1986) found no variation in the wear rate of aluminium alloys with varying silicon contents from 4 to 15 wt.% except that pure aluminium wears slightly more than the aluminium–silicon alloys. They used commercial alloys with small amounts of other elements such as iron, manganese, titanium and copper. A similar observation was also made by Okabayashi and Kawamoto (1968). However, silicon plays a role in the transition load, i.e. the load at which the wear mechanism changes from fine equiaxed particles to laminar particles.

Another controversy concerns the optimum size of silicon particles in wear-resistant aluminium alloys. Aluminium-silicon alloys contain eutectic silicon plus either primary aluminium (hypoeutectic) or primary silicon (hypereutectic). The size of the eutectic and primary silicon particles can be reduced by adding a modifier (sodium or strontium <0.05 wt.%) and a refiner (phosphorus <0.05 wt.%). It is well known that finer silicon particles lead to improved mechanical properties.

The effects of such microstructural refinements on the wear behaviour of aluminium alloys have been observed. It has been reported that modifying the eutectic aluminium–silicon alloy increases the wear resistance of the alloy and its composites (Subramanian and Kishore, 1986), which is in direct contradiction with the study (Pramila Bai *et al.*, 1983) where no beneficial effects were reported. Refinement of primary silicon in hypereutectic aluminium–silicon alloys has been shown to improve the wear resistance (Jaleel *et al.*, 1984). It should be noted that during the sliding process, any

silicon in the near surface region will get fragmented and spherodized to a size range of 1–5 μm , irrespective of its original size (Antoniou and Borland, 1987).

A more recent study by Elmadagli *et al.* (2007) on the influence of microstructure (silicon weight percentage, particle size, morphology and alloy hardness) on the wear behaviour of aluminium–silicon alloys has concluded that increasing the silicon content increased the transition load but had minor effects on wear rates. A similar effect was noted for alloy hardness. On the other hand, a decrease in the aspect ratio or size of silicon particles increased both the wear resistance and transition load.

2.5.3 Hardness

If there is only one mechanical property that controls wear; it is hardness. Its influence on wear has been well recognized in earlier literature. According to Archard (1953), the wear rate of a material increases with applied load and decreases with hardness, as described by the equation:

$$w = k L/H$$

where w = wear rate
 k = wear coefficient
 L = applied load
 H = hardness of the material

Hardness of aluminium alloys can be increased by many methods. However, it should be borne in mind that the method of increasing the hardness matters. For example, work hardening increases the material's hardness but there is no corresponding increase in wear resistance. This is because the subsurface region gets work-hardened during sliding and any prior strain hardening has no effect.

A method to increase hardness is through the solid solution strengthening route. As discussed earlier, many alloying elements are useful in forming solid solution with aluminium, but their influence is limited to their solid solubility limits.

Precipitation, or age hardening, is yet another method of increasing the hardness of aluminium alloys. The presence of nano-sized particles (10 – 150 nm) strengthens the materials through the interaction of dislocations with the particles – looping around or cutting through the precipitates under stress. The peak-aged alloys have been shown to offer the best wear resistance among this group of alloys (Subramanian, 1985). However, the higher temperature developed during sliding under certain conditions could overage the alloy, leading to inferior wear performance. The stability of the second phase may be an important factor in controlling the wear behaviour of aluminium alloys.

Dispersion hardening or strengthening is a technique whereby hard or soft external particles are introduced into the aluminium alloy matrix. This group of materials are also called metal matrix composites (MMC). It should be noted that the incorporation of soft particles such as graphite does, in fact, reduce hardness and therefore the word 'hardening' is a misnomer.

Second phase particles added externally to aluminium alloys are hard particles, such as alumina, zirconia, corundum, silica, fly ash and silicon carbide, and soft particles such as graphite, mica and coconut shell char. The process route is either through liquid metallurgy or powder metallurgy. The addition of soft particles is expected to yield lower friction and thus lower wear rate through solid-lubrication effects in metal-on-metal sliding conditions, whereas the hard particles are for increasing abrasive wear resistance through higher hardness. However, the combination of adding soft and hard particles together to aluminium alloys has also been suggested to improve strength and frictional properties many years ago (Subramanian, 1983).

MMC coatings also form a distinctive group of materials whereby powders of aluminium alloys and hard ceramic particles or soft self-lubricating powders are mixed together and are formed either by a spraying method or a weld overlay technique such as plasma transferred arc (PTA) surfacing. A summary of aluminium-based MMCs that have been studied for wear behaviour are given by Deuis *et al.* (1997).

2.5.4 Counterface

The wear and frictional behaviour of aluminium alloys are determined using laboratory scale wear-test machines. The most popular wear-test methods are pin-on-disc and pin-on-ring machines. There are several other geometries available. The aluminium alloy to be tested for wear resistance can be either of the contacting surfaces or both. As there has been no standard counterface material, several different materials have been used against aluminium alloys in wear testing (Subramanian, 1991a). Aluminium alloy pins are frequently rubbed against steel or cast iron discs. In some cases, aluminum alloys are rubbed against themselves.

Steels containing three levels of hardness were used as counterface materials in a study by Subramanian (1989). The hardness levels varied from 114 to 770 HV. When the hardness of the steel counterface was increased, the wear rate of the aluminium alloy pins decreased and the transition load increased. Here, the transition load refers to the load at which the wear debris changed from equiaxed particles to laminates.

In the same study, copper alloys containing three levels of aluminium were chosen as counterface materials (Subramanian, 1989). The choice of copper was based on the solid solubility concepts postulated over 50 years ago (Goodzeit *et al.*, 1956). When two metals with high mutual solubility are

slid together, they exhibit a greater friction and wear than that of a sliding couple with less mutual solid solubility. When the amount of aluminium in a copper–aluminium alloy is more, the adhesion of aluminium to copper–aluminium alloy is reduced due to partial saturation.

Thermal conductivity of the counterface material plays an important role. The partition of the frictional heat generated at the wearing interface between the aluminium alloy and the counterface material depends on the thermal properties. For example, when a toughened ceramic was used as the counterface, the wear rate was higher and the wear transition occurred at a lower load (Subramanian, 1989, 1991a). Although it was expected that the high hardness of the ceramic would lower the wear rate of aluminium, the poor thermal conductivity of the ceramic disc made the aluminium pin hotter.

Zhang and Alpas (1997) have also found that thermal properties are responsible for wear transitions. The temperatures of the pin and disc were measured. Below the transition load (or speed), the temperature of the pin was lower than that of the disc, but above the transition line, it was *vice versa*. Artificial cooling of the wearing interface extended the wear transition to a higher load and speed.

One of the main reasons why researchers have reported different wear rates for an aluminium alloy was that different counterface materials were used. The counterface materials interact with the aluminium pin differently in terms of asperity size, adhesion of asperities in the wearing surfaces, and heat generation and removal from the wearing interface. In summary, the influence of the counterface on the wear of aluminium alloys is through its hardness, solid solubility and thermal conductivity.

2.5.5 Sliding distance

The initial contact between aluminium pins on a counterface is very important. There are many ways the pin can contact the disc. The pin can have a flat, conical or hemispherical end touching the counterface. If a flat surface is used, the apparent area of contact is supposed to remain constant through the test. But in practice, this may not always be possible due to misalignment of the pin against the disc. If a pin with a hemispherical end is used, it starts off with a point contact (in theory) and the area of contact increases as it wears down, apparently reducing the applied stress or pressure. It is the author's experience that in the first few hundred metres of sliding, the wear rate decreases, reaching an equilibrium or steady state after a certain distance or time (Subramanian, 1989).

As the sliding distance increases, the pin–disc system has enough time to reach an equilibrium where the temperature at the interface is stable. The tribo-layer is also well established due to transfer, back transfer and mechanical mixing at the rubbing surface (Zhang and Alpas, 1997).

2.5.6 Load

The applied load on the wearing surface has a significant effect on the wear rate; wear increases with load (Subramanian, 1989). When the rate of increase in the wear rate of an aluminium alloy changes at critical loads, it often means that the mechanism of wear has changed.

The wear mechanism map to be discussed in a later section has applied load as normalized stress on the vertical axis representing a ratio of the real area of contact to the apparent area.

The effect of applied load on the frictional behaviour as measured by the friction coefficient (i.e. frictional force/applied load) is rarely significant. However, whenever there is a large variation in the friction coefficient, there is a likelihood of observing a change in the wear mechanism and/or wear rate. The range of friction coefficients of aluminium sliding against several metallic counterfaces in air generally varies from 0.4 to 0.6. Attempts to correlate friction coefficient to wear rate rarely has yielded a good correlation.

As the effect of applied load on wear is more pronounced than that of sliding speed, the majority of the published literature has focused on the former.

2.5.7 Sliding speed

The relative speed between the sliding surfaces affects the wear rate and mechanisms of aluminium alloys. The temperature of the sliding surfaces depends on the sliding speed at which the rubbing surface moves in relation to the counterface. The transition from one wear mechanism to another occurs when the sliding speed is increased. At low speeds, the wear rate of aluminium alloys decreases with sliding speed, reaching a minimum, and then increases (Subramanian, 1991b). The trend of decreasing wear rate with speed is due to the increased strength of the asperities with strain rate. It is known that the strength of aluminium alloys increases with the rate of loading, i.e. strain rate. This is true up to a particular speed, above which the wear rate increases. This increase in wear rate is due to softening of the aluminium by frictional heat where the temperature effect becomes dominant.

The wear mechanism map discussed later has sliding speed as normalized velocity on the horizontal axis, representing the ratio of generation to removal of frictional heat.

2.5.8 Temperature

The ambient temperature can influence the wear behaviour of aluminium alloys and their composites. As the test temperature is increased, the hardness of the material decreases, resulting in a larger true area of contact. At high

temperatures, the resistance to crack propagation is diminished and therefore there is accelerated debris formation.

Several studies have focused on the wear behaviour of aluminium-based composites at high temperatures. Deuis and Subramanian (2000) have studied high temperature wear behaviour of MMC coatings produced by plasma transferred arc (PTA) surfacing. Singh and Alpas (1996) and Wilson and Alpas (1997) have extensively studied wear of MMCs. A more recent study by Kumar *et al.* (2009) has presented wear behaviour at test temperatures between 100 and 300°C of aluminium–silicon alloys containing *in situ* formed titanium diboride particles.

All these studies conclude that addition of hard particles reduced wear rates and increased the mild to severe transition loads.

2.5.9 Test methods

There have been several test geometries used under arbitrary conditions, making comparison of wear data from different studies difficult. However, most of the studies have used either pin-on-disc or pin-on-ring geometry with the pin being made of the subject material, i.e. aluminium alloy. There are several counterface materials used, from aluminium (self-mating) through steels and ceramics. The steel counterface had various microstructures, from soft ferrite/pearlite to hard martensite. The effects of counterface materials on aluminium wear behaviour have been discussed earlier.

The size, shape and stiffness of the sample holder should also be monitored, as this will have a significant effect on the wear behaviour of aluminium alloys. If the sample holder acts as a heat sink, there is some cooling and this will influence the transition load and speed.

2.6 Wear maps

Lim and Ashby (1987) introduced the concept of wear mechanism maps for the sliding wear of steel. This is a useful tool to describe the wear behaviour of steel under different sliding conditions, using normalized pressure and normalized velocity. The variables used in the construction of the wear mechanism map are described below:

$$\text{Normalized pressure, } P = F/HA \quad [2.2]$$

$$\text{Normalized velocity, } V = vr/a \quad [2.3]$$

$$\text{Normalized wear rate, } W = w/A \quad [2.4]$$

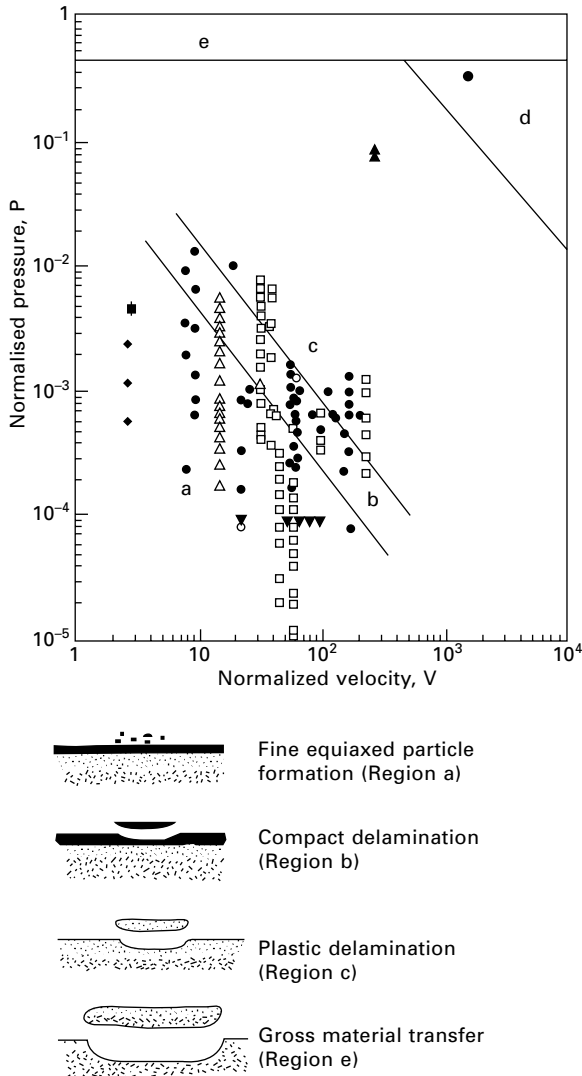
Where F = applied load, N

H = room temperature hardness, N/m²

A = apparent area of contact, m²

v = sliding speed, m/s
 r = radius of the pin, m
 a = thermal diffusivity, m^2/s
 w = wear rate, m^3/m

Following the work of Lim and Ashby (1987), a qualitative wear mechanism map was published for aluminium alloys by Antoniou and Subramanian (1988). Figure 2.1 shows various regions of wear identified by wear



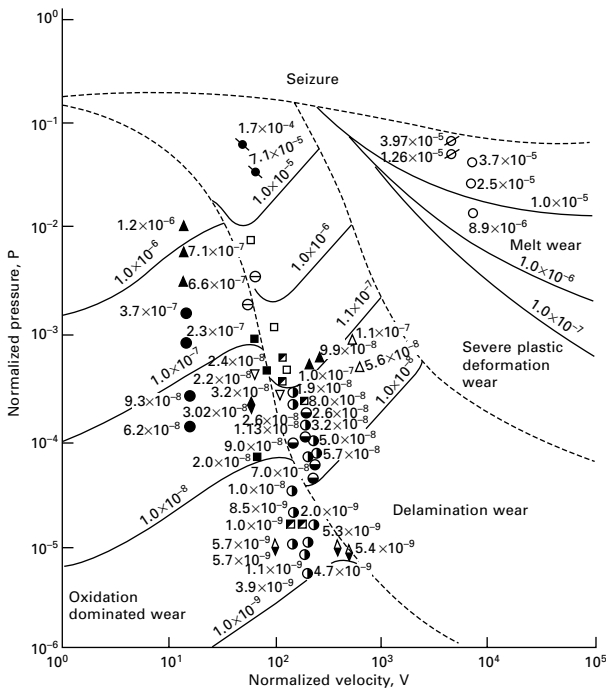
2.1 Regions of wear identified by wear debris morphology and worn surface topography of aluminium and the counterface.

debris morphology and worn surface topography of the aluminium and the counterface. A few years later, Liu *et al.* (1991) produced a quantitative wear map for aluminium alloys with iso-wear rate lines superimposed on the wear mechanism map, Fig. 2.2.

Various identified mechanism regions are summarized in Table 2.2. A brief description of each mechanism is given below (Antoniou and Subramanian, 1988):

Region a – Fine equiaxed particle formation. In this wear regime, tribolayers form on the sliding surfaces of aluminium alloy and the counterface. The tribolayer consists of finely ground and mechanically mixed materials from the sliding surfaces. It occurs through transfer and back transfer of aluminium and counterface materials. The environment may have a role to play, such as through oxidation. The extent of oxidation in the formation of these tribolayers is yet to be proven. There was no evidence for the presence of crystalline oxides but it is speculated that amorphous oxides of aluminium could be present. The presence of iron oxide is likely when steel counterfaces are used.

Region b – Delamination of compact layer. At higher load and/or sliding speed, delamination of the compacted layer occurs. We can also call this



2.2 Quantitative wear map for aluminium alloys with iso-wear rate lines superimposed on the wear mechanism map (Liu *et al.*, 1991).

compact layer a kind of tribolayer, as the constituents are derived from the sliding surfaces of aluminium and the counterface, and possibly through the reaction with the environment. This is a transition zone between the equiaxed particle formation and plastic delamination. The tribolayer continues to exist in this regime. However, the wear debris consists mostly of laminar particles detached from the tribolayer instead of only equiaxed particles as in Region a.

Region c – Plastic delamination. When the applied load and speed are increased further, the temperature of the interface reaches a critical value. This makes the aluminium alloy softer and the depth of subsurface deformation increases. The shear instability created by the frictional force results in the formation of laminar particles from the surface. According to the delamination theory proposed by Suh *et al.* (1977), a crack initiates at a weak point, such as a defect or a second phase particle, and grows due to repeated application of force through the contacting asperities, leading to eventual formation of a laminar particle. The particle consists of aluminium and little or no counterface material. Generally, the environmental reaction product such as oxide is absent under these conditions.

Region d – Melt wear. The surface of the aluminium alloy can reach temperatures close to its melting point when the applied load and sliding speed are very high. The molten film of aluminium would reduce the coefficient

Table 2.2 Wear mechanisms of aluminium alloys under dry sliding conditions (Subramanian, 1991b)

Region	Mechanism	Debris	Worn surface	Subsurface deformation	Counterface	Wear rate, (m ³ /m)
a	Fine, equiaxed particle formation	<5 µm Equiaxed Dark in appearance	Dark in appearance Smooth	Yes	Dark in appearance Fairly smooth	10 ⁻¹³ – 10 ⁻¹²
b	Compact delamination	20–200 µm Laminar Dark in appearance	Dark with metallic spots Smooth and pitted	Yes	Dark in appearance Rough	10 ⁻¹³ – 10 ⁻¹²
c	Plastic delamination	20–200 µm Laminar Metallic	Rough Metallic Pitted	Yes	Rough Transferred aluminium	10 ⁻¹²
d	Melt	Globular	Knobbly	No data	Transferred aluminium	No data
e	Gross material transfer	Irregular chunks	Rough	No	Heavy transfer of aluminium	10 ⁻¹¹ – 10 ⁻¹⁰

of friction in this regime. Wear occurs through the ejection of the molten droplets from the wearing surface. It is very difficult to produce melt wear in aluminium, unlike in steel, which has lower thermal conductivity. Studies exploring the melt wear of aluminium are limited. Further studies are required in this area.

Region e – Gross material transfer. At very high loads and sliding speeds, significant amounts of material get transferred between the aluminium alloy and the counterface. Once the disc is coated with a layer of aluminium, it results in like-on-like metal sliding, leading to the formation of large wear particles. Seizure occurs under these conditions when the real area of contact is equal to the nominal area of contact.

2.7 Future trends

Chemical composition and mechanical and thermal treatments determine the microstructure which, in turn, influences the wear behaviour of aluminium alloys. The wear behaviour is system-dependent, since the test variables such as the counterface affect the wear rate and wear transitions.

One of the tools developed to understand the wear behaviour of aluminium alloys is wear mechanism mapping. These maps describe the wear mechanisms in a diagram of normalized load and normalized speed with iso-wear rate lines. As can be seen from the wear mechanism maps, the majority of wear data exists in the middle of the wear map and there is a need for more data in the very low load and speed regions. Ultra-mild wear data produced by Alpas and his team fills some of the gaps (e.g. Wilson and Alpas, 1997). As wear transitions are linked to the high temperature stability of aluminium alloys, further research should be focused on improving the high temperature strength of these materials as well as designing wear systems with effective heat removal from the rubbing surfaces.

Abrasive wear is also of industrial importance, but the low hardness values of aluminium alloys make them unsuitable for such applications. However, incorporating hard abrasive particles, either through a liquid metallurgy or powder metallurgy route, makes them hard enough to provide sufficient resistance to abrasion for some purposes. More research needs to be carried out in this area. Possible options include matrix hardening, hard particle type and loading, and interface engineering. The development of new *in-situ* composite materials should also be explored. MMC overlay coating is also an option.

2.8 References

- Antoniou R and Borland D W, (1987), *Mater Sci Eng*, 93, 57.
 Antoniou R and Subramanian C, (1988), *Ser Metall Mater*, 22, 809–814.

- Archard J F, (1953), *J App Phys*, 24, 981.
- Deuis R L, Subramanian C and Yellup J M, (1997), *Comp Sci Tech*, 57, 415–435.
- Deuis R L and Subramanian C, (2000), *Mater Sci Tech*, 16, 209–219.
- Elmadagli M, Perry T and Alpas A T, (2007), *Wear*, 262, 79–92.
- Eyre T S and Beesley C, (1976), *Trib Int*, 9, 63.
- Goodzeit G L, Hunnicut R P and Roach A E, (1956), *Trans ASME*, 78, 1669.
- Jaleel T K A, Raman N, Biswas S K and Murthy K S S, (1984), *Aluminium*, 60, 787.
- Kumar S, Subramanya Sarma V and Murthy B S, (2009), *Metall Mater Trans*, 40A, 223–231.
- Lim S C and Ashby M F, (1987), *Acta Metall*, 35, 1–24.
- Liu Y, Asthana R and Rohatgi P K, (1991), *J Mater Sci*, 26, 99–102.
- Okabayashi K and Kawamoto M, (1968), *Univ. of Osaka Prefecture Bulletin*, A17, 199.
- Pramila Bai B N, Biswas S K and Kumtekar N N, (1983), *Wear*, 87, 237.
- Pramila Bai B N and Biswas S K, (1986), *ASLE Trans*, 29, 116.
- Rabinowicz E, (1984), *Wear*, 100, 533.
- Rao K N and Sekhar J A, (1986), *J Mater Sci Let*, 5, 1186.
- Rigney D A, (1988), *Ann Rev Mat Sci*, 18, 141.
- Rohatgi P K and Pai B C, (1974), *Wear*, 28, 353.
- Rooy E L, (1972), *AFS Trans*, 80, 421.
- Singh J and Alpas A T, (1996), *Metall Mater Trans*, 27A, 3135–3148.
- Subramanian C, (1983), *Wear of aluminium – graphite particulate composites*, Master's thesis, Indian Institute of Science, Bangalore, India.
- Subramanian C, (1985), *Proc. Int Conf on Aluminium*, New Delhi, India, 568–572.
- Subramanian C, (1989), *Dry Sliding Wear of Aluminium Alloys: Wear Mechanism Maps and Effects of the Counterface*, Doctoral Thesis, University of Melbourne, Australia.
- Subramanian C, (1991a), *Scr Metall Mater*, 25, 1369–1374.
- Subramanian C, (1991b), *Wear*, 151, 97–110.
- Subramanian C and Kishore, (1986), *J Reinforced Plastics and Composites*, 3, 278.
- Suh N P, (1973), *Wear*, 25, 111–124.
- Suh N P and his co workers, (1977), The delamination theory of wear, *Wear*, 44, 1
- Suh N P, (1986), *Tribophysics*, Prentice-Hall, Englewood Cliffs, NJ.
- Sukumoto M, Iwai I and Murase I, (1986) in Sheppard T (ed), *Aluminium Technology*, 86, 10M, London, 557.
- Vandelli G, (1968), *Alumino*, 37, 121.
- Wilson S and Alpas A T, (1997), *Wear*, 212, 41–49.
- Yamada H and Tanaka T, (1987), *J Japan Inst of Light Metals*, 37, 83.
- Zhang J and Alpas A T, (1997), *Acta Mater*, 45, 513–528.

Tribological properties of titanium-based alloys

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Abstract: Titanium-based alloys (including Ti alloys and TiAl intermetallics) are very attractive for many industrial sectors owing to their unique physical, mechanical, chemical and biological properties. However, titanium and its alloys are characterised by poor tribological behaviour in terms of high and unstable friction, severe adhesive wear, low resistance to abrasion, susceptibility to fretting wear and a strong tendency to seize. This may be related to their inherent characteristics of electron configuration, crystal structure, ineffectiveness of lubrication and low thermal conductivity. The tribological behaviour of TiAl intermetallics are very similar to titanium alloys. This problem can be overcome by changing the nature of the surface, i.e. surface engineering of titanium-based alloys.

Key words: wear, friction, fretting wear, titanium alloys, TiAl intermetallics.

3.1 Introduction

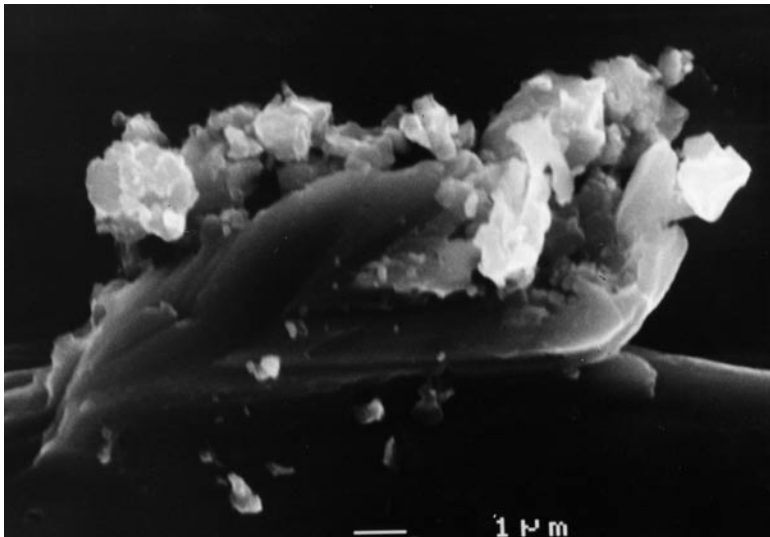
Titanium is the fourth most abundant metal, comprising about 0.63% of the Earth's crust, and it is distributed widely throughout the world. It has also been detected in meteorites, on the moon and in stars (Bomberger *et al.*, 1985). It was discovered as its oxide in 1791 and named after the giants of Greek mythology, the Titans (McQuillan and McQuillan, 1956). Notwithstanding the fact that the pure metal was first extracted in the early part of the last century, titanium alloys have been commercially available only for *circa* 60 years. Therefore, titanium is the best known member of what are often called the 'new metals'.

The primary driving force for the rapid development of titanium and titanium alloys is their unusual combination of properties in terms of high strength-to-weight ratio, excellent resistance to corrosion and outstanding bio-compatibility. Titanium alloys have been the material of choice for the aerospace industry for more than four decades. In view of their unique combination of attractive properties, there is an ever-increasing demand for diversifying titanium alloys into such non-aerospace sectors as biomedical, performance sports, automotive, power generation, off-shore, general engineering and architecture in order to promote wealth creation and to increase the quality of life.

Titanium aluminides, intermetallics of titanium and aluminium, have low

densities, relative high melting points, high strength-to-weight ratios and high specific moduli. In addition, their strength decreases more slowly with increasing temperature than that of disordered alloys. Therefore, titanium aluminides have great potential for high-tech applications, owing to their high specific strength, stiffness and creep resistance at elevated temperature, and an excellent resistance to oxidising environments compared to conventional titanium alloys and steels (Pocci *et al.*, 1994). For example, higher operating temperatures of gas turbine and car engines allow more efficient fuel energy conversion with lower toxic emissions. These attributes have been the driver for substituting steel with titanium alloys or titanium aluminides for weight saving in transportation systems.

However, although titanium long ago crossed the barrier between laboratory curiosity and high-value consumer product, the poor tribological behaviour (in terms of high and unstable friction, severe adhesive wear, low resistance to abrasion, susceptibility to fretting wear and a strong tendency to seize) has restricted, to date, the very large-scale uptake of titanium alloys, especially under dynamically loaded conditions. For example, severe adhesive wear may occur when a titanium surface slides against any engineering surface, whether it is metallic, ceramic or polymeric, under a medium-to-high load, thus forming ‘a handful of debris’ (Fig. 3.1) (Dong, 1997). Titanium aluminides have similarly poor tribological behaviour (Maupin *et al.*, 1993; Li *et al.*, 2006), although they have different chemical compositions and crystal structures as compared with Ti and its alloys. Therefore, it is an



3.1 ‘A handful of debris: a micro-scale hand holding debris’ SEM micrograph taken from Ti wear track (Dong, 1997).

important task from both a scientific and a technological point of view to study the tribological behaviour and mechanisms of Ti-based alloys, thus laying an essential basis for the development of strategies for combating the wear and friction of Ti-based alloys via surface engineering. To this end, in this chapter, the tribological behaviour of Ti-based alloys will be examined, the fundamental characteristics will be discussed and potential mitigation strategies will be put forward.

3.2 Wear behaviour of titanium alloys

3.2.1 Tribocontact and adhesion

Adhesive wear may be distinguished as the most fundamental of the several types of wear, in the sense that adhesion is a basic phenomenon (Burwell, 1957/58).

Nominally-flat metal surfaces are never truly planar but are covered with asperities with a certain height distribution. When two surfaces are brought together, these asperities are flattened by plastic deformation. The summation of individual contact points gives the real area of contact, which is about 10^{-1} – 10^{-4} % of the apparent or nominal areas (Bowden and Tabor, 1950; Greenwood and Williamson, 1966). Real contact area depends on surface topography, the deformation properties of the asperities, and the normal forces and tangential forces which cause junction growth.

At the regions of real contact, strong adhesion or cold-welding occurs and the friction force is essentially the force required to shear the junction formed. With sliding motion present, junction growth occurs and eventually junction shearing takes place. As sliding continues, fresh junctions will form and be ruptured in turn. If the adhesive strength is stronger than the cohesive strength of either of the two materials, then the junction will rupture within the weaker asperity. As a result, material is transferred from one surface to the other and some is eventually detached to form loose wear particles.

Under atmospheric conditions, all metallic surfaces are covered with a layer of oxide and hence the adhesion between oxide layers at the asperity tips is weak, and junctions have low shear strength. However, this oxide layer is generally very thin (about 5–10 nm for Ti) and is easily penetrated by the contacting asperities, especially if the metal is not hard enough to provide sufficient mechanical support for the oxide. Hence the oxide is removed with rubbing and the exposed metal comes into contact. On the other hand, reoxidation of the exposed metal commences immediately, except in a vacuum or in an inert atmospheres. If the process of healing of the surface oxide predominates, the sliding surfaces are separated by the oxide film, with only occasional direct metallic contact, resulting in low friction and wear, and will be accompanied by fine oxidised debris and a smooth surface.

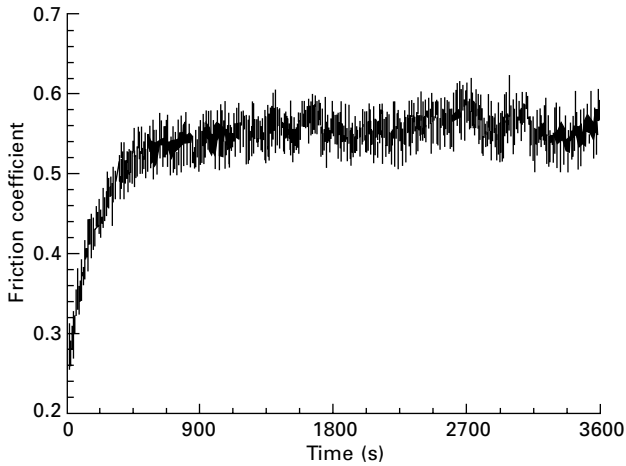
This type of adhesive wear is termed mild wear, or oxidational wear (Quinn, 1992).

By contrast, if the process of damaging the oxide film predominates, then the wear becomes worse and severe wear takes place, characterised by surface roughening and coarse metallic debris. Scuffing, galling and seizure are forms of severe wear with different degrees of surface damage (Tabor, 1987), all of which are reported to occur in titanium alloys (Wayne *et al.*, 1980). Scuffing is localised surface damage associated with local solid-state welding between sliding surfaces (Blau, 1992a). The term is frequently used in describing the breakdown of a fluid or solid lubricant film, leading to unacceptably high friction and severe wear. Galling is a more severe form of scuffing and is associated with gross surface damage; it features a severely roughened surface, and transfer or displacement of large particles. Galling often refers to damage resulting from unlubricated sliding. On further sliding both scuffing and galling can be a destructive process leading to seizure of the surface and consequent gross failure of the sliding system due to catastrophic growth of asperity junctions (Hutchings, 1992).

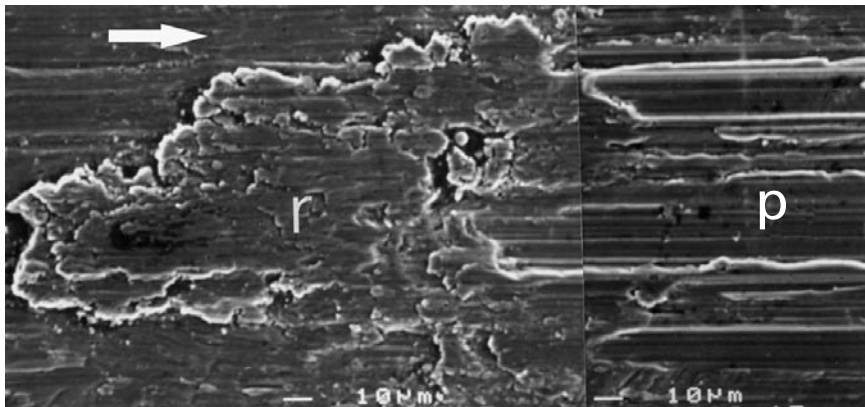
3.2.2 Adhesive wear behaviour of titanium and its alloys

Adhesive wear occurs when a titanium surface contacts with most engineering material surfaces, whether they are metallic or ceramic, under force, in motion. Hence, titanium alloys are particularly prone to adhesive wear, leading to seizure and galling (Rabinowicz, 1954; Miller and Holladay, 1958/59).

The strong adhesion tendency of Ti is clearly reflected in the high and unstable coefficient of friction when titanium slides against itself or other engineering materials. For example, it has been demonstrated that the coefficient of friction of polycrystalline Ti sliding against itself in vacuum (1.33×10^{-7} Pa) ranges from 0.75 to 1.25 (Buckley, 1981). As shown in Fig. 3.2, the friction trace of Ti-6Al-4V alloy sliding against a tungsten carbide (WC) ball in air fluctuates widely throughout the whole testing period, indicative of the 'stick-slip' adhesive behaviour of Ti and its alloys when sliding against most engineering materials (Waterhouse and Wharton, 1974a). This 'stick-slip' behaviour is closely related to the strong adhesion feature of titanium. The real contact area at first increases with increasing tangential force through junction growth and the two surfaces remain in adhesive contact, showing 'stick'. Then, when the applied force exceeds the adhesive strength, the junction ruptures and rapid 'slip' of the two surfaces occurs. This 'slip-stick' cycle is repeated, accounting for the wide fluctuation in the friction trace. Observations of the worn tracks on the Ti-6Al-4V disc revealed deep grooves produced by ploughing ('p' in Fig. 3.3) and recurrent prow-like transverse ridges or adhesive spots ('r' in Fig. 3.3), which are associated with the experimentally recorded fluctuation in the



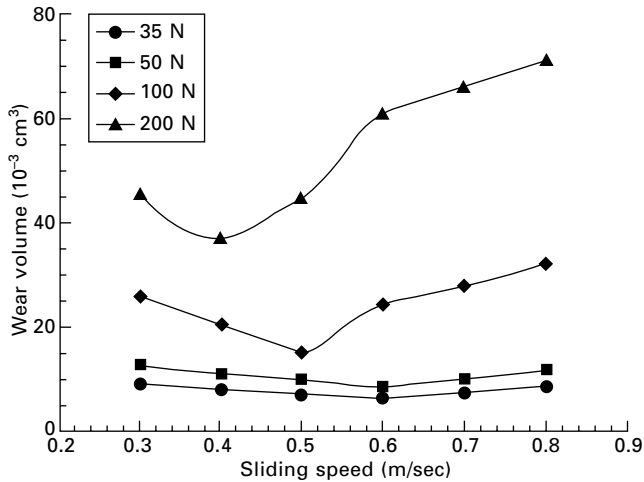
3.2 The friction trace of Ti-6Al-4V alloy sliding against a WC ball.



3.3 Wear track morphologies.

‘stick-slip’ friction process. Severe wear occurs to the titanium disc when unidirectionally sliding against a WC ball slider in air (Fig. 3.3).

Molinari *et al.* (1997) investigated the wear of self-mated Ti-6Al-4V wheels (40 mm in diameter and 10 mm in thickness) in a wheel-on-wheel configuration using an Amsler tribometer. During the tests, one wheel rotated against the other stationary wheel under different loads (35 – 200 N) and the sliding speed between the wheel surfaces ranged from 0.3 to 0.8 m s⁻¹. The wear of the rotating titanium specimen was reported as a function of sliding speed and load as shown in Fig. 3.4. The wear rate increased with the applied load from about 2.57 to 17.99 × 10⁻³ gm⁻¹; for a given load, the wear rate first decreased and then increased with the sliding speed, with this minimum shifting towards lower speeds by increasing the load. The initial



3.4 Effect of load and sliding speed (Molinari *et al.*, 1997).

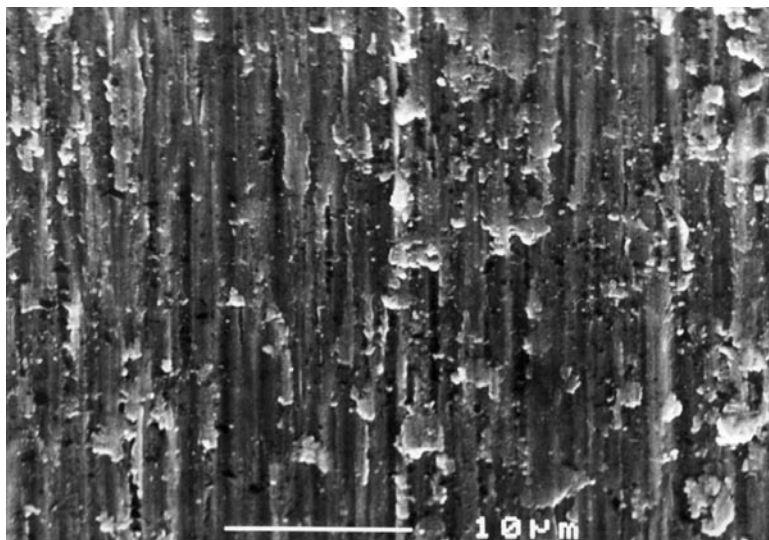
decrease of the wear rate with the sliding speed could be attributed to the formation of oxide film because of the flash temperature induced by friction during dry sliding (i.e. oxidation wear).

Severe adhesive wear of titanium occurs not only under sliding conditions but also under rolling–sliding conditions with oil lubrication. For example a similar wheel-on-wheel configuration was used to study the wear of Ti in a combined rolling–sliding contact (with a sliding ratio of 10%) using a Ti-6Al-4V wheel rolling–sliding against a hardened steel wheel under oil lubrication conditions. The tests revealed severe wear of the Ti-6Al-4V surface with a high wear rate of $2.76 \times 10^{-6} \text{ g m}^{-1}$ (Dong and Bell, 2000). The worn surfaces were very rough, with typical adhesive wear features evidenced by numerous adhesive craters and deep ploughing grooves (Fig. 3.5). Therefore, the poor wear resistance of the Ti surface is associated with the preferential transfer of Ti-6Al-4V onto the steel counterpart and the strong abrasive action of the transferred materials.

3.2.3 Factors affecting adhesive wear of titanium

Electron structure and adhesion

From a fundamental viewpoint, many properties of a material are closely related to its electron structure. Hence, various attempts have been made to correlate tribological properties of a material with its electron structure. Based on Pauling's (1949) findings that the d-bond character (determined by electron structure) for various transition metals are different, Buckley and co-workers (e.g. Buckley and Miyoshi, 1984) correlated the chemical activity and the friction coefficient with the d-bond character, and found



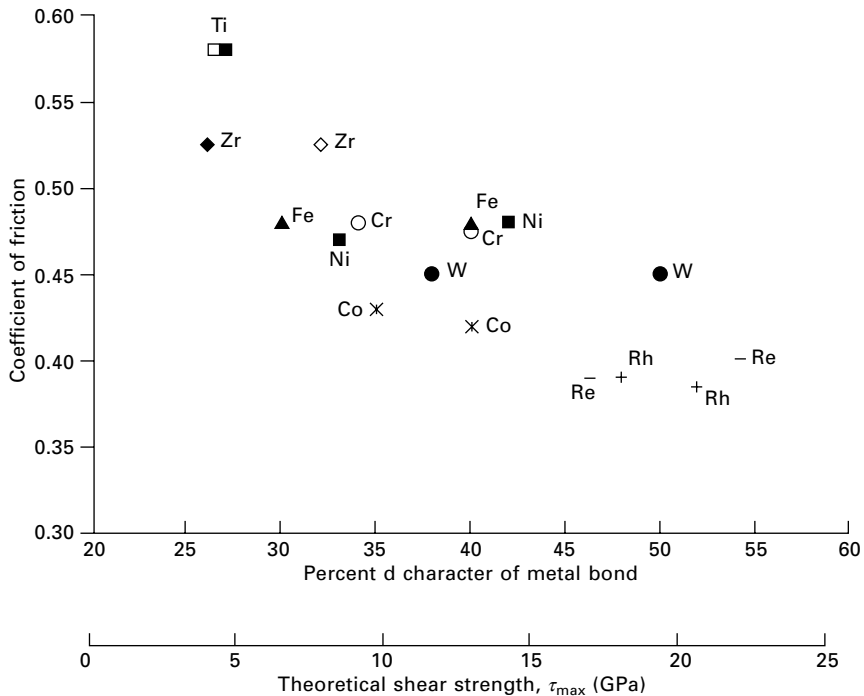
3.5 Wear morphologies of Ti-6Al-4V wheel (Dong and Bell, 2000).

that the greater the percentage of d-bond character, the less active is the metal and hence the lower is the friction, as is demonstrated in Fig. 3.6. It can be clearly seen that since titanium possesses the lowest value of d-bond character (27 %), it has a high friction coefficient.

Likewise, another theory has been developed based on Samsonov's (1973) stable electronic configuration model. It is proposed that in transition metals, the filled (d10), unfilled (d0) and half-filled (d5) are three especially stable electronic configurations, of which the d5-configuration is most stable. So the probability for the formation of a stable electronic configuration is measured in terms of the statistical weight of atoms having stable d5-configurations (SWASC d5). When the SWASC d5 decreases (with decreasing number of electrons in isolated atoms), the proportion of non-localised electrons are correspondingly increased, thus giving rise to high adhesion and hence a high tendency to seize (Upadhyaya, 1982). So the poor tribological behaviour can be explained in terms of low SWASC d value.

Metallic coatings such as nickel, chromium and molybdenum have been applied to titanium to overcome galling and seizure, presumably owing to their high d5 (chromium and molybdenum) and d10 (nickel) statistical weights. Strictly speaking, the tribological behaviour of a material depends not only on the material itself but on the counterpart and conditions prevailing. Thus, the theory based on the electron structure appears to be, to some extent, successful in explaining the poor tribological behaviour of titanium.

This theory explains the seemingly abnormal experimental observations that laser surface alloying with nitrogen or oxygen deep-case diffusion



3.6 Relationship between friction coefficient and d-bond character (Miyoshi and Buckley, 1984). Black symbols denote coefficient of friction as function of theoretical shear strength.

hardening cannot improve the sliding wear resistance of titanium alloys if there is no surface compound layer (titanium nitrides or oxides). Similarly, nano-crystallisation can effectively improve the strength and hardness of titanium, but no significant enhancement of tribological properties during sliding against steel is observed (Garbacz *et al.*, 2007). Li *et al.* (2006) investigated the effect of heat treatment on the mechanical and tribological properties of Ti-Nb-Ta-Zr (beta alloy) and Ti-6Al-4V (alpha+beta alloy) and concluded that heat treatment that improves mechanical properties is not a practical way to improve the wear resistance of these alloys. This is because although such bulk or surface treatments can increase hardness of titanium alloys, they cannot change the nature of titanium. Clearly, the adhesive wear behaviour of titanium is determined by its nature, and increasing the hardness of titanium does not necessarily improve its adhesive wear resistance.

Crystal structure and ductility

As has been discussed in Section 3.2.1, adhesive wear of a material involves metal-metal contact, plastic deformation, cold weld, growth of the junction

and materials transfer. Therefore, the severe adhesive wear tendency of Ti and its alloys is also related to their ease of plastic deformation and high ductility.

Generally, metals with hexagonal structures have superior friction and wear characteristics relative to cubic structured metals (Blau, 1992b; Hutchings, 1992; Rosi *et al.*, 1952). The good tribological properties of these materials may be explained by their plastic deformation mechanisms, which are actually determined by their crystal structure. At room temperature, hexagonal metals plastically deform by slip on the slip plane, the closed-packed basal plane (0001), thus making continuous junction growth impossible, as it requires slip on different slip planes (Rosi *et al.*, 1952).

Alpha titanium, although a hexagonal metal, has an axial ratio c/a of 1.58787, less than the ideal for closest packing (1.633). The lattice of titanium is compressed along the c -axis so the interplanar spacing and the atomic density of this plane are reduced, which tends to make the basal plane less favourable for slip and allows, in order of ease of operation, prismatic $\{10\bar{1}0\}$ and the first-order pyramidal $\{10\ 11\}$ slip to occur (Buckley and Johnson, 1966). Therefore, titanium resembles the cubic metals in having multiple slip systems, and hence behaves more like cubic metals in terms of its high ductility, easy deformation and poor tribological performance.

It thus follows that any measures that reduce the plastic deformation and ductility of Ti and its alloys could more or less decrease their adhesive wear tendency. For example, adding 3%Cu into CP Ti can reduce its ductility and adhesive wear, although its hardness is slightly reduced from 306 to 262HV0.1 (Ohkubo *et al.*, 2003). In addition, Long and Rack (2001) compared the wear of two metastable β titanium alloys (Ti-35Nb-8Zr-5Ta and Ti-15.5Mo-2.3Nb) with Ti-6Al-4V $\alpha + \beta$ alloy under reciprocating sliding conditions against a hardened steel disc. All three titanium alloys have very similar hardness (28–30HRC) but the metastable β titanium alloys possess a much higher reduction in area (55–65%) than the $\alpha + \beta$ alloy (45%). Their tribological test results indicate that although the strength of the metastable β titanium alloys are much higher than that of Ti-6Al-4V $\alpha + \beta$ alloy, the former exhibited a much greater degree of surface deformation and material transfer, and higher average friction, than the latter. Therefore, β titanium alloys normally have a lower adhesive wear resistance than their $\alpha + \beta$ counterparts, probably due to their higher ductility.

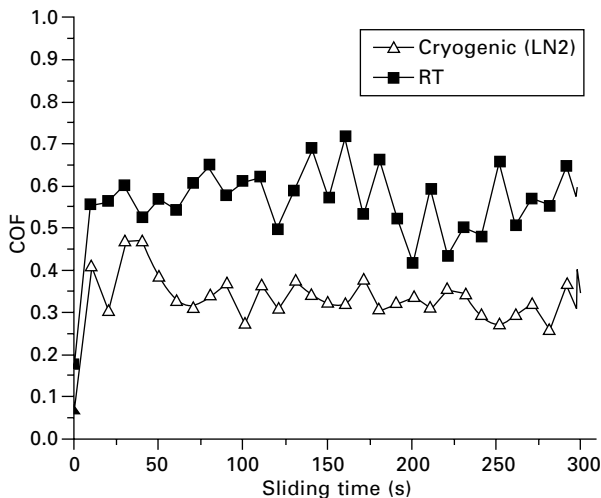
Thermal conductivity

During sliding contact of materials, friction work is transformed to thermal energy, and accumulation of thermal energy tends to maximise the potential energy at the interface (Abdel-Aal, 2003). It is well-known that titanium and its alloys have a much lower (17 W/mK) thermal conductivity than steel (40

W/mK). As a result, the friction-induced thermal energy will increase the flash temperature at the tribocontact of titanium asperities. This will not only increase the adhesion strength due to ease of diffusion but also increase the extent of junction growth due to increased plastic deformation and ductility. Therefore, the high adhesive wear tendency of titanium and its alloys is, to some extent, related to their low thermal conductivity. The above mechanism is supported by the fact that the coefficient of friction of CP Ti becomes lower and more stable when tested at liquid nitrogen temperature than at room temperature (Fig. 3.7) (Basu *et al.*, 2009). The flash temperature at the tribocontact is much higher when tested in air than in liquid nitrogen. Therefore, the deformation mode is changed from dislocation slip at room temperature to twinning at cryogenic temperature. In addition, the reduced friction coefficient may be also related to the change of ductility at low-temperature, but it is known that titanium has a high ductility even at liquid nitrogen temperature.

Ineffectiveness of lubrication

Many sliding surfaces are lubricated to protect against wear and to lower the friction. However, it has been reported that all conventional lubricants (mineral oils and greases) that are successfully used for most metals have been shown to be completely ineffective when applied to titanium alloys (Rabinowicz, 1954). Without effective lubrication, it is difficult to achieve hydrodynamic lubrication because the lubricant film is not sufficiently thick



3.7 Comparison of frictional behaviour of a-Ti/steel tribocouple between LN2 and RT environments at a sliding speed of 0.89 ms^{-1} under 10 N load (Basu *et al.*, 2009).

to keep the surfaces completely apart. Consequently, direct contact between titanium asperities and the counterfaces will occur, leading to boundary lubrication. This unusual effect can mean only that no effective adsorption of the lubricant molecules on the titanium oxide surface has taken place. Additionally, the low heat conductive nature of titanium adds to the problem of the ineffectiveness of lubricants, possibly because this causes higher temperatures at contacting surfaces, resulting in some desorption of the boundary lubricant (Hutchings, 1992).

3.2.4 Abrasive wear

Abrasive wear is the removal of material from a surface by a harder material impinging on or moving along the surface under load. In principle, abrasive wear can involve both plastic flow and brittle fracture (Hutchings, 1992), but for most metals and alloys, abrasive wear is dominated by a plastic deformation mechanism.

At the onset of abrasion, an abrasive particle penetrates into the opposing surface, with the penetration depth being proportional to the ratio N/H (where N is the applied load and H the indentation hardness of the worn surface) (Eyre, 1976). As sliding occurs, the particle will plough the surface, producing a groove, with the material originally in the groove being displaced via a ploughing model and/or removed as debris via a micro-cutting model (Eyre, 1976; Hutchings, 1992). Therefore, abrasive wear rate is directly proportional to the applied load and inversely proportional to the hardness of the abraded material. It has been also found that abrasive wear rates depend, to a large extent, on the hardness ratio between the abraded material and the abrasive (Hutchings, 1992).

It is well-known that titanium and its alloys are soft (200–350 HV), and they cannot be hardened by martensitic transformation as for steel. Therefore, the abrasive wear resistance of titanium alloys is poor. As discussed in Section 3.2.2, during adhesive wear of titanium surfaces, some titanium transfers to the counterpart and thus makes it very rough. This transferred material, in turn, abrades the titanium surface, thus leading to severe abrasive wear. Therefore, adhesive wear and abrasive wear, in most cases, coexist during wear of titanium alloys (Alam and Haseeb, 2002). This is evidenced by the deep parallel grooves found in worn surfaces shown in Fig. 3.5.

Budinski (1991) quantitatively compared the abrasive wear resistance of Grade 2 CP Ti and Ti-6Al-4V with a portfolio of other metallic materials using the ASTM G65 dry sand–rubber wheel abrasion test. The results, given in Table 3.1, clearly demonstrate that both grades of titanium have poor abrasion resistance. The abrasive wear rates of these two titanium materials were about seven times that for 1080 carbon steel and indeed, neither grade had an abrasion resistance comparable to soft austenitic stainless steel.

Table 3.1 Abrasive wear of various materials (Budinski, 1999)

Material	Hardness	Volume loss (mm ³)
6061 T6 aluminium alloy	60HRB	1220
Ti-6Al-4V	36HRC	650
Grade 2 Ti	90HRB	550
316 austenitic stainless steel (SS)	90HRB	260
17-4 precipitation hardening SS	43HRC	220
1018 carbon steel	24HRC	67
D2 tool steel	60HRC	33

Consequently, titanium and its alloys are not recommended for applications involving low-stress abrasion from hard particles.

3.2.5 Fretting wear and fretting fatigue

Fretting wear is a destructive phenomenon that occurs between two contacting surfaces when they experience relative movement at minute displacement under load. According to the relative movement of the mating surfaces, fretting has two modes: (i) gross-slip, where relative movement occurs across the entire contact interface and (ii) partial stick, where slip occurs near the edge of contact with no slip (i.e. stick) in the central region (mixed fretting).

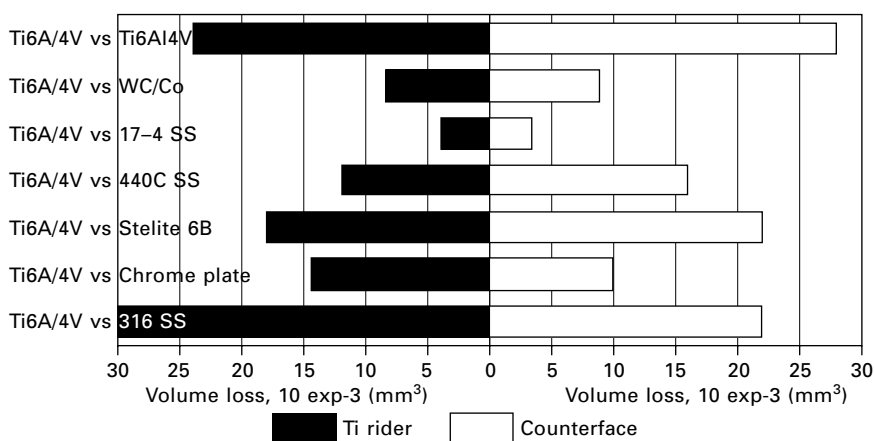
Hager *et al.* (2004) systematically investigated gross slip and mixed fretting wear regimes in Ti-6Al-4V interfaces at room temperature, using an ellipsoid-on-flat rigid-plate test geometry. The transition from mixed to gross slip was observed when increasing the displacement and/or reducing the normal load, which is normally accompanied with a large reduction in coefficient of friction, and especially the change of the shape of frictional logs from elliptical to quasi-rectangular. At or near the transition load or displacement, there is a cycle dependence transition due to the fatigue of formed adhesive junctions in the stick areas. Zhou *et al.* (1997) reported fretting wear induced tribological transformed structure (TTS) in Ti-6Al-4V interfaces owing to accumulation of plastic deformation between the mating surfaces. The TTS layer can form quickly in gross-slip fretting but it takes a long time to form the TTS layer in mixed fretting.

During fretting of titanium alloys, multiple wear mechanisms, such as adhesive, abrasive and oxidative wear, can occur sequentially or simultaneously, and hence fretting wear is not a basic but a complex wear mechanism. It is known from Section 3.2.2 that titanium alloys have a high tendency for adhesion which causes sticking. On the other hand, titanium alloys have a very strong affinity to oxygen, forming lubricous rutile titanium oxide, which can effectively reduce interfacial friction and adhesion. Therefore, oxidation and formation of rutile must play an important role in the fretting wear of titanium alloys.

The effect of oxidation on the fretting wear of CP Ti at an amplitude of 75 microns in air of 50% RH, and in nitrogen, was investigated, and the results indicated that the fretting wear of CP Ti was higher in air than in nitrogen, especially beyond 40 000 cycles (Waterhouse and Wharton, 1974). Waterhouse and Iwabuchi (1985) studied the fretting wear of four titanium alloys, IMI550, 679, 685 and 829 at 20, 400, 500 and 600°C in air. They found that the fretting wear of these four titanium alloys depended strongly on temperature. When tested at a low temperature of 20°C, considerable loose oxide was produced and the wear was high. At intermediate temperatures of 400–500°C, wear debris was compacted together by the fretting action to form small areas of glaze oxide, leading to reduced friction and wear. The lowest fretting wear was observed when tested at 600°C because of the formation of thin and protective oxide films. Therefore, the formation of oxide at elevated temperatures can effectively reduce the fretting wear and coefficient of friction of titanium alloys.

Research has also demonstrated that fretting wear of Ti and its alloys is closely related to the counterface materials (Budinski, 1991). As shown in Fig. 3.8, Ti-6Al-4V is quite susceptible to fretting damage when self-mated and mated against soft 316 austenitic stainless steel; the lowest system damage is obtained with a tribopair of Ti-6Al-4V/Stellite 6B Co-Cr alloy. The test results suggest that the use of a hardened counterface helps to reduce fretting wear of Ti-6Al-4V.

The surface damage caused by fretting wear will act as crack initiation sites. Therefore, the most severe consequence of fretting is a reduction in fatigue strength, i.e. fretting fatigue, when the small amplitude movement arises from the cycling stressing of one of the contact surfaces. Fretting fatigue



3.8 Fretting wear of Ti-6Al-4V rider against various flat counterfaces (Budinski, 1991).

has been identified as one of the causes of in-service damage related high cycle fatigue in the US Air Force (Nicholas, 1999). For example, fretting fatigue is a problem in many aerospace applications, such as the titanium compressor dovetail joint at the blade/disc interface.

Titanium and its alloys are particularly susceptible to fretting fatigue, and mixed fretting wear is the most detrimental to fatigue life. The reductions in fatigue strength of CP-Ti, Ti-2.5Cu and Ti-6Al-4V at 10^7 cycles due to fretting are 38, 55 and 63%, respectively. When tested in a corrosive environment, serious reduction in fatigue strength of high-strength titanium alloys due to fretting was observed, with a strength reduction factor of 2.6–3.6 (Waterhouse and Iwabuchi, 1985). It is known that a reduction in the coefficient of friction can reduce the shear loading and thus reduce the crack driving force (Golden *et al.*, 2007).

3.3 Wear of titanium-aluminium intermetallics

Many researchers have studied the metallurgy and mechanical properties of gamma-based titanium aluminides because of their attractive high-temperature mechanical properties, high stiffness, low density and high oxidation resistance. However, only limited work has been carried out in recent years to study the tribological properties of titanium aluminides, despite the fact that some proposed applications, e.g. valves in car engines and turbine blades in aero engines, involve contacting and relative movement. Indeed, tests of TiAl-based exhaust valves in a motor cylinder showed that serious wear occurred on both the valve tip and stem after running for 533h (Hurta *et al.*, 1995).

3.3.1 Sliding wear of titanium aluminides

Chu and Wu (1995) studied the coefficient of friction (CoF) of titanium aluminides containing 25, 40, 50 and 53 at%Al unidirectionally sliding against a hardened (700 HV) steel surface under unlubricated conditions. The CoF increased with increasing Al content, with a value of around 0.4 for 25 at% Al and 0.6–0.7 for Al content between 40 and 53 at%. It is known that Ti-25Al, Ti-40Al and Ti-53Al alloys consist mainly of single α_2 , $\alpha_2 + \gamma$ and single γ phase, respectively. Therefore, it follows that the γ phase possesses a higher coefficient of friction than the α_2 phase. This is echoed by the more recent reports by Rastkar *et al.* (2000) and Xia (2004) that the friction coefficient of γ -based titanium aluminides (such as Ti-48Al-2Nb-2Mn, Ti-48Al-2Nb-2Cr-1B and Ti-45Al-2Nb-2Mn-1B) fell within the range of 0.5–0.8.

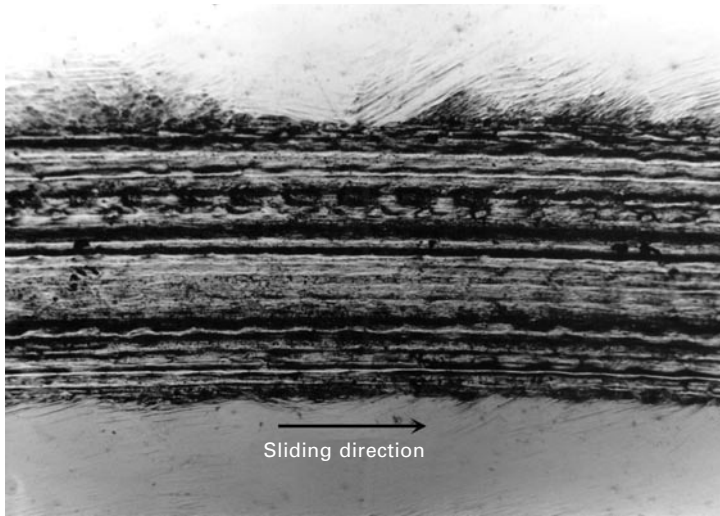
Rastkar *et al.* (2000) investigated the friction and wear behaviour of two gamma-based titanium aluminides, Ti-48Al-2Nb-2Mn and Ti-45Al-2Nb-2Mn-1B using a ball-on-disc configuration sliding against a 10 mm hardened (720 HV) steel ball under loads (stresses) of 3.5 (746MPa), 10 (940MPa) and

20N (1184MPa) in air, without lubrication. The wear loss for both materials increased with sliding distance at all loads; however, except for the initial running wear, the wear measured was larger for Ti-45Al-2Nb-2Mn-1B than for Ti-48Al-2Nb-2Mn after 60m sliding. The average wear rate under 10 N over a total sliding distance of 360 m was about $2 \times 10^{-3} \text{ mm}^3 \text{ m}^{-1}$ and $4 \times 10^{-3} \text{ mm}^3 \text{ m}^{-1}$ for Ti-48Al-2Nb-2Mn and Ti-45Al-2Nb-2Mn-1B, respectively. The inferior wear resistance of Ti-45Al-2Nb-2Mn-1B relative to Ti-48Al-2Nb-2Mn was attributed to crack initiation by the notch-shaped TiB_2 plates observed in the lamellar structure of Ti-45Al-2Nb-2Mn-1B. The wear tracks formed in both materials were characterised by plastic deformation and ploughing with mild oxidation (Fig. 3.9); after etching, the wear track revealed some interlamellar cracks extending into the unworn areas adjacent to the wear tracks. Therefore, it is believed that the wear of gamma-based titanium aluminides during sliding is closely related to the interlamellar slip, which results in the cleavage and fracture of lamellae in the worn area. The fractured lamellae may be fragmented under subsequent abrasion into some wear debris.

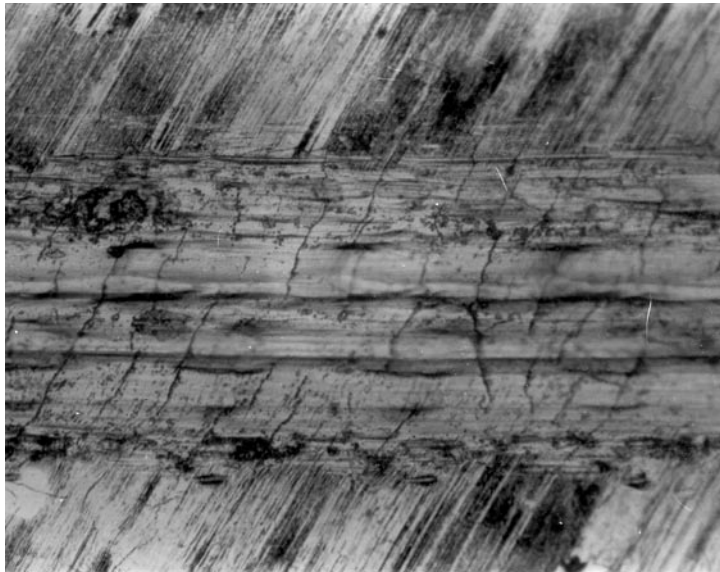
Xia (2004) directly compared the wear of γ -based Ti-48Al-2Nb-2Cr-1B titanium aluminide with the work-horse titanium alloy, Ti-6Al-4V, sliding against an 8 mm WC ball under 10 N load without lubrication. The results (Fig. 3.10) reveal that the γ -based Ti-48Al-2Nb-2Cr-1B displays very high wear volumes, almost the same as the Ti-6Al-4V alloy, with an average wear rate of $2.55 \times 10^{-3} \text{ mm}^3 \text{ m}^{-1}$.

More recently, Li *et al.* (2006) investigated the effect of counterface materials on the sliding wear of γ -based titanium aluminides under 10 N load without lubrication. Figure 3.11a displays the wear loss as a function of sliding distance of the γ -based TiAl, sliding against 8 mm Al_2O_3 , Si_3N_4 , WC and steel balls. Clearly, the wear behaviour of γ -based titanium aluminides is highly counterface dependent; the wear rate of TiAl was the highest with a counterface of Al_2O_3 and it was the lowest when the counterface changed to steel. It is also of interest to find that the wear of the ceramic ball sliders is much higher than WC or steel balls (Fig. 3.11b), which is believed to be related to the interface tribochemical reactions and surface brittle fracture. These results indicate that sliding contact of TiAl intermetallics against ceramics of Al_2O_3 or Si_3N_4 may not be desirable designs, since these tribopairs can result in a very high overall wear loss.

Gialanella and Straffelini (1999) studied the effect of microstructures, equiaxed, duplex and lamellar, on the wear of Ti-48Al-2Cr-2Nb-1B sliding against a M2 (65HRC) disc, using a disc-on-block configuration at a sliding speed of 0.628 ms^{-1} without lubrication. Their results revealed that, when tested under a low load of 50 N, no appreciable differences among these three different microstructures could be detected; under higher loads, lamellar specimens displayed the highest wear and the equiaxed ones displayed the



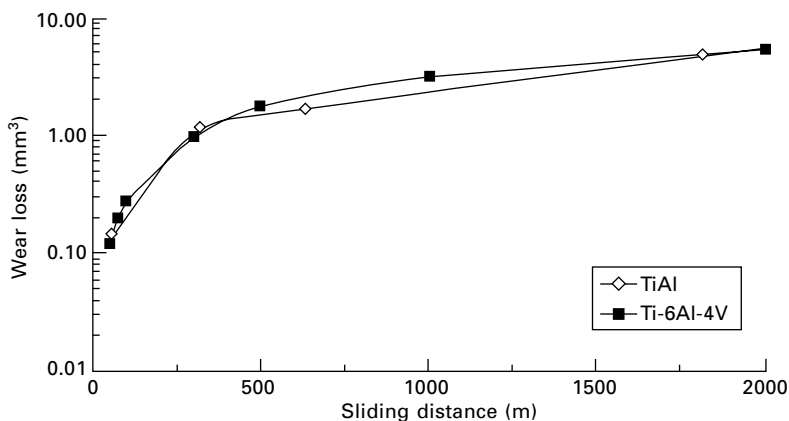
(a)



(b)

3.9 Wear track morphologies showing (a) ploughing and (b) cracks (Rastkar *et al.*, 2000).

smallest. A remarkable improvement in wear resistance was observed when the titanium aluminide specimens were tested without removing the surface layer that resulted from heat treatment. This is because of the formation of the surface oxide layer – a possible way to combat wear of titanium aluminides.



3.10 Comparison of sliding wear of Ti-6Al-4V with TiAl (Xia, 2004).

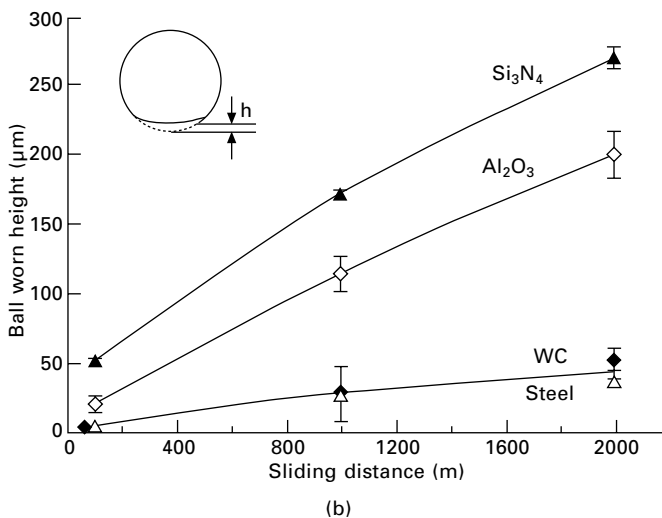
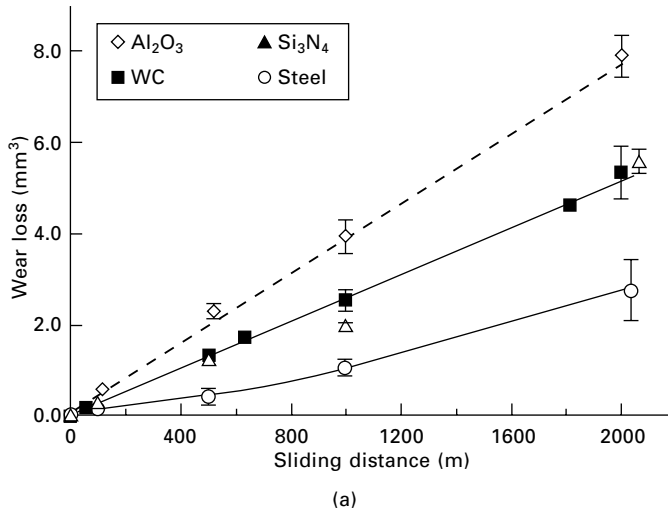
3.3.2 Abrasive wear of titanium aluminides

Because of their good mechanical properties at high-temperatures and superior environmental stability, titanium aluminides may find tribological uses in aggressive environments. For example, extensive research has been conducted to explore the potential applications for low-pressure turbine blades. However, fretting wear and abrasion are major concerns for such aero-engine applications.

The abrasive wear resistance of several titanium aluminides has been compared with steel, titanium alloys and aluminium alloys by Hawk and Alman (1997) using a pin-on-drum abrasive wear testing apparatus. It can be seen from Table 3.2 that, as a whole, the abrasive wear resistance of titanium aluminides against 100 micron garnet (1300 HV) is better than that of CP titanium and of some titanium alloys, although it is inferior to that of stainless steel and hardened tool steel.

3.3.3 Fretting wear of titanium aluminides

Because of their potential applications for low-pressure turbine blades, fretting damage on gamma-TiAl (Ti-48Al-2Cr-2Nb) in contact with Ni-based superalloys at temperatures from 296–823K has been evaluated using Ti-6Al-4V as a benchmark (Miyoshi *et al.*, 2003). The fretting wear tests were conducted using a pin-on-flat configuration at loads from 1–40N, frequencies of 50, 80, 120 and 160 Hz, and slip amplitudes between 50–200 microns for 1–20 million cycles. Severe material transfer was observed on the surface of the superalloy pin after fretting against the gamma-TiAl (Fig. 3.12). This implies that the adhesion between the TiAl and the superalloy is so strong that cohesive bonds in the Ti-48Al-2Cr-2Nb were fractured. The

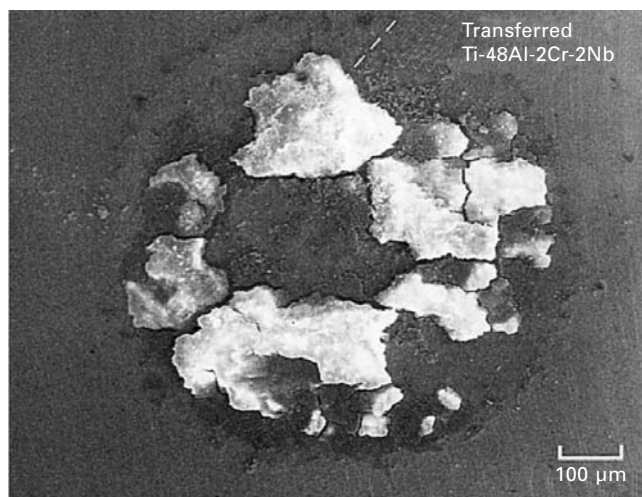


3.11 Effect of counterface materials on the sliding wear of TiAl: (a) Wear loss of the γ -based TiAl and (b) wear loss of the balls (Li *et al.*, 2006).

failed Ti-48Al-2Cr-2Nb transferred to the superalloy surface, and progressive fretting resulted in scuffing or galling. Similar Ti-6Al-4V transfer was also observed on the superalloy, but the degree of Ti-6Al-4V transfer was larger. Therefore, it is essential to combat the fretting wear of Ti-48Al-2Cr-2Nb by surface engineering.

Table 3.2 Abrasive wear factor of titanium aluminides together with some other materials for comparison (Hawk and Alman, 1997)

Material	Hardness (GPa)	Specific wear rate $\times 10^{-3}\text{mm}^3(\text{Nm})^{-1}$
<i>Titanium aluminides</i>		
Ti3Al	2.9	18.1
TiAl	2.4	17.9
Ti-48Al-2Cr-2Nb	2.4	16.3
<i>Steel</i>		
304 SS	1.6	12.8
AISI52100	6.5	8.0
12% Mn steel	2.1	10.3
<i>Ti and its alloys</i>		
CP Ti	3.0	24.2
Ti-8Al-1Mo-1V	3.1	23.6
Ti-10V-2Fe-3Al	2.8	37.8



3.12 Severe material transfer (Miyoshi *et al.*, 2003).

3.4 Conclusions

3.4.1 Wear

Because of their inherent crystal and electronic structure, ineffectiveness of lubrication and low thermal conductivity, titanium alloys are characterised by high adhesion, severe adhesive wear and high-and-unstable friction when sliding against nearly any engineering materials. Titanium and its alloys also suffers from abrasive wear because of relatively low hardness, which cannot be significantly increased by bulk or surface heat treatments.

In addition, titanium and its alloys are quite prone to fretting damage when

coupled to themselves and to austenitic and martensitic stainless steels, mainly due to their high tendency for adhesion and high friction. The surface damage caused by fretting wear will act as crack initiation sites, and titanium and its alloys are particularly susceptible to fretting fatigue because of the high adhesion-induced detrimental mixed fretting wear. The reductions in fatigue strength of high-strength titanium alloys are in the range of 60–70%.

Although the crystal and electronic structure of titanium aluminides differ greatly from that for titanium and its alloys, they have very similar tribological behaviour. The sliding friction coefficient of γ -based titanium aluminides ranges from 0.5 to 0.8; the sliding wear rate of titanium aluminides is almost the same as that of titanium alloys but the wear resistance of the former is marginally better than the latter; and the fretting wear of TiAl is comparable to that of titanium alloys.

3.4.2 Wear mitigation strategies

The poor tribological behaviour of titanium-based alloys is clearly related to their surface nature. Consequently, this problem may be overcome by changing the nature of the surface, i.e. surface engineering of titanium-based alloys, which provides the most promising way to improve their tribological performance.

The adhesive wear resistance of titanium-based alloys can be effectively enhanced by the formation of surface oxide layers during anodising (Chapter 4), plasma electrolytic oxidation (Chapter 5) and ceramic conversion (Chapter 14), or nitride layers during plasma nitriding (Chapter 10), and laser nitriding (Chapter 12).

In addition to these surface treatments, laser cladding (Chapter 13) and thermal spraying (Chapter 7) can increase the surface hardness and thus abrasive wear resistance of titanium-based alloys. Fretting wear of titanium-based alloys can be reduced by low friction and hard coatings (such as diamond-like carbon, DLC) and their fretting fatigue can be effectively addressed by laser peening (Chapter 13).

3.5 Acknowledgements

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3.6 References

- Abdel-Aal H A (2003), 'On the interdependence between kinetics of friction-released thermal energy and the transition in wear mechanisms during sliding of metallic pairs', *Wear*, 254, 884–900.

- Alam M O and Haseeb A S M A (2002), 'Response of Ti-6Al-4V and Ti-24Al-11Nb Alloys to Dry Sliding Wear Against Hardened Steel', *Tribology International*, 35, 357–362.
- Basu B, Sarkar J and Mishra R (2009), 'Understanding friction and wear mechanisms of high-purity titanium against steel at liquid nitrogen temperature', *Metallurgical and Materials Transaction A*, 40, 472–480.
- Blau P J (1992b), 'Appendix: Static and kinetic friction coefficient for selected materials', in ASM International (ed.): *ASM Handbook, Vol 18, Friction, Lubrication and Wear Technology*, ASM, Metals Park, Ohio, 70–75.
- Blau, P J (1992a), 'Glossary of terms', in *ASM Handbook, Vol 18, Friction, Lubrication and Wear Technology*, ASM, Metals Park, Ohio, pp 1–21.
- Bomberger H B, Froes F H and Morton P M (1985), 'Titanium – a historical perspective', in Froes F H, Eylon D and Bomberger N B (eds): *Titanium Technology: Present Status and Future Trends*, The Titanium Development Association, Dayton, Ohio, 1–17.
- Bowden F P and Tabor D (1950), *The Friction and Lubrication of Solids* (Part I), Clarendon Press, Oxford.
- Buckley D H and Johnson R L (1966), *Friction, wear, and adhesion characteristics of titanium-aluminum alloys in vacuum*, NASA TN D-3235, NASA.
- Buckley D H (1981), *Surface Effects in Adhesion, Friction, Wear and Lubrication*, Elsevier Scientific, 1981, p 353.
- Buckley D H and Miyoshi K (1984), 'Friction and wear of ceramics', *Wear*, 100, 333–353.
- Budinski K G (1991), 'Tribological properties of titanium alloys', *Wear*, 151, 203–217.
- Burwell J T (1957/58), 'Survey of possible wear mechanisms', *Wear*, 1, 119–141.
- Chu C L and Wu S K (1995), 'A study on the dry uni-directional sliding behaviour of titanium aluminides', *Scripta Metallurgica et Materialia*, 33, 139–143.
- Dong H (1997), First Prize of Photomicrograph Competition, *11th International Conference on Wear of Materials*, April, San Diego, USA.
- Dong H and Bell T (2000), 'Enhanced wear resistance of titanium surfaces by a new thermal oxidation treatment', *Wear*, 238, 131–137.
- Eyre T S (1976), Wear characteristics of Metals, *Tribology International*, 9, pp 203–212.
- Garbacz H, Gradzka-Dahlke M and Kurzydłowski K J (2007), 'The tribological properties of nano-titanium obtained by hydrostatic extrusion', *Wear*, 263, 572–578.
- Gialanella S and Straffellini G (1999), 'Interplay between oxidation and wear behaviour of the Ti-48Al-2Cr-2Nb-1B alloy', *Metallurgical and Materials Transactions A*, 301, 2019–2026.
- Golden P J, Hutson A, Sundaram V and Arps J H (2007), 'Effect of Surface Treatment on Fretting Fatigue of Ti-6Al-4V', *Int. J. Fatigue*, 29, 1302–1310.
- Greenwood J A and Williamson J B P (1966), 'Contact of nominally flat surface', *Proceedings of Royal Society of London*, A295, 300–319.
- Hager C H, Sanders J H and Sharma S (2004), 'Characterization of mixed and gross-slip fretting wear regimes in Ti6Al4V interfaces at room temperature', *Wear*, 257, 167–180.
- Hawk J A and Alman D E (1997), 'Abrasive wear of intermetallic-based alloys and composites', *Materials Science and Engineering A*, 239–240, 899–906.
- Hurta S, Clemens H, Frommeyer G, Nicolai H P and Sibum H (1995), 'Valves of intermetallics gamma-TiAl-based alloys: Processing and properties', in Blenkinsop

- P A, Evans W J and Flower H M (eds): *Titanium '95, Science and Technology*, The Institute of Materials, UK, 97–104.
- Hutchings I M (1992), *Tribology: Friction and Wear of Engineering Materials*, Edward Arnold, London.
- Li C X, Xia J and Dong H (2006), 'Sliding wear of TiAl intermetallics against steel and ceramics of Al_2O_3 , Si_3N_4 and WC/Co', *Wear*, 261, 693–701.
- Long M and Rack H J (2001), 'Friction and surface behaviour of selected titanium alloys during reciprocating-sliding motion', *Wear*, 249, 157–167.
- Maupin H E, Wilson R D and Hawl J A (1993), 'Wear Deformation of Ordered Fe-Al Intermetallic Alloys', *Wear*, 162–164, 432–440.
- McQuillan A D and McQuillan M K (1956), *Titanium*, Academic Press, New York, Butterworths Science Publication, London.
- Miller P D and Holladay J W (1958/59), 'Friction and wear properties of titanium', *Wear*, 2, 133–140.
- Miyoshi K and Buckley D H (1984), 'Considerations in friction and wear', in NASA (ed.): *Tribology in the 80's*, Vol 1, NASA Conference Publication 2300, 291–320.
- Miyoshi K, Lerch B A and Draper S L (2003), 'Fretting wear of Ti-48Al-2Cr-2Nb', *Tribology International*, 36, 145–153.
- Molinari A, Straffellini G, Tesi B and Bacci T (1997), 'Dry Sliding Wear Mechanisms of the Ti-6Al-4V Alloy', *Wear*, 208, 105–112.
- Nicholas T (1999), 'Critical Issues in High-cycle Fatigue', *Int. Journal of Fatigue*, 21(S), S221–231.
- Ohkubo C, Shimura I, Aoki T, Hanatani S, Hosoi T, Hattori M, Oda Y and Okabe T (2003), 'Wear resistance of experimental Ti-Cu alloys', *Biomaterials*, 24, 3377–3381.
- Pauling L (1949), 'A resonating-valence-bond theory of metals and intermetallic compounds', *Proceedings of the Royal Society of London*, A196, 343–362.
- Pocci D, Tassa O and Testani C (1994), 'Production and Properties of CSM', in J H Schneibel and M A Crimp (eds), *Processing, Properties, and Application of Iron Aluminides*, The Minerals, Metals & Materials Society.
- Quinn T F J (1992), 'Oxidation wear', in ASM international (ed.): *ASM Handbook, Vol 18, Friction, Lubrication and Wear Technology*, ASM, Metals Park, Ohio, 280–289.
- Rabinowicz E (1954), 'Friction properties of titanium and its alloys', *Metal Progress*, 65 (2), 107–110.
- Rastkar A R, Bloyce A and Bell T (2000), 'Sliding wear behaviour of two gamma-based titanium aluminides', *Wear*, 240, 19–26.
- Rosi F D, Dube C A and Alexander B H (1952), 'Mechanism of plastic flow in titanium', *Journal of Metals*, February, 145–146.
- Samsonov G V (1973), *A Configurational Model of Matter*, Consultants Bureau, New York.
- Tabor D (1987), 'Friction and wear – Developments over the last fifty years', *Proceedings of the Institution of Engineers (1987-5) International Conference: Tribology – Friction, Lubrication and Wear Fifty Years on*, 1–3 July, London, Vol 1, pp 157–172.
- Upadhyaya G S (1982), 'An electron approach to the wear mechanism', *Wear*, 80, 1–6.
- Waterhouse R B and Iwabuchi A (1985), 'High Temperature Fretting of Four Titanium Alloys', *Wear*, 106, 303–313.
- Waterhouse R B and Wharton M H (1974), 'Titanium and Tribology', *Industrial Lubrication and Tribology*, 26(1/2), 20–23, 26(3/4), 56–59.
- Wayne S F, Nowotny H and Rice S L (1980), 'Wear of titanium alloys under repetitive

- impulsive loading', in Kimura H and Izumi O (eds): *Titanium 80, Science and Technology (Proceedings of the 4th World Conference on Titanium)*, 1895–1906.
- Xia J (2004), *Development of novel surface engineering technology to combat wear of Al-containing intermetallics*, PhD thesis, The University of Birmingham, UK.
- Zhou Z, Sauger E, Liu J J and Vincent L (1997), 'Nucleation and early growth of tribologically transformed structure (TTS) induced by fretting', *Wear*, 212, 50–58.

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Abstract: Light metals and alloys can form native oxide films on their surfaces that offer only limited protection to surface degradation. Anodising refers to electrochemical anodic oxide film formation; it is one of the most popular methods to increase wear- and corrosion-resistance of light alloys, especially under light loads. Anodic films are most commonly applied to protect aluminium alloys and are discussed here in detail; magnesium and titanium alloys can also be anodised, which is described at the end of this chapter. Anodised light alloys have been exploited in a wide range of industrial sectors such as automotive, marine and aerospace. More recently, porous anodic alumina films have found their application in nanoscience and nanotechnology.

Key words: native oxide, anodising, wear-resistance, corrosion-resistance, nanotechnology.

4.1 Introduction

Lightweight metals, such as aluminium and its alloys, have inherent resistance to atmospheric corrosion due to the presence of a protective film (in the form of an oxide (Al_2O_3) or hydroxide ($\text{Al}_2\text{O}_3 \times \text{H}_2\text{O}$)) that forms immediately after the metal is exposed to air. This native oxide film is about 2.5 to 10 nm thick (Henley, 1982) and thus can offer only a limited protection in aggressive (e.g. marine-coastal) environments. The protective properties may be enhanced by further oxidising the surface, e.g. thermally, chemically or electrochemically. Anodising is distinct from chemical conversion coatings processes in that the surface is oxidised electrolytically and a much thicker film can be formed (Sheasby and Pinner, 2001). The process derives its name from the fact that the part to be treated becomes the anode in an electrolytic cell (unlike in electroplating). Compared to other surface engineering techniques, anodising is distinguished by utilising a controlled oxidation attack on the metal substrate, which results in conversion of the consumed metal layer into surface oxide film. Anodic oxide layers on Al are typically 5 to 25 μm thick; hence they can be used not only for decorative but also for protective purposes, e.g. to improve wear- and corrosion-resistance of the parent metal. Depending on anodising conditions, both thin non-porous (or barrier type) and thicker porous films can be produced.

Anodising has been known since the 1920s but became of commercial importance only twenty years later. The first anodising process, developed

by Bengough and Stuart (1923), was a chromic acid process used for the protection of Duralumin seaplanes (Sheasby and Pinner, 2001). Anodic films are most commonly applied to protect aluminium alloys, although processes also exist for other light-weight metals, including magnesium and titanium; a brief discussion of anodising of these materials is included in final parts of this chapter. However, for the present, this discussion will be specific to aluminium and its alloys. This process is not a useful treatment for iron or carbon steel because these metals exfoliate when oxidised, i.e. the iron oxide (also known as rust) flakes off, constantly exposing the underlying metal to corrosion.

Traditionally, anodising is performed for the corrosion protection of aircraft, vehicles, boats, trains, buildings, household articles, sporting goods, office articles, and electronics (ASM, 2003). It is also used to prevent galling of threaded components and to make dielectric films for electrolytic capacitors. More recently, porous anodic films have found application in nanoscience and nanotechnology, including fabrication of microporous anodic oxide membranes (AOMs) for catalytic and sensor devices as well as templates for nanowire manufacturing (Bocchetta *et al.*, 2003; Martin, 1996; Holland *et al.*, 2000; Daub *et al.*, 2007).

4.2 Formation of anodic films

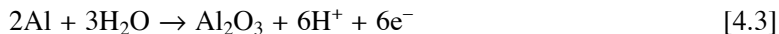
When aluminium is anodically polarised in an electrolyte, negatively charged anions in the solution migrate to the anode where they are discharged with the loss of electrons. In aqueous solutions, anions usually contain oxygen, which reacts chemically with the aluminium. In reality, anodic films contain hydrated forms of the oxides. The metal oxide formation reactions may be considered to occur via the anodic dissolution of metal to form the corresponding cations:



followed by reaction between the metal cation and ionic oxygen:



The net reaction of anodic oxidation of Al is usually given as follows:

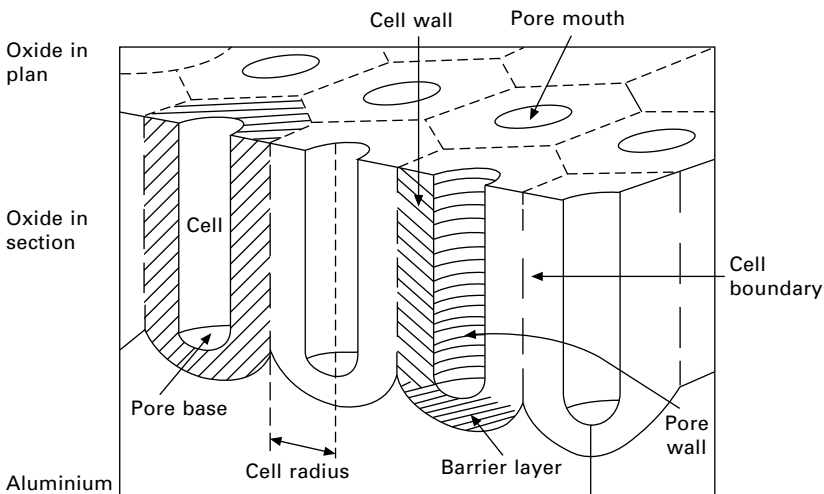


The result of the anodic oxidation depends on a number of factors, particularly the electrolyte (its nature, concentration and temperature) and the conditions of electrolysis (current and voltage). In simple terms, the following processes can occur at the anode:

- (i) If the products of anodic reaction are essentially insoluble in the electrolyte, a strongly adherent barrier-type film is formed on aluminium. The barrier

film growth continues until its resistance prevents current from reaching the anode. These films are extremely thin and dielectrically compact. They may be formed in a number of relatively neutral pH salt solutions of which borate or tartrate electrolytes are common examples. Such films are formed at relatively high voltages; they are used in capacitor production and in the electronics industry, where dielectric protection of very thin aluminium coatings formed by vacuum deposition techniques is typically required.

- (ii) If the reaction products are sparingly soluble in the electrolyte, an adherent film is formed as above, but the film growth is accompanied by localised field-assisted dissolution, which produces a regular array of essentially parallel-sided pores in the film (Fig. 4.1). These pores allow continuing current flow and thus film growth. Electrolytes used are generally acidic and include sulphuric, phosphoric, chromic and oxalic acids. The films formed are used to enhance the adherence of paints, lacquers or adhesives, and, as they may be very hard and many microns thick, they find extensive application for protective and decorative purposes.
- (iii) If the reaction products are moderately soluble, electropolishing of Al may be possible under these conditions, if a suitable electrolyte is used.
- (iv) If the anode reaction products are fully soluble in the electrolyte, then the metal is dissolved until the solution is saturated. This scenario takes place in some strong inorganic acids and bases (Sheasby and Pinner, 2001) that are used for electrochemical machining of Al.



4.1 Schematic representation of a porous anodic film showing the principal morphological features (Sheasby and Pinner, 2001).

Among these anodic processes, (i) and (ii) will be dealt with and are described in more detail below; however, (iii) and (iv) are not in the scope of this chapter. Initial emphasis is given to the barrier layer formation and thickening, which is the main process during the formation of barrier-type anodic films. Although barrier anodising is not the main focus here, it relates closely to porous anodising and, in some aspects, has been the subject of greater investigation. Important factors that distinguish porous and barrier-type films are detailed. Subsequently, the initiation of pores is described, followed by a review of the factors that control the porous morphology and how it may be modified. This has relevance to colouring processes, and properties such as hardness and corrosion resistance (Sheasby and Pinner, 2001).

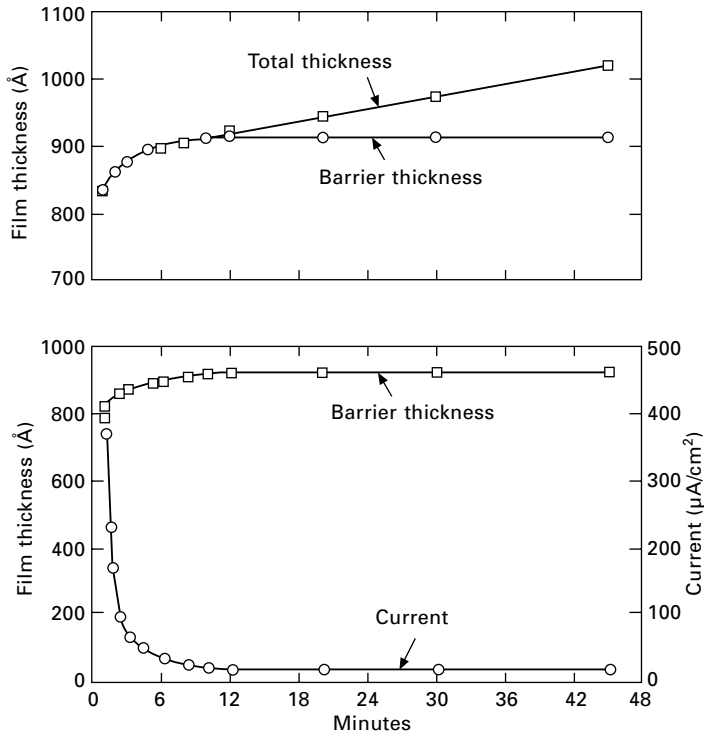
The oxide growth in terms of thickness and chemical structure depends on several factors, such as applied potential or current density, temperature, and, of special interest, the solution composition. Barrier type films with high electrical resistivity are favoured in solutions in which the oxide is almost insoluble, and this usually requires almost neutral solutions. Porous oxides of low solubility are developed in acidic solutions (Benjamin and Khalid, 1999).

4.2.1 Barrier layer formation

There appears to be no clear demarcation between types of anodic films (Parkhutik and Shershulsky, 1992), with porous films developing under certain conditions from previously formed barrier films. Subsequent film growth in the porous mode relies strongly on the presence of the barrier layer at the bottom of the pores. To provide a better understanding of anodising processes, it is therefore important to consider the following two key aspects of the film formation: determination of the interface (i.e. the metal/oxide or the film/solution) at which the barrier film growth occurs and establishment of what enables pores to form and propagate (Sheasby and Pinner, 2001).

Barrier layer thickness

It is commonly observed that the barrier layer thickness is proportional to the anodising voltage, with small variations determined by the nature of the electrolyte. Holland and Sutherland (1952) obtained film growth thicknesses under unit voltage of 1.3 nm/V in 3% ammonium tartrate solution, whereas capacitance measurements by Ginsberg and Kaden (1961) gave values of 1.4 nm/V for films formed in barrier film-forming electrolytes and 1.15 nm/V for the barrier layers of porous anodic coatings. Figure 4.2 shows that some porous oxide may be formed in a supposedly barrier film-forming electrolyte, when anodising at constant voltage, after the limiting barrier thickness has been achieved (Sheasby and Pinner, 2001).



4.2 Film growth in ammonium tartrate electrolyte (Hunter and Towner, 1961).

Anion and cation migration

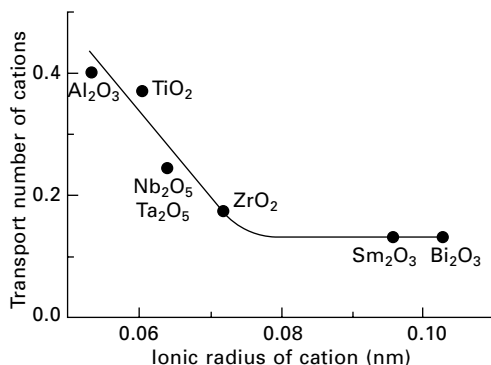
There has been considerable work investigating whether film growth is due to the migration of aluminium cations across the film to produce oxide by reaction with the electrolyte, or due to oxygen-bearing anions moving across the film to oxidise the metal surface, or both. Originally, it was believed that oxygen moved across the film (Schenk, 1948; Rummell, 1936; Anderson, 1944). Schenk (1948) appreciated that the ionic diameter of oxygen and the atomic diameter of aluminium are very large, but as the discharge potential of oxygen is low, he postulated that oxygen ions are first discharged at the solution interface, diffuse across the oxide, and are then reionised near the metal surface to react with Al^{3+} . Hoar and Mott (1959) suggested that the smaller hydroxyl ions carry the current and produce protons at the metal interface, which then move back across the film to combine with O^{2-} from the electrolyte, and subsequently the process repeats. This prompted work to determine the hydration of anodic films (Heine and Pryor, 1963; Brock and Wood, 1967). It was discovered that only the outer regions of films formed in aqueous tartrate solutions were hydrated, but Brock and Wood

(1967) found no hydration in films produced in a non-aqueous glycol-based solution. Thus, it was deduced that O^{2-} rather than OH^- is mobile. Various tracer techniques, such as radioactive tracers, ion implantation, nuclear microanalytical techniques, and transmission electron microscopy of ultramicrotomed sections have been used to understand the ionic transport through anodic films (Sheasby and Pinner, 2001).

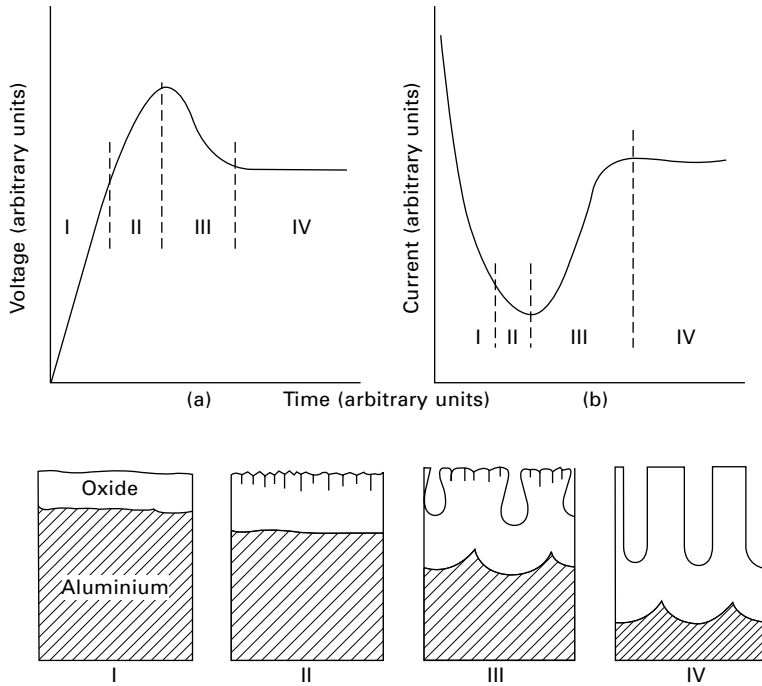
Detailed investigations have also shown that metal cations in most of the anodic films are not completely immobile. The transport number of cations depends mainly upon their ionic radius (Fig. 4.3), being about 0.40 for Al_2O_3 , 0.37 for TiO_2 (Habazaki *et al.*, 2000) and 0.3 for MgO . The numbers indicate that the barrier film growth on these metals occurs at both interfaces, although metal oxidation at the metal/oxide interface prevails.

4.2.2 Porous film growth and morphology

Porous anodic films formed on aluminium in electrolytes such as sulphuric acid are characterised by a very uniform morphology. Pores are approximately cylindrical, situated in generally close-packed hexagonal cells, and separated from the substrate by a thin layer of oxide. Many of these features are determined by the anodising voltage as described below. Thus, the course of porous film development is revealed by monitoring the change of voltage when anodising at constant current, or current when anodising at constant voltage (Fig. 4.4). The compact barrier layer thickens during Stage I. Incipient pores develop in the barrier film during Stage II, while the classical film morphology starts to arise during Stage III. Steady-state propagation of the pores continues through Stage IV. However, the thickness of the porous film depends on the amount of charge passed. Consequently, when anodising at a constant current density, the film thickness is proportional to the anodising



4.3 Relationship between the transport number of cations in anodic films on valve metals and ionic radii of cations (Habazaki *et al.*, 2000).



4.4 Schematic diagrams showing the development of a porous anodic film on aluminium under (a) constant current conditions, and (b) constant voltage conditions (Parkhutik and Shershulsky, 1992).

time. This relationship falls down for thicker films and those produced under particularly aggressive solution conditions, where the effects of chemical dissolution become significant.

The anodic reaction that leads to film growth takes place mainly at the metal/oxide interface, and therefore the film is effectively growing from within rather than building up on its outer surface. This means that the outer part of the film is in contact with the electrolyte for the full anodising time, and, depending on conditions, may become considerably dissolved chemically (without field enhancement) by the end of the anodising process. Underlying regions of the film are progressively attacked to lesser extents. Thus, the pores are tapered, being wider at their mouths than near the aluminium substrate. It then follows that the maximum achievable film thickness depends on the ability of the electrolyte to chemically dissolve the film. When anodising has been continued for sufficient time that the pore walls at the outer surface are vanishingly thin, then, although anodising may continue to produce film material at the metal/oxide interface, no further net film thickening takes place.

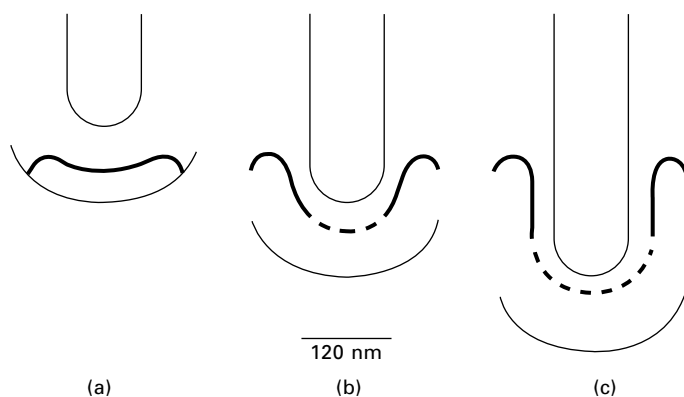
Understanding the factors that control this balance between the rate of

film formation and the rate of film dissolution forms a vital part of practical anodising technology (Sheasby and Pinner, 2001). Tracer studies employed by the group of G.E. Thompson (Garcia-Vergara *et al.*, 2006a, 2006b) have shown that the porosity of anodic alumina films is essentially of mechanical origin, initiated by the instability of the film under growth stresses when the anodising conditions do not allow formation of new film material at the film/electrolyte interface (corresponding to about 60% current efficiency). The film growth is accompanied by film material displacement from the barrier layer towards the cell walls (Fig. 4.5). This displacement arises under the influence of growth stresses and the barrier layer plasticity caused by the ionic transport processes.

4.3 Structural evolution of anodic films

4.3.1 Crystallisation processes

During the development of the science associated with the structure of anodic films, such films have variously been described as amorphous, microcrystalline, γ - Al_2O_3 , γ' - Al_2O_3 or η - Al_2O_3 . Material is amorphous if it is X-ray indifferent, i.e. no spotty diffraction pattern can be obtained. Nanocrystalline describes such material where the crystalline size is less than about 40 nm. γ - Al_2O_3 is a transition alumina produced during the thermal transformation of boehmite to corundum (Wefers and Misra, 1987). It has a tetragonally deformed spinel-type structure and contains cation vacancies and several percent hydroxyl ions. η - Al_2O_3 is also a transition alumina but arises from the decomposition of bayerite. According to Verwey (1935), the



4.5 Schematic diagrams showing the relative distributions of W tracer in anodic films at intervals of 60 s of anodising at 500 mA/dm² in 0.4M phosphoric acid solution at 20°C: (a) 180 (b) 240 and (c) 300 s. The distribution of (c) assumes a similar displacement of tungsten as in the previous 60 s (Garcia-Vergara *et al.*, 2006b).

O^{2-} ions in γ' - Al_2O_3 are arranged in a face-centred cubic lattice, and the smaller Al^{3+} ions are distributed statistically in the interstices between the oxygen ions, with about 70% of the aluminium ions having a coordination number of six, the rest having four.

γ - Al_2O_3 has been found by X-ray diffraction in films produced in oxalic acid (Schmid and Wasserman, 1932), concentrated sulphuric acid (Tajima *et al.*, 1959) and boric acid (Burgers *et al.*, 1932). Recently, Ono and co-workers (1990) have determined lattice parameters from electron diffraction patterns of films formed in chromic, phosphoric and sulphuric acids, which had undergone crystallisation under the electron beam. They concluded that the film material is comparable to η - Al_2O_3 .

Trillat and Tertian (1949) investigating, by electron diffraction, coatings of 1 μm and 20 μm thickness obtained in sulphuric acid on 99.99% aluminium. They found a crystal structure consisting of a mixture of the monohydrate and either the γ -oxide or a non-classified transition form at the extreme top layer. The lower layers of both coatings were amorphous. It must be remembered, however, that in the presence of moisture, the amorphous oxide coating is gradually transformed into the monohydrate, as during hydrothermal sealing, which may provide some explanation of the results of Trillat and Tertian (Sheasby and Pinner, 2001).

It is worth noting at this stage that the dielectric breakdown of anodic films can lead to the local formation of crystalline material. Plasma electrolytic oxidation (PEO) is a modification of the standard anodising process, using pulses of voltage greater than the dielectric breakdown potential for the oxide film. This process can be used to grow thick (tens or hundreds of micrometres), largely crystalline, oxide coatings on valve metals (Al, Mg, Ti, etc.) and is discussed further in Chapters 5 and 6.

4.3.2 Oxygen evolution

Oxygen evolution is a collateral electrode process that sometimes accompanies the main reaction of anodic oxidation. It usually becomes visible to the unaided eye during anodising at relatively high voltages (80 V) (Dimogerontakis *et al.*, 1998). In neutral solutions, the oxygen evolution can take place either from the discharge of the hydroxyl ions [4.4] or from the disintegration of the water molecules [4.5]:



Other possible routes are associated with the structural evolution of the anodic oxide film during its formation, e.g. crystallisation of amorphous anodic oxide, formation of individual oxide phases of alloying elements, and substrate impurities as well as spinel phases. In these cases, released

oxygen is often trapped inside the film, forming occluded porosity. Following reactions [4.4] and [4.5], the oxygen release implies appearance of electronic conductivity in originally dielectric oxide film, which is characteristic of pre-breakdown anodising stages.

Various kinetic mechanisms of the oxygen evolution reaction have been proposed (Antropov, 1977). Its rate is determined by the slowest step, which can be one of the following: discharge of hydroxyl ions or water molecules, recombination of oxygen atoms, electrochemical desorption of hydroxyl radicals, and formation and decomposition of unstable intermediate oxides of a metal present in the electrode.

4.3.3 Incorporation of anionic species

The knowledge of the nature/composition of anodic oxides as regards the incorporation of species such as electrolyte anions is of specific importance for both the understanding of the electrochemical mechanism of oxide production and growth, and the scientific and technological applications of porous anodic alumina films (Patermarakis *et al.*, 1999). Incorporated anionic species are considered as primary electron sources in the breakdown theory of anodic oxide films (Albella *et al.*, 1991). Their presence and distribution in the film are therefore crucial to ensure high dielectric properties of anodic oxides (e.g. in capacitor applications) or, if necessary, control breakdown phenomena (e.g. in advanced high-voltage anodising processes, see Chapters 5 and 6).

Electrolyte anions are always incorporated in the barrier layer and, through the mechanism of porous layer growth, in the pore walls. They extensively determine the oxide nature/composition across the walls and along the surface of pores and properties, such as reactivity, catalysis and porosity. A bell-like distribution of anions across the barrier layer and a qualitatively similar parabola-like one, have been verified for washed and dried films after anodisation. But during the film growth, the real distribution of anions is a monotonic one. Anions enter the barrier layer through suitable micro-crevices with widths comparable to molecular sizes and their local concentration decreases from the pore base surface towards the metal (Patermarakis *et al.*, 2001).

4.3.4 Internal stress and defect formation

Oxide films and coatings are potentially very effective in developing hard, wear- and corrosion-resistant surfaces. However, many properties of anodic films are controlled or influenced by local defects or non-uniformities in the barrier layer, such as stress-induced breaks in the oxide, local regions of crystalline oxide and, on a larger scale, the effects of second phase particles

at the metal surface (Sheasby and Pinner, 2001). The growth of oxide films is accompanied by the development of stresses in the oxide films, which can be both beneficial and harmful. So, the ultimate thickness to which an anodic oxide film may grow without cracking or detachment depends on its ability to relieve the growth stresses (Moon and Pyun, 1998). Compressive stresses are more favourable than tensile, because they increase resistance to fatigue failure. Conversely, crack initiation, stress corrosion, and decrease of fatigue limit can serve as examples of a detrimental effect of tensile residual stresses.

The presence of stresses in oxide films and their effects on cracking, spalling and decohesion of oxide films has been recognised for some time (Krishnamurthy and Srolovitz, 2003). There have been relatively few attempts to investigate the mechanisms that produce the observed stress distributions in films produced by oxidation. The earliest explanation for the origin of these stresses was offered by Pilling and Bedworth (1923), who proposed that these stresses were due to the difference in molar volumes of the oxide and the metal. Stresses generated within the oxide films may be either compressive or tensile. The sign of these stresses may not be attributed simply to the relationship between the volumes of oxide and metal from which the oxide is formed, as stress measurements have shown that the magnitude and sign of the stresses is dependent upon the oxide formation conditions, e.g. in the case of anodising, conditions such as surface preparation, electrolyte pH, current density, and electrolyte composition (Archibald, 1977).

4.4 Practical anodising processes

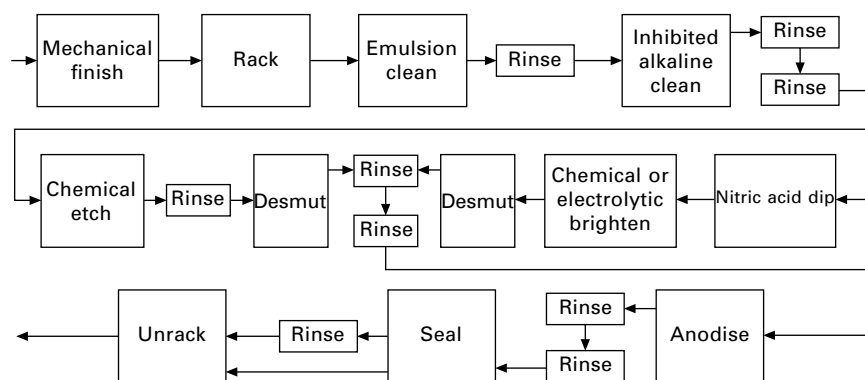
For the anodic oxidation of aluminium, the most widely used processes are based on sulphuric acid and chromic acid. The sulphuric acid processes are most generally used for the production of decorative, protective, and hard, wear-resistant coatings. The chromic acid processes are employed where maximum protection is required with a minimum loss of metal section (The Canning Handbook, 1982). Other processes, used less frequently or for special purposes, use sulphuric acid with oxalic acid, phosphoric acid, or oxalic acid alone (Table 4.1). Except for thicker ($\geq 25 \mu\text{m}$) coatings produced by hard anodising (see Section 4.4.3) processes, most anodic coatings range in thickness from 5 to 18 μm (ASM, 1994). The sequence of operations typically employed in anodising, from surface preparation through sealing, is illustrated in Fig. 4.6.

4.4.1 Chromic acid process

The earliest commercial anodising development (in Britain by Bengough and Stuart in 1923) was with chromic acid electrolytes and their names are

Table 4.1 Anodising processes for aluminium and its alloys (ASM, 2003)

Solution composition	Concentration (wt%)	Temperature (°C)	Current density (A/dm ²)	Voltage (Vdc)	Appearance and other characteristics
<i>Chromic acid</i>					
Chromic acid (CrO ₃)	10	45–55	0.3–1	40–50	Greyish
<i>Sulphuric acid</i>					
Sulphuric acid (H ₂ SO ₄)	5–25	15–25	0.8–3	15–20	Transparent
Aluminium sulphate	0.1–5				
<i>Oxalic acid</i>					
Oxalic acid	3–5	20–30	1–1.5	25	Yellowish
<i>Phosphoric acid</i>					
Phosphoric acid	3–10	20–30	0.5–2	40–100	Light blue
<i>Hard anodising</i>					
Sulphuric acid	10–20	0–5	2–4	25–60	Transparent, Hardness > 600 HV
Aluminium sulphate	0.1–10				
Oxalic acid	1				
<i>Alkaline anodising</i>					
Sodium hydroxide	8–12	10–20	1–4	30–70	Resistant in basic solutions
Hydrogen peroxide	2–3				
Sodium phosphate	0.1–0.5				
<i>Alternating current anodising</i>					
Sulphuric acid	15–30	0–40	3–12	15–30 a.c.	Soft, flexible, sulphide included



4.6 Typical process sequence for anodising operations (ASM, 1994).

still widely used to describe chromic acid anodising. Due to the passivating ability of chromic acid, this anodising process is preferred for components such as riveted or welded assemblies where it is difficult or impossible to remove all of the anodising solution. This process yields a yellow to dark-olive finish, depending on the anodic film thickness although the colour is grey on high-copper alloys. Chromic acid anodising solutions contain from 3 to 10 wt% CrO_3 . A solution is made up by filling the tank about half full of water, dissolving the acid in the water, and then adding water to adjust to the desired operating level. The maximum reproducible film thickness obtainable is about 8–10 μm on most alloys, but 6061 produces only about 5 μm and the aluminium–copper alloys about 2.5 μm .

In the last decade, significant effort has been directed to environmental issues related to the disposal of waste electrolyte, by developing new anodising processes (Thompson *et al.*, 1999; Iglesias-Rubianes *et al.*, 2007). However, the relationships between anodising conditions, electrolyte composition and corrosion performance are still a source of debate, and a fundamental understanding of the anodising behaviour of the practical alloys would assist the development of replacements for chromic acid (Saenz de Miera *et al.*, 2008).

4.4.2 Sulphuric acid process

The basic operations for the sulphuric acid process are the same as for the chromic acid process. Parts or assemblies that contain joints or recesses that could entrap the electrolyte should not be anodised in the sulphuric acid bath. The concentration of sulphuric acid in the anodising solution is 5 to 25 wt%. The variables that need to be controlled are acid concentration, impurities in the anodising bath, electrolyte temperature, anodising voltage and current density, agitation of the electrolyte, and the composition and condition of the alloy being anodised. Further details about these variables and their effect on subsequent operations and on the final product can be found elsewhere (Brace and Sheasby, 1979).

4.4.3 Hard anodising

Hard anodising is a term used to describe the production of anodic coatings with film hardness or abrasion resistance as their primary characteristic. They are usually thick, by normal anodising standards (>25 μm), with higher hardness of typically > 600 HV on aluminium alloys, and they are produced using special anodising conditions (very low temperature, high current density, special electrolytes). They find application in general engineering for components which require a very wear-resistant surface, such as pistons, cylinders and hydraulic gear. The coatings produced are grey to black in

colour and are less-porous than with conventional anodising. They are often left unsealed, but may be impregnated with materials such as waxes or silicone fluids to give particular surface properties (Sheasby and Pinner, 2001). Not all aluminium alloys can be hard anodised. The 5xxx and 6xxx series alloys respond well to hard anodising, whereas 2xxx, 7xxx alloys and others, including casting alloys with high copper and silicon content, do not. For the higher silicon and copper-containing alloys, the anodised layer tends to be highly porous and of low hardness.

4.4.4 Barrier layer processes

The thickness of the porous-type anodic films obtained by the usual anodising processes, viz. sulphuric, chromic or oxalic acid processes, may be a disadvantage in cases where the metal is very thin and would be dissolved during normal film growth. Such an example is provided by the aluminium deposits obtained by evaporation in high vacuum (Weil, 1956) and commonly used for reflectors in optical instruments, as well as in car headlamps, electric torches, etc. For such deposits, which are usually below 0.5 μm in thickness, solutions must be used which produce barrier-type coatings (Sheasby and Pinner, 2001).

The films formed in barrier layer electrolytes are much thinner than those formed in electrolytes which have some solvent action on the film as it forms. The use of distilled water is more important with non-solvent anodising solutions than with solvent-type solutions. The film thickness depends almost entirely on the forming voltage, being approximately 1.3–1.4 nm per volt. The choice of voltage also depends on other factors, such as the bath resistance and the need to avoid sparking. Adequate films are usually formed in about 45 minutes; the need for forming periods greater than twice this usually indicates defects or dirt in the metal surface, and the product is unlikely to make a satisfactory electrolytic capacitor. In contrast with the films formed in solvent electrolytes, barrier layer films do not require sealing; they are merely washed and dried (Henley, 1982). The most commonly used barrier type electrolytes for protective purposes are ammonium tartrate and boric acid solutions. The process parameters and further detail can be found elsewhere (Sheasby and Pinner, 2001; Henley, 1982).

4.5 Pre-treatment processes

Pretreatment of the aluminium before anodising is essential in all cases, though it may be needed for a variety of reasons. In the simplest case, the material may need only to be cleaned or degreased, but in others it may require more complicated treatments to remove the air-formed oxide film or modify the surface appearance. Such surface oxides may be formed

during casting or heat treatment and can be removed by etching in alkaline or acid solutions. Alloys containing magnesium, during high temperature heat treatment or during storage in slightly humid conditions, tend to build up a layer of magnesium oxide on the surface which is insoluble in alkaline solutions, and attempts to etch in caustic soda may lead to a very rough and patchy surface as the etch acts selectively in removing the oxide skin by undercutting. This oxide is readily removable in nitric or sulphuric acid and it is always a wise precaution to institute an acid dip before alkaline etching of magnesium alloys (Short and Sheasby, 1974). However, in most cases the pretreatment will establish the required appearance for the application involved.

4.6 Anodising equipment

4.6.1 Tanks

Anodising tanks are usually constructed in mild steel, lined with suitable acid-resistant materials such as polypropylene, PVC, or rubbers such as neoprene. Lead-lined tanks, with the lead lining acting as the cathode, have also frequently been used. Further detail about the tank material can be found elsewhere (Sheasby and Pinner, 2001).

4.6.2 Refrigeration and temperature control

The control of temperature in the anodising electrolyte is of fundamental importance in almost all processes, and temperature control to within $\pm 1^\circ\text{C}$, or even $\pm 0.5^\circ\text{C}$, of the desired temperature is often necessary. This frequently requires a refrigeration system, as not only does the electrical energy input to the tank have to be removed, but the formation of aluminium oxide from aluminium is itself an exothermic process. Cooling can be achieved either by means of cooling coils in the anodising tank, or by pumping the electrolyte through an external heat exchanger.

4.6.3 Agitation and exhaust system

Agitation of the electrolyte is also an essential requirement for successful anodising, mainly to ensure that heat is taken away from the surface of the film and that the electrolyte temperature is uniform. The most common method of agitation is by means of air which must be clean and free from oil. This is fed from a blower or compressor to perforated PVC or polypropylene pipes, which are held along the bottom of the anodising tank. All anodising baths should be fitted with fume extraction systems, as the hydrogen evolved at the cathodes carries with it a fine mist of the acid electrolyte.

4.6.4 Power supply

Both rectifiers and motor generators have been used for anodising, but developments in rectifier technology and the general use of silicon rectifiers has meant that generators are little used today. For normal sulphuric acid anodising, a 24 V rectifier is suitable, but for chromic acid anodising or anodising in organic acid based electrolytes, voltages up to 60 or 70 V are needed. Even higher voltages may be used in the case of hard anodising and for the production of barrier-type films. In recent times, anodising using pulsed power supplies is being increasingly recommended (Yokoyama *et al.*, 1982). These power supplies are particularly effective in situations where high anodising current densities are required, or where difficult alloys are being processed, such as those with high copper contents. Both improved corrosion resistance and increased abrasion resistance are claimed for coatings produced by pulsed current anodising (Yokoyama *et al.*, 1982; Colombini, 1988; Juhl and Moller, 1997). In practice, these rectifiers allow anodising at higher rates than normal (Colombini *et al.*, 1983) without the danger of 'burning' of the anodic coating.

4.6.5 Cathodes

Whilst with lead-lined tanks the tank walls can be used as cathodes, in most cases it is normal to employ separate cathodes. This gives greater flexibility in terms of materials, and allows appropriate arrangement of the cathodes along the length of the tank. In some cases, such as chromic acid anodising, anode-cathode area ratio is important, and this can be controlled more readily with separate cathodes. Cathode materials used include lead, stainless steel, aluminium and graphite; and sheet, rod, bar and shaped electrodes are all used. In the case of sulphuric acid anodising, aluminium is the normal electrode material, usually in the form of 1050 or 1200 alloy plates or 6063 extrusions. The benefit of these over lead has been described by Grubbs (1981), who found reduced energy costs with aluminium and indicated a minimum anode-cathode distance of 25 cm.

4.6.6 Jigging

The objective in jigging is first to form a positive contact with the work, and second to make handling as easy as possible without running the risk of deforming the work in jigging or unjigging, or by movement between loose points of contact, etc. Points of contact should be chosen with care, preferably, of course, in positions which are hidden from the eye, as no film is formed at such points. Three or more points of contact may be necessary in order to avoid movement of the part within the jig. Each contact point should not

be allowed to carry more than 10–20 amperes, though this is to some degree dependent on the gauge of metal of which the article is made.

Jigs for anodising are often referred to as racks. Ideally, when made from aluminium, the jig material should be of the same or a similar alloy type to the material being anodised, or at least from a material that does not tend to rob the work of current by consuming more than its share. If possible, jigs should be designed to allow reasonable spacing between articles and to hold them parallel to the cathodes, as although the throwing power of most anodising electrolytes is good, significant variations in anodic film thickness will occur if work is too densely packed or is at very different distances from the cathodes (Sheasby and Pinner, 2001).

4.7 Post-treatment processes

4.7.1 Colouring

The colouring of anodic oxides is accomplished by using organic and inorganic (e.g. ferrite ammonium oxalate) dyes, electrolytic colouring, precipitation pigmentation, or combinations of organic dyeing and electrolytic colouring. After the anodising step, the parts are simply immersed in the subject bath for colouring. Dyeing consists of impregnating the pores of the anodic coating, before sealing. The depth of dye adsorption depends on the thickness and porosity of the anodic coating. The dyed coating is transparent, and its appearance is affected by the basic reflectivity characteristics of the aluminium. For this reason, the colours of dyed aluminium articles should not be expected to match paints, enamel, printed fabrics, or other opaque colours (ASM, 1994).

The main requirements of anodic films that are to be dyed are: (i) that the coating is of adequate thickness, the precise thickness varying with the shade to be dyed, i.e. dark colour tones will require thicker coatings; (ii) that it is sufficiently porous and absorptive; (iii) that the coating itself has a suitable colour; and (iv) that it is free from blemishes due to scratches, porosity, pits, etc., and from differences in metallurgical structure such as grain size variation or segregation. Many types of organic dyes are in use, including both acid and basic types. Alizarin dyes, complex dyes, indigo dyes and even cotton dyes, diazo dyes, etc. are employed. The colour obtained is a function of the anodic film and the degree of dispersion of the dye.

4.7.2 Sealing

In addition to breakdown of the anodised article by corrosion of the base metal through film defects, the anodic film may itself be attacked and destroyed, also allowing metal corrosion to occur. This is prevented by sealing the

oxide film, which can be carried out in a number of different ways, having varying efficiencies. When the article is not expected to have a long life, the sealing generally need only be sufficient to prevent staining and leaching of the colouring matter, but when the surface is expected to withstand attack for a long period, it is essential to ensure that the oxide film has been made as unreactive as possible by the sealing process (Conference on Anodising Aluminium, 1961).

When properly done, sealing in boiling deionised water for 15 to 30 minutes partially converts the as-anodised alumina of an anodic coating to an aluminium monohydroxide known as Boehmite. It is also common practice to seal in a hot aqueous solution containing nickel acetate. Precipitation of nickel hydroxide helps in plugging the pores. The corrosion resistance of anodised aluminium depends largely on the effectiveness of the sealing operation. Sealing will be ineffective, however, unless the anodic coating is continuous, smooth, adherent, uniform in appearance, and free of surface blemishes and powdery areas. After sealing, the stain resistance of the anodic coating also is improved. For this reason, it is desirable to seal parts subject to staining during service.

4.8 Anodising magnesium

Three methods of anodising magnesium are widely employed by industry. One uses only the internal voltage generated as a result of a galvanic couple, and two use an external power source. The first method, often referred to as galvanic anodising or the Dow 9 process, uses a steel cathode electrically coupled to the magnesium component to be anodised. Dow 9 coatings have no appreciable thickness and impart little added corrosion resistance. However, the resulting coating is dark brown to black, which makes it useful for optical components and for heat sinks in electronic applications. This coating also serves as an excellent paint base. The other two anodising processes, known as the HAE and Dow 17 processes, use an external power source. Both processes produce an anodic layer about 50 μm thick, but they differ in that the solution used for Dow 17 coatings is acidic whereas the HAE process employs an alkaline bath (ASM, 1994) as detailed in Table 4.2.

4.8.1 HAE process

The HAE anodic coating is named after its inventor, Harry A. Evangelides, who patented the coating in 1952. This treatment is effective on all forms and alloys of magnesium, provided no other metals are inserted or attached to the magnesium workpiece. Alternating current is applied to form the coating and the voltage typically does not exceed 125 V. The treatment

Table 4.2 Anodising processes for magnesium alloys (Brandes and Brook, 1992)

Solution composition	Concentration (g/l)	Temperature (°C)	Current density (A/dm ²)	Time and voltage	Remarks
<i>HAE process</i>					
Potassium hydroxide	120	<35	1.2–1.5	90 min at 85 V approx.	Matt, hard, brittle, corrosion resistant, dark brown, 25–50 µm thick, abrasion resistant
Aluminium	10.4			a.c. preferred	
Potassium fluoride	34				
Trisodium phosphate	34				
Potassium manganate	20				
<i>Dow 17 process</i>					
Ammonium bifluoride	232	70–85	0.5–5	10–100 min up to 110 V a.c. or d.c.	Matt, dark green, corrosion resistant, 25 µm thick approx., abrasion resistant
Sodium dichromate	100				
Phosphoric acid	88				

produces a two-phase coating (as in the Dow 17 process). With a current density of 1.2–1.5 A/dm², the terminating potential of 65–70 V for the thin (5 µm) light-tan coating is reached after 7–10 minutes, and for the thick (50 µm), dark brown, vitreous, relatively brittle and highly abrasive layer, the terminating potential of 80–90 V is reached after 60 minutes (Groshart, 1985; Karimzadeh and King, 1996; Ghali, 2000; www.tagnite.com). Upon sealing, the HAE treatment provides excellent corrosion resistance. The dark brown coating is hard, with good abrasion resistance, but it can adversely affect the fatigue strength of the underlying magnesium, particularly if it is thin (Gray and Luan, 2002).

4.8.2 Dow 17 process

Dow 17, one of the first anodised magnesium coatings, was invented in the mid-1940s by the Dow Chemical Company, and can be applied to all forms and alloys of magnesium. It may be applied using either alternating or direct current, while the voltage normally does not exceed 110 V. This process produces a two-phase, two-layer coating. The first layer is deposited at a lower voltage and results in a thin, approximately 5 µm, light-green coating. The overlayer is formed at a higher voltage. It is a thick, dark-green coating of approximately 25 µm, which has good abrasion resistance, paint base properties and corrosion resistance. For thin, light-green coatings, the

voltage can be terminated at 64 V a.c.; for thick green coatings, at 90 V a.c. (Hawkins, 1993; Karimzadeh and King, 1996). However, within less than one minute, a transparent film can be formed, without affecting the metallic look of the alloy (Gross, 1961).

4.8.3 Limitations

Even though magnesium and its alloys can be anodised by either d.c. or a.c. current in nearly any solution which can carry current and not dissolve the magnesium or the coating faster than it can form (Groshart, 1985), the main problem remaining is the porosity/defect density of MgO coatings, which is based on the volume coefficient of 0.85 for the oxide if compared with 1.38 for Al₂O₃ coatings. For a reasonable protective oxide layer, the volume coefficient of the oxide should be larger than 1 to guarantee a dense and defect-free coverage of the metal surface. Furthermore, the hardness of MgO is rather low; thus it can be more easily removed or damaged. The overall performance is not much better compared to conversion coatings, and the anodising process is more expensive.

It is remarkable that most of the older low voltage treatments are based on chromate-containing solutions, which are known to be quite effective in corrosion protection of magnesium alloys, but whose use is already or will be further limited due to the health and environmental issues involved with the use of chromates. In contrast to conversion coatings, not much research is performed to develop alternative chrome-free, low voltage anodising baths. Only a limited number of more recent activities to develop such new processes or treatment baths are known (Takaya, 1989; AIF, 2005) and none of them seems to be industrially used so far. Most of the successful more recent developments concentrate on high (above the breakdown) voltage anodising (i.e. plasma electrolytic oxidation), using discharges in the electrolyte to modify the surface. These treatments of magnesium and its alloys are described in more detail in Chapter 6.

4.9 Anodising titanium

While extremely corrosion resistant itself, titanium and its alloys are often anodised to impart properties other than corrosion resistance. For instance, in wear situations, titanium components are prone to galling (see Chapter 3). To overcome this tendency, titanium is often anodised in a caustic electrolyte. Two methods of anodising titanium are used in industry: acid anodising and alkaline anodising. Both processes can produce a porous TiO₂ film on the surface of titanium, but acid anodising can form a very thin oxide layer (<0.1 µm), while a relatively thick oxide film (< 4 µm) can be produced by alkaline anodising. The purpose of anodising titanium is to enhance its

wear resistance (alkaline anodising) and/or to impart desirable aesthetic appearance (via acid anodising).

By controlling the terminal voltage during acid anodising, vivid colours from silver to blue (Fig. 4.7) can be obtained. These are interference colours. A thin layer of titanium oxide is produced during the anodising process. White light falling on the oxide is partially reflected and partially transmitted and refracted in the oxide film. The light that reaches the metal/oxide surface is mostly reflected back into the oxide. Several reflections may take place. A phase shift occurs during this process, along with multiple reflections. The degree of absorption and number of reflections depends on the thickness of the film (Table 4.3). The light that was initially reflected from the oxide surface interferes with the light that has travelled through the oxide and been reflected off the metal surface. Depending on the thickness of the oxide, certain wavelengths (colours) will be in-phase and enhanced while other wavelengths will be out of phase and dampened. Hence, the observed colour is mainly determined by the oxide thickness, which itself is dependent on the applied voltage. At any given voltage, the oxide film grows to a specific thickness and then stops when the resistance increases to a point where no current is being passed. The phenomenon of voltage-controlled oxide thickness indicates that the colour is also voltage controlled. Decorative anodising has been widely utilised by the jewellery industry for years and can also be used to colour-code tools and hardware according to size and type, and for hobby items (bicycles, golf clubs, paint guns, etc.) (Metalast, 2000); these coatings are now finding functional use for medical (Sudarshan and Braza, 1991) and dental instruments (ASM, 1994).



4.7 Anodised titanium, with oxide layer increasing in thickness from the bottom up (Titanium Information Group, 2006).

Table 4.3 Relationship between formation voltage, thickness and colour of anodic films on titanium anodised in phosphoric/sulphuric acid (Titanium Information Group, 2006)

Formation voltage	Thickness (nm)	Colour
0	1.5	Silver
2	2.5	Silver
4	10.5	Gold colour just detectable
6	13.2	
8	16.0	Very pale gold
10	18.0	Pale gold
12	27.0	Rich gold
14	24.2	Dark gold
16	25.4	Dark gold with a purple tint
18	26.0	Dark gold/purple
20	27.2	Purple with a gold tint
22	34.9	Blue/purple
24	36.4	Dark blue
28	46.9	Mid blue
30	61.0	Light blue
32	71.5	Pale blue

Thicker oxide films, able to withstand relatively higher loading, are produced by alkaline anodising processes. Codeposition of low friction polymers simultaneously with the growth of the anodic film provides both surface hardness and optimum corrosion resistance and lubricity. Anodising of titanium alloys can reduce friction and wear and can, to some extent, prevent galling and seizing by conjunction with dry film lubricants (Jenkins, 2003).

4.9.1 Acid anodising

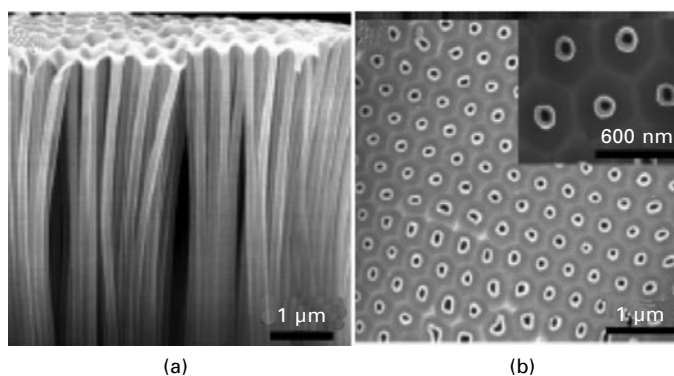
Contrary to popular belief, acid anodising of titanium, which thickens the oxide film, confers only a minimum improvement to wear resistance. The anodic film also serves to reduce the inward diffusion of oxygen at elevated temperature and of hydrogen under conditions of galvanic charging. Many electrolytes are effective; 80% phosphoric acid + 10% sulphuric acid + 10% water produces a sound coherent film with potential raised from 0 to 110 V over 10 minutes. Galling can be significantly reduced by acid anodising, for example on threaded components, by conjunction with compressive surface treatment, and with a dry film lubricant. Ti-6Al-4V bolts used on the successful Heidrun riser had an epoxy polyamide molydisulphide coating applied over a peened and anodised surface (Titanium Information Group, 2006).

4.9.2 Alkaline anodising

Thicker oxide films, able to withstand relatively higher loadings, are produced by an alkaline anodising processes such as TiodizeR. Long established alkaline-base proprietary finishes, such as CanadizingR, control the oxide film thickness and density so that one or more of a series of dry film lubricants may be applied and ‘locked-in’ to the surface. Canadized coatings have been used successfully to prevent galling at the joints and in the drive shaft of the titanium core sample drill tubes used in NASA’s exploration of the moon (www.azom.com).

4.10 Future trends

Anodising is one of the most promising surface treatments for such lightweight metals as aluminium, titanium and magnesium because it can increase wear- and corrosion-resistance, as well as provide aesthetic appearance and electrical insulation. More recently, porous anodic films produced on aluminium in solutions such as phosphoric, oxalic, sulphuric, and chromic acid have found their application in nanoscience and nanotechnology. Renewed interest has been paid to this type of film, primarily due to the possibility of producing membranes with highly ordered porous structures. Indeed, these membranes can be easily obtained by detaching the anodic oxide layer from the metal substrate and dissolving the barrier film at the base (see Section 4.2.2 and Fig. 4.1) in order to open the bottom of the pores (Bocchetta *et al.*, 2003). These microporous anodic oxide membranes (AOMs) can be used for catalytic and sensor devices, and as templates for the growth of nanowires where ordered structures are required (Fig. 4.8).



4.8 $\text{TiO}_2/\text{Ni}/\text{TiO}_2$ nanotubes obtained using atomic layer deposition (ALD). The tubes shown in (a) are removed from the alumina membranes. The tubes in (b) are embedded in the membranes (Daub *et al.*, 2007).

The limits of anodising, a 60-year-old technology, were broadened by the development of hard anodising processes, which can fabricate relatively thicker coatings with higher hardness or abrasion resistance than normal anodising. However, the problems of environmental concerns, high cost, wear, corrosion, heat and electrical resistance persist. A recently developed anodising process also known as plasma electrolytic oxidation (PEO), can address these problems as environmentally-friendly PEO can achieve much higher hardness (up to 23 GPa) and thickness (up to 200 μm) than conventional anodising (Yerokhin *et al.*, 1999). This process has opened new vistas in the anodising of lightweight metals. Previously difficult-to-anodise alloys can now be processed with relative ease. The improved surface characteristics, wear- and corrosion-resistance of PEO coatings make them much more attractive for replacing conventional anodising processes. The general properties of PEO compared to conventional d.c. anodising are highlighted in Table 4.4. The scope for industrial use of this technology is also quite promising due to the process flexibility, low capital cost and environmentally-friendly precursor materials utilised. The oxide coatings are produced by anodic polarisation at high voltage in a non-aggressive electrolyte, in which the oxide film can develop. At a critical potential, the electric field is sufficient to break down the oxide with the onset of electrical sparks and can lead to thermal ionisation together with microarc discharge phenomena (Khan, 2008). The oxide film can be fused and alloyed with elements in the electrolyte. PEO processes can occur at a high local temperature and pressure in the discharge channels. The oxide coatings generally consist of a porous top layer, a dense intermediate layer and a thin inner layer. Plasma electrolytic oxidation coatings are generally compact, thick, hard, and electrically and thermally insulating; adhesion to the substrate metal is very high. More

Table 4.4 General comparison of conventional d.c. anodising and PEO coating technologies (Walsh *et al.*, 2009)

Property	Conventional d.c. anodising	More recent PEO techniques
Cell voltage (V)	20–80	120–300
Current density (A dm^{-2})	<10	<30
Substrate pretreatment	Critical	Less critical
Common electrolytes	Sulphuric, chromic, or phosphoric acid	Neutral/alkaline pH 7–12
Maximum scale	Can be $>1000 \text{ m}^2 \text{ day}^{-1}$	Usually $<10 \text{ m}^2 \text{ day}^{-1}$
Ability to coat alloys containing intermetallics	Relatively poor	Improved
Oxide thickness (μm)	<10	<200
Hardness	Moderate	Relatively high
Adhesion to substrate	Moderate	Very high
Temperature control	Critical	Not so important

detailed information regarding PEO process on aluminium, titanium and magnesium metals and their alloys is provided in later chapters.

4.11 References

- AiF (2005), *Entwicklung kostengünstiger Anodisierverfahren für Magnesiumlegierungen für funktionelle und dekorative Anwendungen*, Schlussbericht AiF-Vorhaben-Nr. 71ZN, Schwäbisch Gmünd, Forschungsinstitut für Edelmetalle und Metallchemie
- Albella J.M., Montero I., Martinez-Duart J.M. and Parkhutik V. (1991), 'Dielectric breakdown processes in anodic Ta₂O₅ and related oxides; A review' *J. Mater. Sci.* **26**, 3422–3432
- Anderson S.J. (1944), *Appl. Phys.*, **15**, 477
- Antropov L. (1977), *Theoretical Electrochemistry*, 2nd ed, Mir Publishers, Moscow
- Archibald L.C. (1977), Internal stresses formed during the anodic oxidation of titanium, *Electrochim. Acta*, **22**, 657–659
- ASM (1994), *ASM Metal Handbook* 1994, Surface Engineering, Vol. 5
- ASM (2003), *ASM Metal Handbook* 2003, Corrosion: Fundamentals, Testing, and Protection, Vol. 13A
- Bengough G.D. and Stuart J.M. (1923), *Brit. Pat.* 223994
- Benjamin S.E. and Khalid F.A. (1999), Stress generated on aluminium during anodisation as a function of current density and pH, *Oxidation of Metals*, **52**, No. 314, 209–223
- Bocchetta P., Sunseri C., Chiavarotti G., Di Quarto F. (2003), *Electrochim. Acta*, **48**, 3175–3183
- Brace A.W. and Sheasby P.G. (1979), *The Technology of Anodising Aluminium*, Technicopy Ltd, England
- Brandes E.A. and Brook G.B. (1992), *Smithells Metals Reference Book*, 7th ed., Butterworth-Heinemann, Oxford, UK
- Brock A.J. and Wood G.C. (1967), *Electrochim. Acta*, **12**, 395
- Bryan J.M. (1950), *J. Soc. Chem. Ind.*, **69**, 169–173
- Burgers J.W., Claassen A. and Zernicks D. (1932), *Z. Phys.*, **74**, 599
- Colombini C. (1988), *Trans. Inst. Met. Fin.*, **66**, 142–143
- Colombini C., Montorsi A. and Dalla Barba W. (1983), *Ossidare Oggi*, **3**, No. 1, 35–37
- Conference on Nodising Aluminium (1961), *Proceedings at the University of Nottingham*, published by The Aluminium Development Association
- Daub M., Knez M., Goesele U. and Nielsch K. (2007), *J. Appl. Phys.* **101**, 09J111
- Dimogerontakis T., Kompotiatis L. and Kaplanoglou I. (1998), 'Oxygen evolution during the formation of barrier type anodic film on 2024-T3 aluminium alloy', *Corrosion Science*, **40**, No. 11, 1939–1951.
- Garcia-Vergara S.J., Iglesias-Rubianes L., Blanco-Pinzon C.E., Skeldon P., Thompson G.E. and Campestrini P. (2006a), Mechanical instability and pore generation in anodic alumina, *Proc. R. Soc. A* **462**, 2345–2358
- Garcia-Vergara S.J., Skeldon P., Thompson G.E. and Habazaki H. (2006b), A flow model of porous anodic film growth on aluminium, *Electrochim. Acta*, **52**, 681–687
- Ghali E. (2000), 'Magnesium and magnesium alloys', in *Uhlig's Corrosion Handbook*, 2nd ed., edited by R. Winston Revie, John Wiley & Sons, 793–830
- Ginsberg H. and Kaden W. (1961), Study of the growth process of primary films on the surface of aluminium, *Proc. Aluminium Development Assoc. Conference on Anodising*, Nottingham, Preprint No. 8, p. 101

- Gray J.E. and Luan B. (2002), Protective coatings on magnesium and its alloys – a critical review, *Journal of Alloys and Compounds*, **336**, 88–113
- Groshart E. (1985), Magnesium – Part II: Design for finishing, *Metal Finishing*, **83** (11), 57–59
- Gross W.H. (1961), Moderne Verfahren zur Oberflächenbehandlung von Magnesium und seinen Legierungen; *Metall*, **15** (6); 551–555
- Grubbs C.A. (1981), *Plating and Surface Finishing*, **68**, No. 11, 32–34
- Habazaki H., Takahiro K., Yamaguchi S., Shimizu K., Skeldon P., Thompson G.E. and Wood G.C. (2000), Importance of amorphous-to-crystalline transitions for ionic transport and oxygen generation in anodic films, *Phil. Mag. A*, **80**, No. 5, 1027–1042
- Hawkins J.H. (1993), Assessment of protective finishing system for magnesium; *50th Annual World Magnesium Conference*; May 11–13, 1993; Washington DC, International Magnesium Association
- Heine M.A. and Pryor M.J. (1963), *J. Electrochem. Soc.*, **110**, 1205
- Henley V.F. (1982), *Anodic oxidation of aluminium and its alloys*, Pergamon Press, England
- Hoar T.P. and Mott N.F. (1959), *J. Phys. Chem. Solids*, **9**, 97
- Holland E.R., Li Y., Abbott P. and Wilshaw P.R. (2000), *Displays*, **21**, 99–104
- Holland L. and Sutherland N. (1952), *Vacuum*, **2**, 155–159
- Hunter M.S. and Towner P.F. (1961), Determination of the thickness of thin porous oxide films on Al, *J. Electrochem. Soc.*, **108**, (2), 139–144
- Iglesias-Rubianes L., Garcia-Vergara S.J., Skeldon P., Thompson G.E., Ferguson J. and Beneke M. (2007), *Electrochim. Acta*, **52**, 7148
- Jenkins M. (2003), *Materials in sports equipment*, Woodhead Publishing Limited, Cambridge, England
- Juhl A.D. and Moller P. (1997), *Proc. of Aluminium 2000 Conf.*, Cyprus, **1**, 303–311
- Kaiser Aluminium and Chemical Corp. (1959), Brit. Pat. 820583
- Karimzadeh H. and King J.F. (1996), *Salt spray performance of HAE, Dow 17 and Tagnite coatings*; Report MR10/DATA/270; Magnesium Elektron Limited.
- Khan R.H.U. (2008), 'Characteristics and stress state of plasma electrolytic oxidation coatings', PhD thesis, The University of Sheffield, UK.
- Krishnamurthy R. and Srolovitz D.J. (2003), *Acta Materialia*, **51**, 2171–2190
- Martin C.R. (1996), *Chem. Mater.* **8**, 1739–1746
- Metalast Technical Bulletin (2000), *Titanium anodizing, An in house evaluation*, Metalast
- Moon Sung-Mo and Pyun Su-II (1998), The mechanism of stress generation during the growth of anodic oxide films on pure aluminium in acidic solutions, *Electrochim. Acta*, **43**, Nos. 21–22, 3117–3126
- Ono S., Ichinose H., Kawaguchi T. and Masuko N. (1990), *Corrosion Science*, **31**, 249
- Parkhutik V.P. and Shershulsky V.I. (1992), Theoretical modelling of porous oxide growth on aluminium, *J. Phys. D: Phys.* **25** 1258–1263
- Patemarakis G., Chandrinos J. and Moussoutzanis K. (2001), Interface physicochemical processes controlling sulphate anion incorporation in porous alumina and their dependence on the thermodynamic and transport properties of cations, *J. Electroanalytical Chemistry*, **510**, 59–66
- Patemarakis G., Moussoutzanis K. and Nikolopoulos N. (1999), Investigation of the incorporation of electrolyte anions in porous anodic Al₂O₃ films by employing a suitable probe catalytic reaction, *J. Solid State Electrochem* **3**, 193–204
- Pilling N.B. and Bedworth R.E. (1923), The oxidation of metals at high temperatures, *J. Inst. Met.*, **29** 529–582

- Rummell T. (1936), *Z. Physik*, **99**, 518–551
- Saenz de Miera M., Curioni M., Skeldon P. and Thompson G.E. (2008), Modelling the anodising behaviour of aluminium alloys in sulphuric acid through alloy analogues, *Corrosion Science* **50** 3410–3415
- Schenk M. (1948), *Werkstoff Aluminium u. seine Anodische Oxydation*; A. Francke A.G., Berne
- Schmid E. and Wassermann G. (1932), *Aluminium*, **4**, 100
- Sheasby P.G. and Pinner R. (2001), *The surface treatment and finishing of aluminium and its alloys*, Vol. 1, 6th Ed., © Finishing Publications Ltd, UK.
- Short E.P. and Sheasby P.G. (1974), *Trans. Inst. Met. Fin.*, **52**, 66–70
- Sudarshan T.S. and Braza J.F. (1991), Surface Modification Technologies V, *Proceedings of the Fifth International Conference*, held in Birmingham, UK, pp 89–100
- Tajima S., Soda M., Mori T. and Baba N. (1959), *Electrochim. Acta*, **1**, 205–216
- Takaya M. (1989), Anodizing of magnesium alloys in KOH–Al(OH)₃ solutions, *Aluminium*, **65** (12), 1244–1248
- The Canning Handbook (1982), *Surface Finishing Technology*, Birmingham, England
- Thompson G.E., Zhang L., Smith C.J.E. and Skeldon P. (1999), *Corrosion*, **55**, 1052
- Titanium Information Group (2006), *A Designers and Users Handbook, Surface Treatment of Titanium*
- Trillat J.J. and Tertian R. (1949), *Rev. Aluminium*, **26**, 315–19
- Verwey E.J.W. (1935), *J. Chem. Phys.*, **3**, 592
- Walsh F.C., Low C.T.J., Wood R.J.K., Stevens K.T., Archer J., Poeton A.R. and Ryder A. (2009), *Trans. Inst. Met. Fin.*, **87**, No 3, 122–135
- Wefers K. and Misra C. (1987), *Alcoa Technical Paper No. 19*, revised, Aluminium Company of America
- Weil F.C. (1956), *Electroplating and Metal Finishing*, **9**, No. 1, 6–10
- Yerokhin A.L., Nie X., Leyland A., Matthews A. and Dowey S.J. (1999), *Surf. Coat. Technol.* **122**, 73
- Yokoyama K., Konno H., Takahashi H. and Nagayama M. (1982), *Plating and Surface Finishing*, **69**, No. 7, 62–65

Plasma electrolytic oxidation treatment of aluminium and titanium alloys

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Abstract: This chapter gives a review of the plasma electrolytic oxidation (PEO) technique from scientific, technological and application points of view. The first section of the chapter reviews the historic development and advantages of the PEO process. Section 5.2 stresses the growth phenomenon and formation mechanism of PEO coatings. Section 5.3 discusses the effects of power source types and key process parameters (such as electrolyte composition, electrical parameters and solution temperature) on coatings. Section 5.4 discusses how this process can be applied in improving wear, corrosion protection, and other functional performance including anti-friction, thermal protection, optical, and dielectric. The final section gives a view of new process explorations.

Key words: plasma electrolytic oxidation (PEO), coating, aluminium alloy, titanium alloy, property.

5.1 Introduction

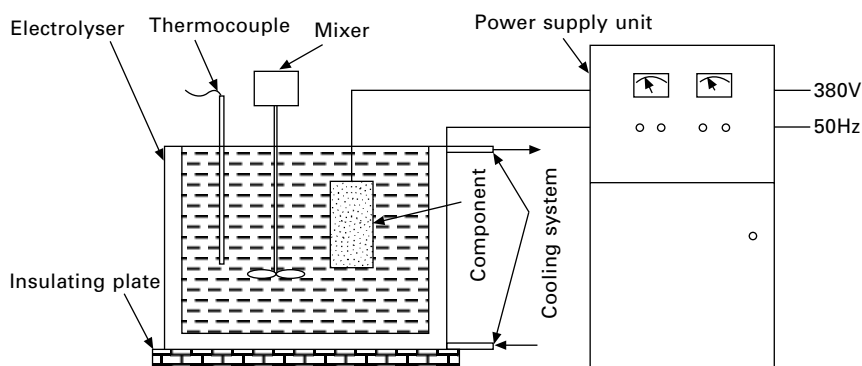
5.1.1 Historic notes

A relatively novel surface modification technique, normally known as ‘plasma electrolytic oxidation’ (PEO), also called ‘microarc oxidation (MAO)’ (Yerokhin *et al.*, 1998a,b) is attracting ever-increasing interest in fabricating oxide ceramic coatings on light alloys based upon Al, Ti and Mg. PEO treatment can enhance their corrosion- and wear-resistance properties, or confer various other functional properties including anti-friction, thermal protection, optical and dielectric, as well as a pre-treatment to provide load support for top layers. Based on the fact that it is rather difficult to catch and analyse the instant discharge event, understanding of the discharge nature is still slight due to the scarcity of experimental proofs, which also leads to the use of various terms such as ‘microplasma oxidation (MPO)’ (Xin *et al.*, 2001; Timoshenko and Magurova, 2000; Rudnev *et al.*, 1998; Magurova and Timoshenko, 1995a; Gerasimov *et al.*, 1994), ‘anodic spark deposition (ASD)’ (Brown *et al.*, 1971; Van *et al.*, 1977; Wirtz *et al.*, 1991; Rudnev *et al.*, 2001) and ‘anodic oxidation by spark deposition’ in Germany (ANOF) (Districh *et al.*, 1984; Krysmann *et al.*, 1984; Kurze *et al.*, 1986a, 1986b, 1987) in modern scientific literatures.

PEO is based on conventional anodic oxidation of light metals and their

alloys in aqueous electrolyte solutions, but operated above the breakdown voltage, which results in formation of plasma micro-discharge events. This allows the formation of coatings composed of not only predominant substrate oxides but of more complex oxides containing the elements present in the electrolyte. Figure 5.1 shows a typical schematic of the equipment used. The microstructure and properties of the coatings can be tailored by the careful selection and matching of electrolyte and electrical parameters; thus wide applications can be found in industrial sectors including automotive, aerospace (see Chapter 18), marine, textile, electronic (3C products), biomedical and catalytic materials (Chigrinova *et al.*, 2001; Atroshchenko *et al.*, 2000; Huang *et al.*, 2000; Hirohata *et al.*, 1999). The PEO technique experienced a long historical development. In the 1930s, Günterschultze and Betz (1934) investigated the phenomenon of spark discharge. It was not until the 1960s, when advances were made for producing cadmium niobate on the cadmium anode in an electrolyte containing Nb using spark discharge by McNiell and Gruss, that the practical application value of spark discharge was firstly exploited (McNiell and Gruss, 1966; McNiell and Nordbloom, 1958). From 1970, utilizing surface discharge to deposit oxide coatings on light metals was studied extensively in Russia, followed by America, Germany and other countries. The early industrial applications could be traced back to the late 1970s. However, the poor quality and low growth efficiency of the coatings delayed further development of this technique.

From the 1980s on, new developments of electrolyte, from acidic to alkaline, and power supply regime, from direct current to pulse current, enabled efficient formation of high quality coatings, especially in the last decade. For example, companies such as Keronite (UK), Magoxid-coat (Germany) and Microplasmic (USA) have devoted effort to the commercial exploitations of PEO coatings for the improvement of wear- and corrosion-resistance properties of light alloys. In the meantime, scientific research in



5.1 Schematic of the equipment for plasma electrolytic oxidation treatment.

many countries including Russia, China, Japan, UK, Germany and Australia has greatly contributed to the scientific understanding of PEO mechanisms and to the development of novel functionally structured PEO coatings. Future trends are expected to further explore new functional PEO coatings and to extend their industrial applications.

5.1.2 Advantages of the PEO process

The PEO technique has many advantages (Patel and Saka, 2001): (i) A wide-range of coating properties, including wear-resistance, corrosion-resistance and other functional properties (such as thermo-optical, dielectric, thermal barrier are conferred); (ii) no deterioration of the mechanical properties of the substrate materials is caused because of negligible heat input; (iii) high metallurgical bonding strength is measured between the coating and the substrate; (iv) there is the possibility of processing parts with complex geometric shape or large size; (v) equipment is simple and easy to operate; (vi) cost is low, as it has no need of experience vacuum or gas shielding conditions; (vii) the technique is ecologically friendly, as alkaline electrolytes are employed, and no noxious exhaust emission is involved in the process, meeting the requirement of green environment-friendly surface modification technology.

Compared with conventional anodizing and hard anodizing, PEO exhibits many excellent characteristics (Volynets *et al.*, 1991), as shown in Table 5.1. Although conventional anodizing in strongly alkaline solutions can produce coatings up to several microns thick, they are still too thin to provide effective protection against wear and corrosion, and therefore are used mainly for decoration. The PEO method, derived from conventional anodizing but enhanced by spark discharge events when the applied voltage exceeds the critical value of the insulator film, can generate thicker ceramic coatings with excellent properties, e.g. high hardness, good wear and corrosion properties, and excellent bonding strength with the substrate, compared with the conventional anodizing method. The process has demonstrated great successes in offering improved surface oxidation treatment of Mg, Al and Ti alloys, replacing the conventional acid-based anodizing processes and/or conversion treatments, which contain hexavalent chrome and other environmentally hazardous substances.

This chapter aims to give an overview of the PEO technique from scientific, technological and application points of view. Discussion on the latest developments will enable engineering designers to realize the potential of the PEO technique for manufacturing high-performance light alloy components and stimulate research into developing new coating materials for advanced applications of light alloys.

Table 5.1 Comparison of PEO process with conventional anodizing and hard anodizing

	Ordinary anodizing	Hard anodizing	PEO
Applied voltage (V)	10~50	20~120	150~800
Current density (A/dm ²)	0.5~2.5	1.5~3.0	5~20
Process flow	Chamfer→degreasing →acid neutralization → oxidation→ sealing	Chamfer→degreasing →acid neutralization → oxidation→ sealing	Degreasing → oxidation → (sealing), need no pretreatment ~Tens of mins
Oxidation time (min)	10~60	30~120	
Working temperature (°C)	0~30	<10	<50 (allows wide variation)
Electrolyte specie	Acid	Acid	Weak alkaline
Coating hardness (HV)	150~300	300~600	800~2000 (Al alloy) 300~600 (Mg alloy) 400~700 (Ti alloy)
Coating thickness (μm)	0.1~3	40~70	Up to 200 μm (adjustable)
Coating composition	Amorphous	Amorphous	A mixture of amorphous and nanocrystalline oxides
Wear resistance	Low	High	Highest
Corrosion resistance	Low	Medium	High
Elec. insulator	Low	Medium	High
Porosity	High	High	Low
Fatigue loss	Low	High (~47%)	Medium (~23%)
Environmental issue	Pollution, containing acid	Severe pollution, containing chrome	Eco-friendly

5.2 Fundamentals of the PEO process

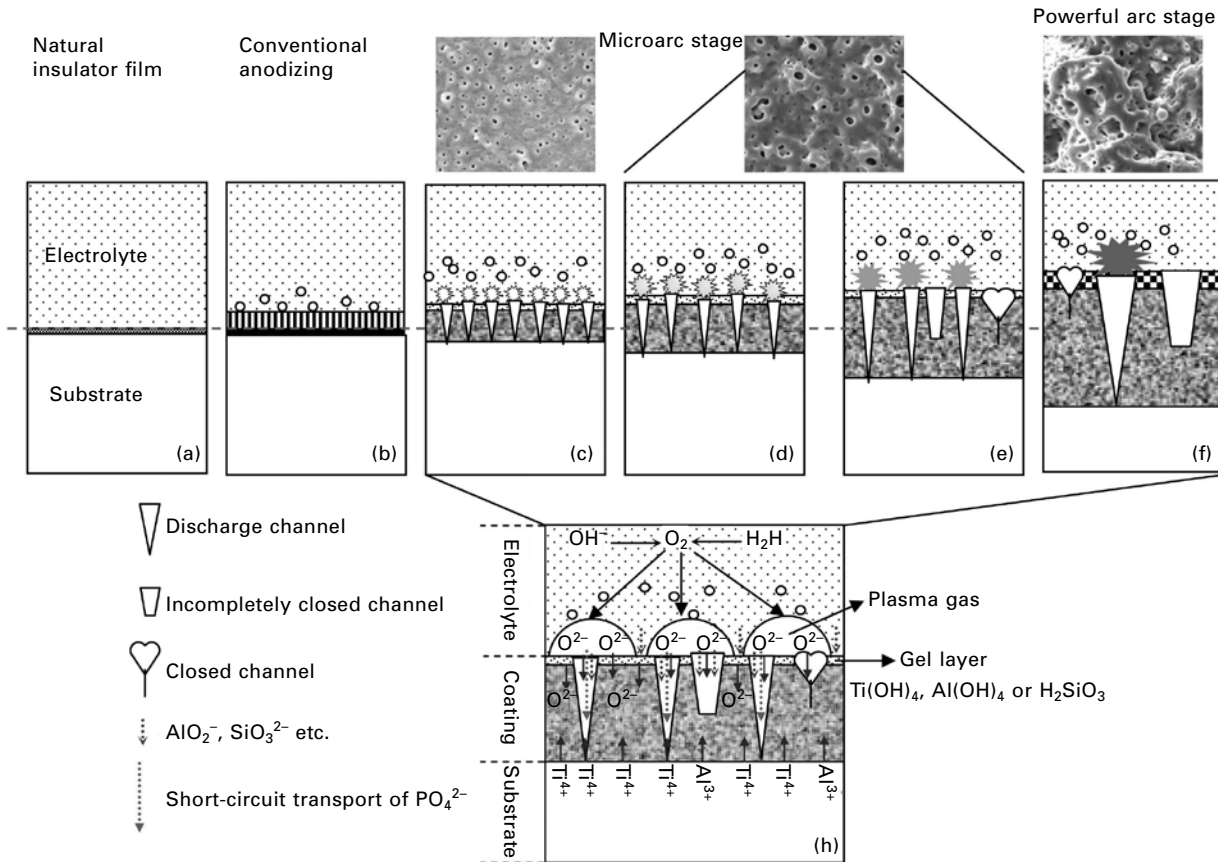
Plasma electrolytic oxidation proceeds accompanied by the evolution of spark discharge phenomena. Focusing on the nature of the spark discharge, previous researchers have proposed a variety of micro-oxidation mechanism models, such as an electronic ‘avalanche’ (Vijh, 1971), an electronic tunnelling effect (Ikonopisov *et al.*, 1977a,b), oxide film discharge centre (Krymann *et al.*, 1971) and contact glow discharge electrolysis (Yerokhin *et al.*, 2003). However, the discharge and growth mechanism of the coating is still controversial due to the scarcity of experimental proof, which is attributed to the difficulty

in catching the instant discharge event, particularly the local physical and chemical processes occurring in the discharge zones. Yerokhin *et al.* have suggested a coating formation mechanism from the chemistry point of view (Yerokhin *et al.*, 1999). Here, we add the further step of the coating formation mechanism, the breakdown-channel-melting effect (Fig. 5.2), based on an analysis of plasma micro-discharge oxidation phenomena and coating structure, as well as chemical reactions at the substrate/coating/electrolyte interfaces from the standpoint of materials science. The corresponding voltage – time curve is shown in Fig. 5.3.

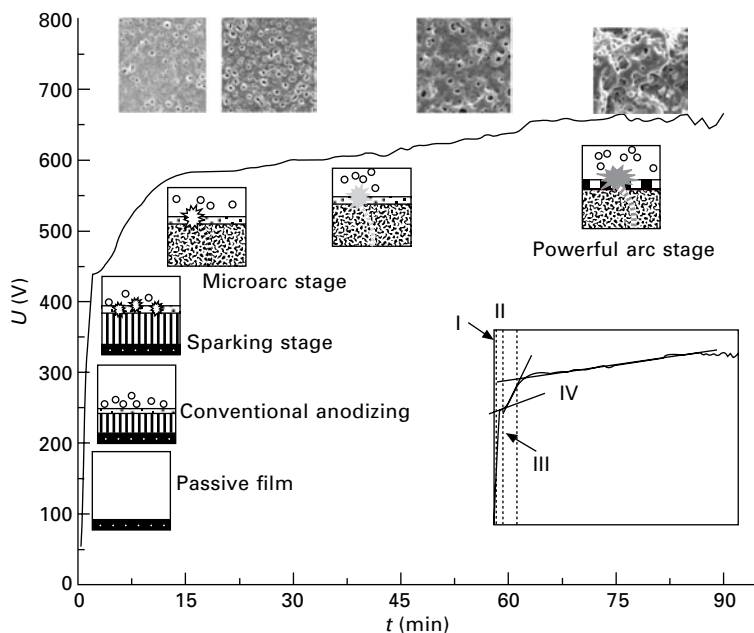
5.2.1 The coating growth phenomenon

Regardless of what kind of electrolyte systems or electrical parameter control modes (constant current or constant voltage) are applied, the basic formation mechanism of PEO coatings is similar. Taking the constant current mode as an example, Fig. 5.3 gives a schematic of the discharge phenomena and coating structure changes during the micro-discharge oxidation process. It is well known that there exists a very thin, natural, passive film on substrate metal surfaces (also shown in Fig. 5.2a), which could provide a very limited protective effect. As the applied voltage increases, a large number of gas bubbles are produced, which is the traditional anodizing stage with the formation of a porous insulation film with a columnar structure perpendicular to the substrate (Fig. 5.2b). When the voltage exceeds a certain threshold (i.e. breakdown voltage), dielectric breakdown occurs in some scattered weak regions across the insulating film, accompanied by the phenomenon of spark discharge (Fig. 5.2c). In this case, a large number of fine, uniform, white sparks are generated on the sample surface which result in the formation of a large number of small uniform micropores.

In constant current mode, in order to ensure effective coating breakdown, the voltage as feedback is forced to increase and reach a relatively stable value (Fig. 5.3). The colour of the sparks also gradually changes from white through yellow to orange-red, while the number decreases. In the yellow to orange-red sparks stage, coating growth rate is faster, this is known as the microarc stage. With the coating thickness increases, the voltage value increases. Meanwhile the number of sparks reduce but their intensity increases, which induces rather rougher surface morphologies (Figures 5.2d and e). With further increase of the voltage, the strong large dot arc discharge appears and bursts with ear-piercing noise (Fig. 5.2f). This causes a splash of the coating materials and local serious ablation characteristics, thus forming a porous and loose part of the PEO coating. To obtain high-quality coatings, this arc discharge stage should be avoided as far as possible.



5.2 Schematic of various chemical reactions and structural evolution developed during plasma electrolytic oxidation process of titanium alloy.



5.3 Schematic of discharge phenomena and coating microstructure developed during plasma electrolytic oxidation process.

5.2.2 Formation mechanism of PEO coatings

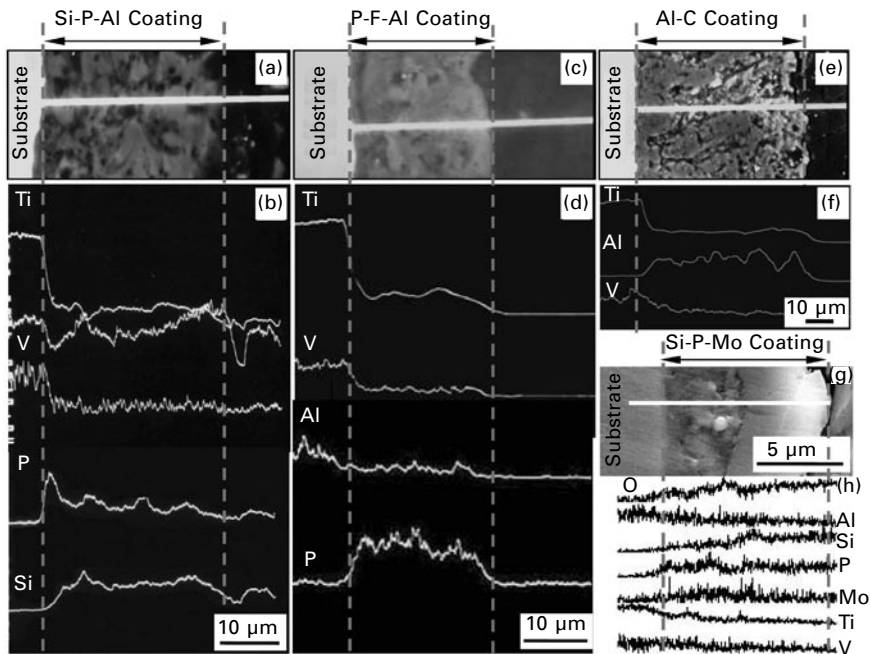
The coating formation process under micro-discharge can be broadly classified into the following three steps: First of all, a large number of dispersed discharge channels are produced as a result of micro-regional instability when the breakdown voltage is reached, as shown in Fig. 5.2c. The induced electron collapse effect makes the coating materials move into the discharge channels rapidly because of the high temperature ($\approx 2 \times 10^4^\circ\text{C}$) at, or around, the centre of discharge and the high pressure ($\approx 10^2$ MPa) in less than 10^{-6} s (Yerokhin *et al.*, 1999). Under a strong electric field force, anionic components such as PO_4^{3-} and SiO_3^{2-} enter the channels through electrophoresis. At the same time, passages, under the effect of high temperature and high pressure, allow alloying elements of the substrate to melt or diffuse into the channels. Secondly, the oxide products are solidified under the rapid cooling of the proximity electrolyte, thus increasing the coating thickness in the local area near to the discharge channels. When the discharge channels become cooled, the reaction products deposit on the channel walls to close the discharge channels. Finally, the produced gases are driven to escape out of the discharge channels, and as a result, the residual blind holes with ‘volcano’ shapes are maintained. When the oxidation continues, the above process repeats in the

relatively weak regions of the entire coating surface, thus promoting the overall uniform coating thickness.

In Region I of Fig. 5.3, voltage linearly increases with time, corresponding to the traditional anodizing stage, in which a very thin insulating film (as shown in Fig. 5.2b) forms, complying with Faraday's Law of 100% current efficiency. In Region II, the voltage increase slows with the decreased oxide film growth rate, which is attributed to the competition of anode coating growth and dissolution. In Region III, voltage increases rapidly to exceed the critical value, a large number of dispersed discharge channels (as shown in Fig. 5.2c) are produced as a result of micro-regional instability caused by breakdown and, at the same time, are accompanied by a large release of oxygen. The emergence of this large amount of oxygen is the main reason for lowering the current efficiency, and the mechanism of the release of oxygen has been discussed in a review (Yerokhin *et al.*, 1999). In Region IV, the voltage remains stable; this is known as the microarc stage. At the end of the stage, the strong dot arc discharge appears.

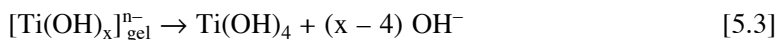
Each spark discharge event corresponds to a discharge channel throughout the coating, resulting in breakdown, channelling, melting and solidification effects, as follows:

- (i) *Discharge induced ion 'short circuit' migration.* By analysing element distribution across a section of distinct coatings formed in different electrolyte systems, it is assumed that PO_4^{3-} ion transports by 'short circuit' to the proximity of the substrate-coating interface and participates in chemical reactions, i.e. migrates through the discharge channels rather than through the diffusion effect. Elements, P from P-containing electrolyte and Ti from the substrate, are predominant in the neighbouring region of interface between coating and substrate (Fig. 5.4), implying that newly-formed products appear mainly near to the coating-substrate interface, which form through the complex reactions in discharge channels by the participation of all kind of ions (mainly electrolyte anions). Why can P easily transport near to the interface by the 'short circuit', while Si and Al migrate slower and mainly dominate in the outer coating? This depends on ionic mobility: the PO_4^{3-} ion does not so easily form a gel, as compared with Si and Al in the form of $\text{Al}(\text{OH})_3$ and H_2SiO_3 gel respectively, and therefore, PO_4^{3-} ion is more easily dragged to the region of the coating-substrate interface through the discharge channel under the high electric field effect. The investigation of species separation during coating growth on aluminium also evidences the mechanism, leading to an inner coating layer with P species nearest to the metal and Si species nearest to the coating surface (Monfort *et al.*, 2007).
- (ii) *Discharge induced coating in-growth.* Substrate metal (Ti as an



5.4 Line scanning of elements along the cross-section of PEO coatings on Ti6Al4 alloy: (a) (c) (e) (g) cross-section of morphologies of coatings; (b) (d) (f) (h) line scanning profiles of elements. Note: marked code represents the coating formed in different electrolyte systems – Si-P-Al coating ($\text{Na}_2\text{SiO}_3\text{-KOH}(\text{NaPO}_3)_6\text{-NaAlO}_2$), P-F-Al coating ($(\text{NaPO}_3)_6\text{-NaF-NaAlO}_2$), Al-C coating ($\text{NaAlO}_2\text{-Na}_2\text{CO}_3$), Si-P-Mo coating ($\text{Na}_2\text{SiO}_3\text{-KOH}(\text{NaPO}_3)_6\text{-Na}_3\text{Mo}_4$).

example) evolves into the discharge channels by dissolution, melting or sputtering, and then undergoes the chemical reactions:

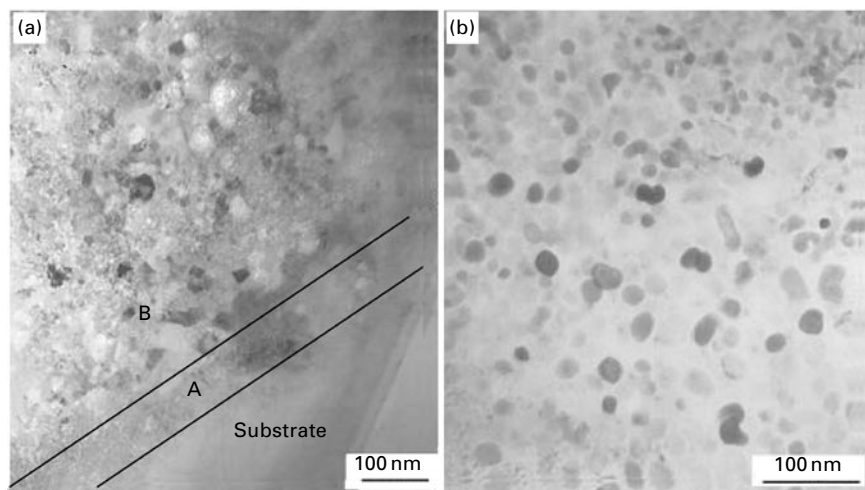


Under the rapid cooling effect of the cold proximity substrate, the generated melting oxide products near to the coating–substrate interface solidify to form a fresh nano-crystalline layer with small uniform nano grains (Fig. 5.5a in A Zone), while the nano grains in this layer are subject to gradual growth under the metallurgical process caused by the repeated discharge. Nie *et al.* (2002) also showed that the coating close to the interface exhibits a nanoscale polycrystalline microstructure

with an amorphous + nanocrystalline inner layer (1.5 μm thick) and a nanocrystalline intermediate layer (50–60 nm) in the coating formed on the Al alloy. Therefore, it is believed that formation of the very thin nanocrystalline layer is a universal characteristic of the PEO process, regardless of the substrate species. The nanocrystalline layer is constantly produced by ‘eating’ the substrate and moves towards the substrate; this is also considered as the main inner growth mechanism.

It should be noted that the very thin nanocrystalline layer near to the interface is a universal characteristic of the PEO process, regardless of the substrate species, while the grain size and phase composition of bulk coating away from the interface shows great distinction, depending on substrate species and electrolyte components. For example, TEM analysis indicates that the TiO_2 coating formed in silicate or phosphate dominated electrolyte mainly is nanocrystalline structured, combined with a small amount of amorphous phase (Fig. 5.5b), which is also confirmed by Matykina *et al.* (2009). The Al_2TiO_5 coating formed on Ti alloys in NaAlO_2 dominated electrolyte (Wang *et al.*, 2005b) as well as the Al_2O_3 coating formed on Al alloys (Guan *et al.*, 2008b) show a much larger grain size, generally at a μm scale.

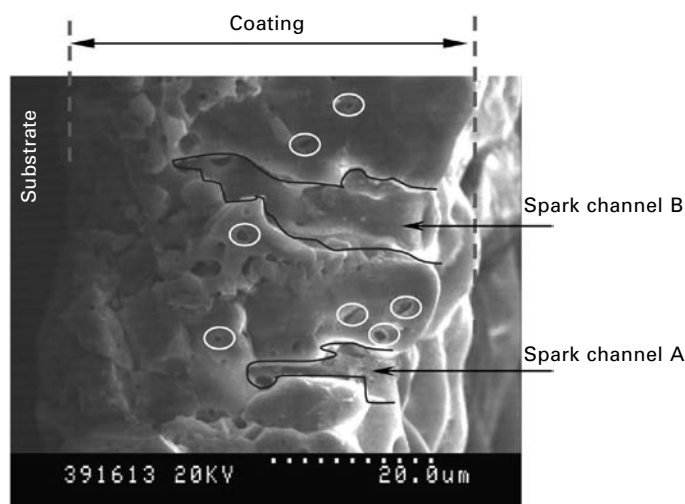
- (iii) *Discharge induced inner and outer growth of the coating.* It should be noted that the growth of coating above and below the original substrate surface is simultaneous. The inner growth is attributed to the continuous formation of a nanocrystalline layer by eating the substrate, while the oxide products of the chemical reactions occurring in the discharge



5.5 TEM images of (a) the inner layer near coating/substrate interface and (b) the dense layer deviating from the interface in the coating formed on Ti6Al4V.

channels are mainly responsible for the formation of the outer layer. The melting oxide products solidify to deposit on the inner wall of the discharge channel, and tend to close the channel, which enhances the growth of the compact inner layer. However, the produced excessive oxygen gas has to be compressed to escape from the channel, which causes the partial melting products to spray out and deposit on the margin of the channel, thus increasing the outer layer thickness in the local area near to the discharge channels. As a result, the residual blind holes with ‘volcano’ shapes are maintained. Therefore, the outer layer generally has a loose nature. Interestingly, not all channels are completely closed. In Fig. 5.6, channel A is not well closed and extends and terminates in the outer looser layer, while channel B significantly extends near the dense layer. The unclosed discharge channels facilitate the formation of a relatively thick coating, by allowing electrolyte to penetrate deep into the growing layer during the process.

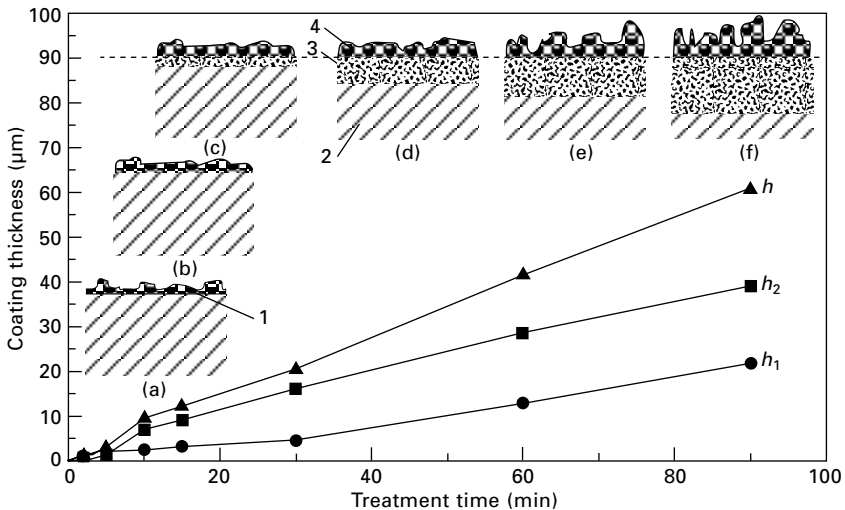
The small pores (ellipse indicating the retained pores in Fig. 5.6) in the bulk coating may form as a consequence of oxygen entrapment in the molten metals in the vicinity of localized discharge channels which occur during coating formation. In Section 5.4.1, the effects of retained pores in the coating will be discussed. The excessive oxygen gas evolution inevitably reduces the current efficiency (Yerokhin *et al.*, 1999; The *et al.*, 2003). It is estimated that the current efficiency of the oxide coating formation is generally as low as 10–30% (Snizhko *et al.*, 2004), while it can increase up to about 60% depending on the electrolyte additive and oxidation stages (Guo *et al.*, 2005).



5.6 Cross-section morphology of coating formed on Ti6Al4V in $(\text{NaPO}_3)_6\text{-NaF-NaAlO}_2$ solution (ellipses show the retained pores).

As mentioned previously, the coating growth above and below the original substrate surface is simultaneous. Figure 5.7 presents a schematic of the growth thickness evolution of the PEO coating. It can be seen that in the initial stages of oxidation (Fig. 5.3 Region I), the coating thickness increases rapidly, and the outer growth dominates with a loose and porous structure, as shown in Figures 5.7 a and b. In the middle stages of oxidation (Fig. 5.3, Regions II ~ IV), the growth rate of the coating slightly decreases, accompanied by the dominant inner growth of a dense coating, as shown in Figures 5.7c, d and e. With increasing oxidation time, the porous layer thickness in the outer coating increases. In the later Region IV of Fig. 5.3, the appearance of large and long-life sparks results in a looser and rougher coating surface (Fig. 5.7f). During the whole growth process, the inner growth is predominant; generally, the outer growth thickness of the coating registers as low as 30% of the total coating, variations depending on distinct alloy and electrolyte compositions. Therefore, PEO coating causes little change in the finished dimensions, making it suitable for production of precision components. If necessary, the outer growth layer can be polished to return to the original dimensions.

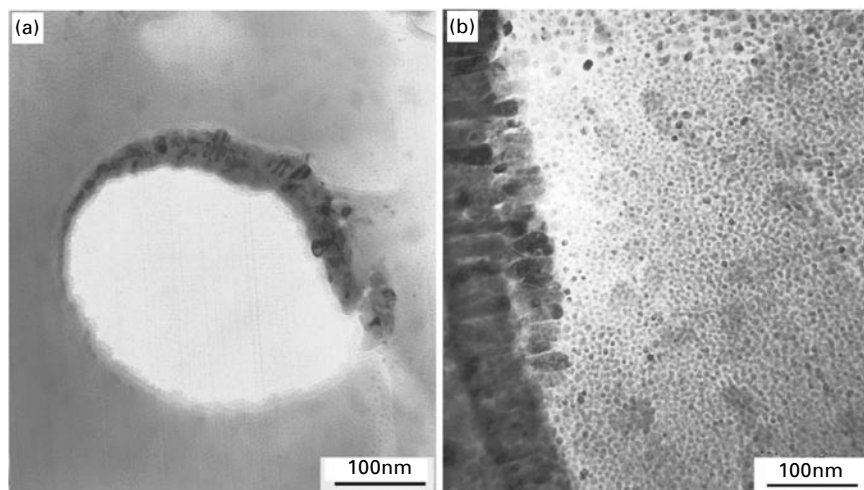
- (iv) *Discharge induced involvement of surface sediments into the coating.* Depending on particular electrolyte systems, insoluble and poorly-



5.7 Schematic of growth thickness evolution of plasma electrolytic oxidation coating: 1 = conventional anodizing film; 2 = substrate; 3 = inner growth layer; 4 = outer growth layer; (a) (b) in the initial stage; (c) (d) (e) in the medium stage; (f) in the final stage, the surface roughening of the coating is striking. h = whole thickness; h_1 = outer growth thickness; h_2 = inner growth thickness.

movable gels such as $\text{Al}(\text{OH})_3$ or H_2SiO_3 continuously deposit on the coating surface (Fig. 5.2h), the subsequent discharge process inducing the hydrated polygels to pyrolyse to form oxide products, which further involves the outer layer through channel effect. The different gel products from electrolytes deposited on the surface sediment layer will inevitably result in distinct external phases (such as SiO_2 , ZrO_2 , Al_2O_3 in the coating, which can be tailored to specially structured coatings for various applications, thus enhancing the design flexibility of coatings. In Section 5.3.2, the diversity of coating composition will be discussed depending on the electrolyte species.

- (v) *Discharge induced repeated melting–solidification process.* The coating of nanocrystalline grains combined with a small amount of amorphous phase forms as a result of solidification of melting products under rapid cooling by the cold substrate and electrolyte, as shown in Fig. 5.5b. The instantaneous temperature gradient around the discharge channel makes it easier to generate the columnar crystal structure along the edge of the discharge channel (Fig. 5.8). At the same time, the as-formed coating products are subjected to the melting–cooling–crystallization process under the instantaneous local heating and cooling cycle caused by the repeated discharge (corresponding to Fig. 5.2c ~ f phases), which leads to the formation of complex oxides as well as the possible transformation of metastable to high temperature stable phases (e.g. anatase to rutile phase transformation).

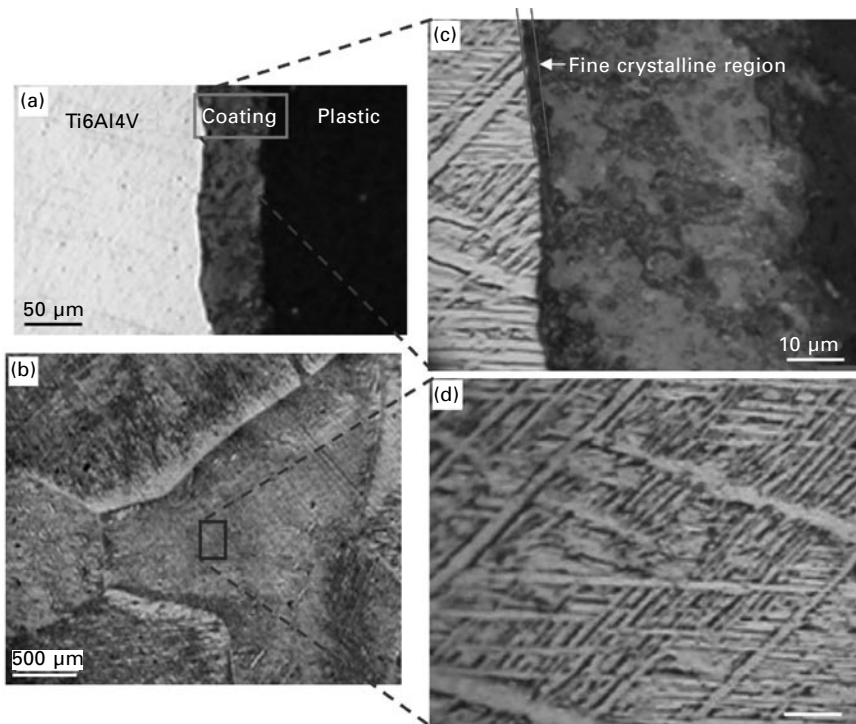


5.8 Pores remained after spark decaying and columnar crystal microstructure grown on pore walls of plasma electrolytic oxidation coating formed on Ti6Al4V alloy.

- (vi) *Discharge induces no changes of substrate microstructure.* Generally, the discharge event tends to occur in the coating–substrate interface or regions near the interface, accompanied by the formation of discharge channels through the coating. While the partial high-energy micro area (channel) caused by the discharge is quenched instantly, it is not enough to induce any change of substrate texture neighbouring to the coating–substrate interface (Fig. 5.9).

5.3 PEO power sources and process parameters

Both intrinsic factors (electrolyte compositions and pH) and extrinsic factors (power source types, electrical parameters, and electrolyte temperature) affect the formation and microstructure of PEO coatings. The composition and concentration of electrolyte and electrical parameters used during the process play a crucial role in obtaining the desired coatings with special phase components and microstructure.



5.9 Texture of Ti6Al4V substrate after plasma electrolytic oxidation: (a), (c) at the coating/substrate interface; (b), (d) far from the interface.

5.3.1 Power sources

Figure 5.1 shows a typical schematic of the equipment for PEO treatment. During PEO treatment, the parts are immersed in the solution, serving as one polar, while the stainless steel plates installed on the inner walls of the electrolyser are used as the counter polar. The coatings are prepared in an electrolyte solution (acid or alkaline) using a specially designed power source which can provide a high voltage and a strong current. The spark discharge induced by the applied high voltage leads to localized high temperature and high pressure, allowing the formation of coatings composed of not only predominant substrate oxides but of more complex oxides containing compounds that involve the components present in the electrolyte.

The specially designed power source for the PEO plays a decisive role in the preparation of the high-quality coatings desired for commercial applications. To some degree, the evolution of the power source demonstrates the developmental progress of the PEO technique. Various types of power sources, such as DC sources (Kuhn, 2003; Verdier *et al.*, 2005; Shi *et al.*, 2006), DC-pulsed sources (Zhao *et al.*, 2005; Nie *et al.*, 1996; Han *et al.*, 2007), AC sources (Arrabal *et al.*, 2008b; Magurova and Timoshenko, 1995b; Timoshenko and Magurova, 2000; Wang *et al.*, 2009; Yerokhin *et al.*, 1999) and bipolar pulsed sources (Yerokhin *et al.*, 2005; Jin *et al.*, 2006; Belov *et al.*, 2002; Shatrov, 2001a,b; Jaspard-Mécuson *et al.*, 2007; Timoshenko and Magurova, 2005) distinguished by different electrical regimes have been applied to produce oxide ceramic coatings on light alloys such as Al and Ti alloys. The adjustable flexibility of electrical regimes enables one to regulate the surface discharge characteristics over a wide range, which is closely related to the coating growth, microstructure and associated properties.

The DC power source developed before the 1970s were used only on a lab scale for preparing thin coatings on simple parts due to the limited controllability and flexibility of the PEO process caused by the difficulty in regulating the surface discharge. Since then, the invention of DC-pulsed and AC sources has greatly supported the rapid development and practical applications of the PEO technique. DC-pulsed sources allow control of the discharge duration by adjustment of the pulse duty cycle. In this way, the power energy can be used more efficiently with reduced energy consumption induced by interval discharge, and the corresponding microstructure and composition of the coatings can be tailored. A larger current density output is needed for the higher applied voltage (generally 800 V) due to the additional polarization caused by the creation of a charged double layer, thus extensive industrial applications are severely limited. In the case of an AC source, the additional polarization of the electrode can be avoided, meanwhile maintaining controllability of the discharge duration by setting the half-wave and full-wave using diode rectifier circuit. The full-wave power source is

inclined to accelerate the growth of the anodic films, and the half-wave one mainly contributes to the uniformity and fineness of the films (Wang *et al.*, 2009). However, the limitations in the power (typically 10 kW) and current frequency (mains frequency only) are the principal disadvantages of these sources that restrict commercial upscaling (Yerokhin *et al.*, 1999).

Recently, a novel bipolar pulse source, which can supply higher power and a wide range of frequencies, has been developed. It is attracting great interest for industrial production due to the strong appeal of obtaining a much more compact coating at a relatively low cost of energy consumption. Yerokhin *et al.* (2005) recently made a comparison between aluminium oxide layer properties obtained by 50 Hz AC and bipolar pulsed modes of PEO, confirming that the bipolar pulsed process is able to improve the coating morphology, particularly by reducing the thickness of the porous outer layer. Investigations from the literature (Jin *et al.*, 2006; Belov *et al.*, 2002; Shatrov, 2001a,b; Jaspard-Mécuson *et al.*, 2007; Timoshenko and Magurova, 2005) have all shown the importance of the pulse initiation delay and duration using bipolar pulsed sources at high frequency (up to kHz range). The significantly better properties of the bipolar pulsed samples can be attributed to the higher frequency current pulses, which enable the creation of shorter and more energetic micro discharge events. As a result, they have a more dense coating, resulting in a higher micro hardness and a lower friction coefficient compared to the DC samples (Jin *et al.*, 2006).

5.3.2 Effects of electrolyte

The intrinsic effects of the electrolyte can be summarized as follows: (i) first and most important, promoting metal passivation to form a thin insulating film, which is a necessary prerequisite for dielectric breakdown to induce spark discharge; (ii) as the medium for conducting current, transmitting the essential energy needed for anode oxidizing to occur at the interface of metal/electrolyte; (iii) providing the oxygen source in the form of oxysalt needed for oxidation; (iv) finally and also interestingly, allowing components present in the electrolyte to be incorporated into the coatings, further modifying or improving the properties of the PEO coatings.

To meet the prerequisite for dielectric breakdown, additives to promote strong metal passivation (such as silicates, aluminates and phosphates) are widely used as basic constituents of the electrolytes. The three groups have the following advantages: (i) they allow the sparking voltage to be easily reached, thus saving time; (ii) components present in the electrolyte (such as SiO_3^{2-} , AlO_2^- and PO_4^{3-}) are easily incorporated into the coatings by poly-reactions and deposition, thus increasing the coating growth rate; (iii) usage of environmentally friendly and inexpensive electrolytes produce wear-

and corrosion-resistant coatings which are beneficial for the commercial producer.

It has been proved by experiments that simple alkaline electrolytes are unfeasible for commercialization of the process, because of lower coating growth rates and very high energy consumption. Thus, a complex electrolyte composition is commonly desirable for investigation and commercial applications. Examples from the published information on the coating phases formed on Al and Ti alloys using complex electrolytes mainly containing strong passive silicates (aluminates or phosphates) are summarized in Table 5.2 (Voevodin *et al.*, 1996; Wu *et al.*, 2005; Lv *et al.*, 2006) and Table 5.3 (Wang *et al.*, 2005b, 2006a, 2004), respectively. Various other specially selected electrolytes and their combinations have been successfully developed in order to provide diverse functional coatings with biocidal or catalytic,

Table 5.2 Coating phase constituents formed on Al alloy in complex electrolytes mainly containing strong passive silicates (or phosphates)

Ref.	Electrolyte group	Substrate	Electrolyte composition	Phase composition of coating	Potential applications
Voevodin <i>et al.</i> , 1996	Silicate	B95 alloy	Na ₂ SiO ₃ , 2–20g/L KOH, 2–3 g/L	Al ₂ O ₃ , SiO ₂ Al-Si-O compound	Wear resistance, corrosion resistance
Wu <i>et al.</i> , 2005	Silicate	Al-Zn-Mg alloy	NaOH, 2 g/L Na ₂ SiO ₃ , 4 g/L	α -Al ₂ O ₃ dominated, γ -Al ₂ O ₃	Wear resistance, corrosion resistance
Lv <i>et al.</i> , 2006	Phosphate	Pure Al	(NaPO ₃) ₆ , 0.008 M NaOH, 0.025 M	α -Al ₂ O ₃ γ -Al ₂ O ₃ AlPO ₄	Biocidal, corrosion resistance

Table 5.3 Coating phase constituents formed on Ti alloy in complex electrolytes mainly containing strong passive silicates (aluminates or phosphates)

Ref.	Electrolyte group	Substrate	Electrolyte composition	Phase composition of coating	Potential applications
Wang <i>et al.</i> , 2006a	Silicate	Ti6Al4V	Na ₂ SiO ₃ (NaPO ₃) ₆ NaAlO ₂	Rutile dominated, anatase	Wear resistance, corrosion resistance
Wang <i>et al.</i> , 2005b	Aluminate	Ti6Al4V	NaAlO ₂ Na ₂ CO ₃	Al ₂ TiO ₅	Wear resistance, corrosion resistance
Wang <i>et al.</i> , 2004	Phosphate	Ti6Al4V	(NaPO ₃) ₆ NaF NaAlO ₂	AlPO ₄ dominated, TiO ₂	Biocidal, corrosion resistance

biomedical, ferroelectric, and semiconducting properties on alloys surfaces. The scope regarding electrolyte selection and relevant properties will be partially described in Section 5.4.

For specific purposes, anion additives such as Na_2WO_4 or K_4ZrF_6 for enhanced wear and corrosion resistance, as well as fine powder additives such as hard, high melting point materials (SiC , ZrO_2), dry lubricants (graphite, PTFE), colouring agents (Cr_2O_3 , V_2O_3) and bioactivity HA, can be introduced into the electrolytes, integrating cataphoretic effects to be incorporated into the coating.

Experiments carried out by Wang *et al.* (1999) revealed that the addition of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ salt to the electrolyte marginally increases the ratio of the thickness of the internal dense layer to the total coating thickness, while the coating deposition rate decreases. Super-hardness phases of m- ZrO_2 and t- ZrO_2 have been incorporated into the coatings on Mg alloys (Luo *et al.*, 2009; Mu and Han, 2008) and Ti alloys (Yao *et al.*, 2008) by introducing soluble K_4ZrF_6 into the electrolytes, and the as-obtained coating containing the ZrO_2 component is beneficial for the enhancement of wear and corrosion protection as well as heat insulation.

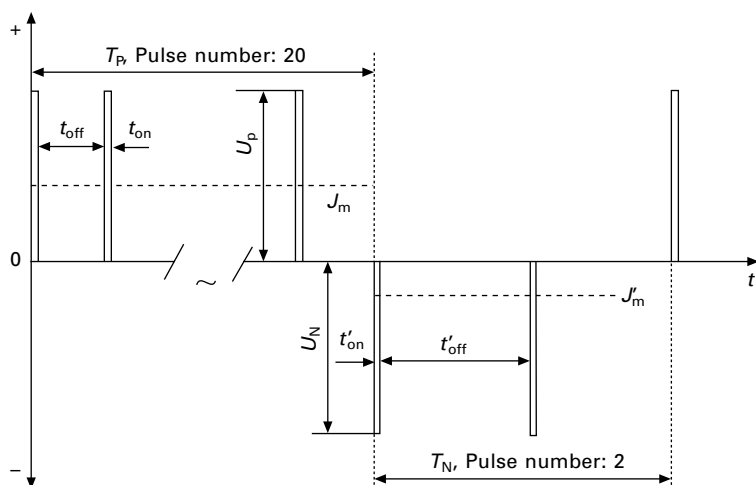
Arrabal *et al.* (2008a,b) have reported that zirconia particles can be incorporated into coatings formed by DC and AC PEO treatments of magnesium, and these coatings have comprised two main layers with zirconia particles incorporated preferentially into the inner layer regions and at the outer layer. Though relatively little zirconium is present in the inner layer, it can be evidenced that nanoparticles suspended in the electrolyte can reach the inner layer via short-circuit paths. Investigations conducted by Wang *et al.* (1999) indicated that the addition of silicon carbide (SiC) powder to the electrolyte reduces the ratio of the dense layer thickness to the total coating thickness. The SiC phase is entirely present in the external porous layer of the coating and thus does not enhance the wear resistance of the PEO coatings.

As well as the limit of greater power consumption, the short service lifetime of the electrolyte is another obstacle and challenge for industrial applications, which also affects the reproducibility of coatings and increases costs by having to update the electrolyte. In fact, almost all the published literature involves the development and optimum of electrolytes (including composition and concentration) for desirable coating properties, while issues on stability of the electrolyte restrict extensive applications. Therefore, selection of reasonable stabilizers and further optimization of the electrolyte composition to improve long-term stability is still an important research direction. In addition, on-line surveying and maintenance of electrolytes is another problem ahead of industrial producers. A possible way is to detect the real-time conductivity of the electrolyte and try to maintain a constant value by the addition of adjusting components.

5.3.3 Effects of electrical parameters

The larger amount of the porous outer layer of the coating leads to lower mechanical hardness, and thus worse performance. Much effort has been devoted to limit or to suppress the growth of the porous layer during PEO treatment. A way to achieve this requirement is to optimize the electrolyte composition. Another approach consists of using special current regimes such as bipolar pulses of current combined with optimal electrical parameters. In Section 5.3.1, it was established that the bipolar pulsed process is able to improve the coating morphology, especially by reducing the thickness of the porous outer layer by much shorter and less energetic micro discharges in the high frequency range.

A typical bipolar pulsed source, as an example, and the effects of electrical parameters (voltage, current, duty cycle and frequency) on the microstructure of the coatings formed on Ti6Al4V are therefore now discussed. The corresponding parameters and waveforms of the bipolar pulsed power source are given in Fig. 5.10. The pulse parameters (voltage or current, pulse on and off time, and working time for positive and negative pulse packets) can be adjusted independently of each other using respective electronic amplifiers. The independent adjustment of different current pulse parameters provides great flexibility in selecting the discharge intensity adequate for a specific coating microstructure. From our experience, it is the positive pulse rather



5.10 Schematic of bipolar pulse output of plasma electrolytic oxidation power supply unit: (t_{on} : positive pulse on time; t_{off} : positive pulse off time; t'_{on} : negative pulse on time; t'_{off} : negative pulse off time; T_p : working time for positive pulse packet; T_N : working time for negative pulse packet; J_m : positive average current density; J'_m : negative average current density).

than the negative pulse that plays a crucial role in the formation of the coating microstructure. The negative pulse is interspersed with the positive pulses only as a means to interrupt the spark discharges, permit the surface to cool, and induce the re-conversion of soluble components into metal oxide. Therefore, the number of pulses in the positive packet is much more than that in the negative packet, as shown in Fig. 5.10, twenty and two for the number of positive and negative pulses in one packet, respectively.

The sparking discharge duration and intensity depend on the pulse-on time and energy, respectively. The single pulse energy E_p is defined as:

$$E_p = \int_0^{t_p} U_p I_p dt \quad [5.5]$$

where U_p is the pulse voltage, I_p the pulse current and t_p the pulse-on time. Therefore, a change in the pulse cycle can regulate the surface discharge characteristics, which are responsible for the growth, microstructure and phase composition of the coatings.

Taking PEO of Ti6Al4V substrate as an example, only one parameter at a time was allowed to change in detecting the evolution of coating characteristics. Table 5.4 summarizes the effect of positive pulse parameters on the growth and microstructure of PEO coatings. It has been established from Table 5.4 that coating growth rate and surface morphologies depend mainly on the single pulse energy of the discharge. When increasing pulse voltage (reducing frequency, increasing duty cycle, or increasing current density), the single-pulse discharge energy rises, thus the coating product mass by a single pulse increases, finally resulting in increasing growth rate of the coating. In addition, increase of the single-pulse discharge energy leads to rapidly rising temperature in the local discharge zones by heat accumulation, which induces a much stronger hot plasma effect. As a result, larger size

Table 5.4 Effect of positive pulse parameters on growth and microstructure of microarc oxidation coatings formed on Ti6Al4V

Electrical parameters	Coating thickness	Surface morphology	Phase composition
Voltage (V) 350,400,450,500,550	Voltage ↑, Growth↑ (4~33μm)		Anatase TiO ₂ dominated,
Frequency (Hz) 1800,1400,1000,600,200	Frequency↓, Growth↑ (6~36μm)	Surface porosity↓, pore diameter,	changes as rutile dominated, transforms
Duty cycle 4%, 8%,12%,16%, 20%	Duty cycle ↑, Growth ↑ (10~35μm)	surface roughness	anatase to rutile (TiO ₂).
Current density (mA·cm ⁻²) 40,60,80,100,120	Current density ↑, Growth ↑ (17~21μm)		Slight phase transformation

pores are formed on the coating surface leading to high surface roughness. Meanwhile, the increasing single-pulse discharge energy is responsible for the phase transformation from anatase to rutile TiO_2 . Experiments conducted on D16 aluminium alloy (wt.%: Mg 1.2~1.8, Mn 0.3~0.9, Cu 3.8~4.9, Si 0.5, Zn 0.3, Fe 0.5, Ti 0.1, Al bal.) by Kuskov *et al.* (1990) also revealed that discharge intensity increase caused by increasing voltage and current density leads to higher coating hardness, which is attributed to increasing $\alpha\text{-Al}_2\text{O}_3$ content.

Generally, for a certain electrolyte system and alloy substrate, the coating growth rate and surface morphologies can be tailored by the optimization of electrical parameters. Recently, a controlled oxidation mode by stepped adjusting of electrical parameters has been proposed to improve the density of coatings (Wang *et al.*, 2005a), taking a constant current density of $60\text{mA}\cdot\text{cm}^{-2}$ combined with the stepwise adjustment of the positive duty cycle to make the coating more dense and homogeneous in structure. During the first stage, the coating grows quickly at a relatively high duty cycle of 8%; while in later stages, smaller grains are produced because of the stepwise decrease in the duty cycle (to 2%) and these partly seal the originally formed bigger pores and cracks. A stepped decreasing current density conducted by Liang *et al.* (2007a) significantly improved the microstructure of oxide coatings compared with the constant current density mode, which is associated with changes in behaviour of spark discharges by the decaying current density in the later stage leading to sealing of the originally formed large micropores.

In essence, the effect of relative distance between the electrodes on the process can be attributed to the discharge intensity. Experimental results by Wei *et al.* (2007a) show that anode currents decrease with larger distances, and the current flowing through the front surface of the sample is higher than that through the back surface. The higher current density induces the strong discharge intensity, thus leading to the thicker and harder coating, which explain the fact that the front surface has better tribological properties and higher corrosion resistance than the back surface. Thus, to produce a uniform coating, it is better to use double or multi cathodes and maintain the equal distance from the sample surface.

5.3.4 Influences of alloy compositions

Alloys with a high content of Si (such as high-silicon die castings) or Cu (such as high-copper aluminium alloys) are rather difficult to anodize with traditional anodizing processes. This problem can be resolved by using the PEO process although it has the disadvantages of local flaws at Si (or Cu) aggregation sites and slightly higher power wastage. Silicon and copper are the main elements that cause irregular features in the PEO coating (He *et al.*, 2009). The irregular degree increases with increasing silicon content in

the alloy, while it still achieves a coating with Si up to 20%, though the hardness value declines due to high porosity.

Irregular features in the micro texture of the substrate alloy can affect the initial growth of the coating. Duan *et al.* (2007) found that PEO films formed on the α -phase in AZ91D alloy had a higher growth rate than those on the β -phase, and the growth of PEO films formed on the β -phase was mainly by virtue of lateral growth of the oxide films formed on the α -phase. This can be attributed to the higher reactivity of the α -phase, which tends to release more Mg^{2+} to participate in film formation reactions under the effect of the high electric field and high Joule heat (Ambat *et al.*, 2000).

Light metal–matrix composites reinforced by particles or fibres, with their outstanding combination of low density, high specific strength and high specific stiffness, have promising applications in the automotive, aeronautic and recreational industries. However, they become more susceptible to corrosion in various environments, due to either localized corrosion, or galvanic reaction between the reinforcements and the matrix, and selective corrosion at the interface because of the formation of new compounds compared with the corresponding light alloy. Conventional anodizing has been used to prepare thin coatings on metal-matrix composites such as Al8090/SiC (Shahid, 1997), A6061/(Al_2O_3)p (Picas *et al.*, 2007), when the particles or whiskers existing in the interface disrupted severely the continuity of the thin film, so the protection properties were limited. Recent investigations (Xue *et al.*, 2006; Xue, 2006; Arrabal *et al.*, 2009; Lee *et al.*, 2008; Wu *et al.*, 2007; Wang

Table 5.5 Coating formed on metal-based composites by PEO process

Ref.	Substrate*	Incorporated species dimension	Electrolyte (base)	Phase composition	Coating Application
Xue <i>et al.</i> , 2006; Xue, 2006	2024/15% SiCp	~12.8 μm	Na_2SiO_3 , 6–10 g/L KOH, 1–2 g/L	mullite, α - Al_2O_3 , γ - Al_2O_3 , amorphous SiO_2	Corrosion resistance
Arrabal <i>et al.</i> , 2009	ZC71/12% SiCp	~2 and 20 μm	Na_2SiO_3 , 0.05M KOH, 0.1 M	MgO, Mg_2SiO_4	Corrosion resistance
Lee <i>et al.</i> , 2008	A356/20 %SiCp	–	Na_2SiO_3 , 15 g/L NaAlO_2 , 3 g/L	α - Al_2O_3 , γ - Al_2O_3	Corrosion and wear resistance
Wu <i>et al.</i> , 2007; Wang <i>et al.</i> , 2006c, 2005	AZ91/22% $\text{Al}_{18}\text{B}_4\text{O}_{33}\text{w}$, AZ91/22% SiCw	–	Na_2SiO_3 , 15 g/L KF, 8 g/L KOH, 8 g/L	MgO, Mg_2SiO_4 and MgF_2	Corrosion resistance

* w = whisker, p = particle

et al., 2006c, 2005c; Cui *et al.*, 2007) (Table 5.5) have indicated that PEO is very promising as a replacement for conventional anodizing to fabricate high-performance coatings on Al or Mg based composites. However, the reinforcement phases (such as particles, whiskers or fibres) in the metal matrix of the composites inevitably affect the microarc discharge process and lower the efficiency of coating growth (Picas *et al.*, 2007; Xue *et al.*, 2006; Lee *et al.*, 2008), because they destroy the integrity of the barrier layer at the initial oxidation stage. Xue *et al.* (Shahid, 1997) believed that most SiC reinforcements are melted, to become silicon oxides, due to high-temperature sintering in the spark discharge channel. However, Arrabal *et al.* insist that SiC particles are incorporated largely unchanged into the coatings (Xue *et al.*, 2006). Though the surface properties are enhanced after PEO treatment, the deteriorating effect of the coated surface on the mechanical properties of the bulk composite cannot be ignored. A recent study has indicated that PEO surface treatment decreases the UTS and elongation of the Mg-based materials (Arrabal *et al.*, 2009), which may be induced by more structural flaws of the coating and substrate–coating interface.

5.4 Properties and applications of PEO coatings

5.4.1 Basic and unique characteristics of PEO coatings

Surface porosity

Depending on the spark discharge essence as described in Section 5.2, pore formation in the coatings is inevitable. Evidence is presented by Curran and Clyne (2006) for the presence of sub-micrometre, surface-connected porosity in such coatings on aluminium alloys, at levels in the order of 20%. High porosity (up to 40%) was found on coatings formed on Mg alloys (Popova *et al.*, 1999).

This porosity has an important influence on various properties and characteristics of coatings (Curran and Clyne, 2006). The pores on the coating surface are largely inter-connected, which can provide natural ‘cages’ for surface impregnation with a wide variety of compounds, including paints, lubricants, sol–gels and polymers (such as PTFE), to achieve duplex coatings for enhanced properties (partially reviewed in Section 5.5.1). The porosity may be partially responsible for the low stiffness and the low thermal conductivity of the coatings. A reduced stiffness limits the differential thermal expansion stresses and a low conductivity favours an effective thermal barrier function, which is beneficial for the thermal protection of the substrates (as will be discussed in Section 5.4.5). Porosity in the coating can induce adverse effects, such as reduced hardness leading to low wear resistance, and poor corrosion resistance from the penetration of corrosive liquids through the pores (as will be discussed in Sections 5.4.2 and 5.4.3).

High adhesive strength between substrate and coating

It has been mentioned that high adhesive strength of coatings can be achieved using the PEO process. However, such statement is mostly based on experimental observations rather than on direct experimental data. Recently, scratch tests have been applied to evaluate the adhesive strength of PEO coatings formed on titanium alloys. However, various conclusions have been drawn. Yerokhin *et al.* (2000) measured the adhesive strength of coatings formed in different electrolytes, and found that the highest critical load L_{c2} (96 N) was obtained in coatings formed in $\text{KAlO}_2/\text{Na}_3\text{PO}_4$ electrolyte. However, using the same method, other investigators (Gnedenkova *et al.*, 2001a; Huang *et al.*, 2003) and this author found no effective data owing to lack of the distinct acoustic launching signals caused by coatings failure. Possibly, this is attributed to the higher adhesion strength of coating to substrate compared with the internal strength of the coatings. A shear test conducted by Wang *et al.* to evaluate the adhesion property indicated that PEO coatings have a high adhesion strength of 110 MPa for an Al_2TiO_5 dominated coating (Wang *et al.*, 2005b) and 40 MPa for an AlPO_4 predominant coating (Wang *et al.*, 2004), respectively. The AlPO_4 predominant coating, mainly relying on the deposit of external components, showed the lower adhesion. Generally, the more prevailing the cohesive failure, the stronger is the adhesive strength of coating to substrate is. In general, the thicker the coating, the weaker the adhesion strength of coating to substrate is.

Internal stress of the coating

It is well known that the internal stress of a coating affects physical and mechanical properties such as hardness, adhesion, wear resistance and fatigue cracking. Therefore, evaluating the residual stress in the PEO coating is very valuable as a measure for mechanical damage. Recently, $\text{Sin}^2\psi$ X-ray diffraction technique was conducted by Khan *et al.* (2005) to evaluate the residual stresses in oxide ceramic coatings produced on BS Al 6082 alloy, indicating that internal normal stress in the coatings ranged from $-111 (\pm 19)$ MPa to $-818 (\pm 47)$ MPa and shear stress ranged from $-45 (\pm 27)$ MPa to $-422 (\pm 24)$ MPa, depending on the applied duty cycle and frequency parameters used during pulsed unipolar PEO treatment. Guan *et al.* (2008a) reported, based on a finite element method, that the compression strength of the coating is about 600 MPa. In addition, a four-point bending test was conducted to reveal the mechanism of cohesive cracking and spallation in the coating. This indicated that plastic deformation in the substrate is due to interfacial crack extension, so the interface crack mode of the coatings is ductile.

5.4.2 Wear resistance properties

Wear resistance properties of coatings mainly depend on hardness. The hardness of PEO coatings formed on light alloys (Al, Mg and Ti) ranges from 400–2000 HV, mainly depending on the alloy species and the coating phase compositions formed in various electrolytes. For example, distinguishing by the phase products, the hardness of Al_2O_3 dominated coatings on Al alloys is high, ranging from 800–2000 HV; MgO -predominant coatings on Mg alloy are of low hardness, from 300–600 HV; while, TiO_2 coatings on Ti Alloys maintain a moderate hardness of 400–700 HV. As summarised in Tables 5.2 and 5.3, for a certain substrate, the coating phase compositions can be tailored according to the different electrolyte systems (silicates, aluminates or phosphates). Among them, Al_2O_3 (especially $\alpha\text{-Al}_2\text{O}_3$) phase incorporated in the coating by high aluminate content electrolytes imparts higher hardness. In addition, hard SiC or ZrO_2 particles can be introduced into the electrolytes, and are incorporated into the coating by integrating cataphoretic effects, which further promotes the hardness.

Due to the high hardness and high adhesion strength of PEO coatings, they are promising as alternatives to replace the conventional hard anodizing process materials. A comparative investigation carried out on 6061Al by Krishna *et al.* (2006) has indicated that the hard-anodized coatings reduced the abrasive wear rate of 6061 Al alloy by a factor of two, while the PEO coatings reduced the wear rate by a factor of 12–30. Micro crack driven damage accumulation and coating removal in the form of flakes is the wear mechanism associated with PEO coatings. Tribological performance of PEO coatings under diverse wear modes such as abrasion, erosion and sliding wear was found to be comparable to that of detonation sprayed alumina coatings and bulk alumina (Krishna *et al.*, 2003).

In terms of energy savings, low friction and low wear loss are desirable to reduce the friction between sliding pairs. Therefore, recent investigations have focused on fabricating antifriction coatings on titanium alloys by the PEO method (Wang *et al.*, 2006a; Gnedenkov *et al.*, 2000, 2001b; Yerokhin *et al.*, 2000). Generally, TiO_2 dominated coatings formed on Ti alloys in phosphate or silicate electrolyte reduce the friction coefficient down to 0.1–0.2 against steel in light load conditions of less than 10 N, which is possibly attributed to the nanocrystalline structure and low friction nature of the TiO_2 material. Voevodin *et al.* (1996) found that an $\text{Al}_{0.26}\text{Si}_{0.08}\text{O}_{0.66}$ coating formed on B95 alloy has the lowest friction coefficient, of 0.15–0.25, depending on the test environment. Application of this coating decreased the wear rate of components fabricated from an Al-based alloy by several orders of magnitude and permitted operation of coated friction pairs at 1 GPa contact load.

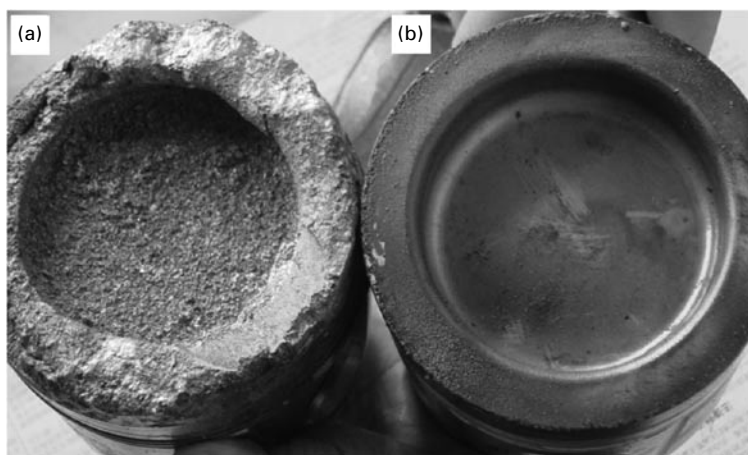
The high wear resistance provided by PEO coating endows light alloys

with great potential for replacing steel rotating or structural frames. Similarly, coated magnesium parts can replace aluminium parts or coated aluminium can replace titanium parts. The weight saving effect by such replacements produces great commercial efficiency by improved performance or reduced fuel consumption in the automotive, aircraft and aerospace industries (see Chapter 18).

PEO-coated engine parts have increased durability and promote combustion efficiency. An example is a PEO treated piston in a natural gas engine. The coating (of 30 μm thickness) was prepared on a ZL108 aluminium alloy piston using a silicate electrolyte. Figure 5.11 demonstrates the damage morphologies for an uncoated and a PEO coated piston after a rig test. After a 380h sliding test, pit corrosion appeared on the contact surface of the uncoated piston. After a 1000h test, severe damage, with top loss by ablation, occurred on the uncoated piston specimen (Fig. 5.11a), while the coated piston kept a complete surface without any pit corrosion or flakes (Fig. 5.11b).

5.4.3 Corrosion resistance properties

Among light alloys, Mg alloy is most active and thus sensitive to corrosion, followed by Al alloy and Ti alloy. PEO can significantly improve the corrosion resistance properties of Mg and Al alloys. Electrochemical impedance spectroscopy results show that the porous outer layer of the coating formed on AM50 magnesium alloy is inconsequential with respect to corrosion, as the corrosion resistance depends on the compact inner layer of the coating



5.11 Macro morphologies for (a) damaged uncoated piston and (b) complete plasma electrolytic oxidation coated piston after indoor test for 1000h.

(Ghasemi *et al.*, 2008); exactly the same is true for PEO treated Al and Ti alloys. This is largely because corrosive liquids can easily penetrate through the porous outer layer to contact the compact inner layer, so the inner layer plays the critical role in the inhibition of corrosion.

A large discharge intensity (even arc sparks) is responsible of high porosity through the layer, which is unfavourable for anti-corrosion performance. So many studies are devoted to avoid the formation of the porous ceramic layers, in different ways: e.g. by the use of complex electrical anodic regimes, such as alternating and pulsed voltage or current signal during PEO treatment (Mécuson *et al.*, 2005, 2007). As discussed in Section 10.4.1, the pores existing in the coating surface provide natural ‘cages’ for the surface impregnation of sealing additives (boiling water, chromate, silicate, phosphate, sol–gel and organic species) to enhance the corrosion resistance properties (Zhang *et al.*, 2007). When sealed, PEO coatings on aluminium will withstand over 2000 hours in salt fog (ASTM B117) while coated magnesium can withstand over 1000 hours. Figure 5.12 shows an example on a PEO-treated seawater filtering device of ZL114 aluminium alloy for a corrosion resistance application in a marine environment. By sealing with a silicate salt, the coating with a thickness of 20 μm formed in phosphate solution can endure salt spray exceeding 1500 hours with no sign of corrosion attack.

Galvanic corrosion is a major obstacle to the coupled use of light alloys with other metals. Light alloys (especially Mg and Al) are more active in the galvanic series and always act as an active anode when contacting other metals. In industrial applications, light alloys will unavoidably be in contact with steel, Cu and other metal components. PEO coating has proved effectively



5.12 Plasma electrolytic oxidation treated seawater filtering device of ZL114 aluminium alloy for corrosion resistance.

in insulating or blocking direct contact between light alloys and other metals, thus eliminating galvanic corrosion (Xue *et al.*, 2007; Barchiche *et al.*, 2008; Gordienko *et al.*, 1993). Galvanic studies of the coated Al alloy coupled with copper, conducted by Xue *et al.* (2007) indicates that treatment with a thick PEO coating can suppress the galvanic corrosion of LC4 alloy

5.4.4 Dielectric properties

Barium titanate is an important functional material in the electronics industry because of its superior dielectric, ferroelectric, piezoelectric, pyroelectric, and electro-optical properties. Using those characters, BaTiO₃ films formed on Ti by PEO may find application in ion sensors, biosensors and pH sensors because of their high dielectric constant. Crater-shaped and large-grained BaTiO₃ films are formed at voltages above 60 V by PEO (Wu and Lu, 2001; Lu *et al.*, 2002).

Ceramic products (such as Al₂O₃, SiO₂, ZrO₂) formed on light alloy surfaces have high electrical resistance and breakdown strength, so possess a great potential for insulating coatings. The coatings formed in silicate-rich electrolytes have a greater thickness with a higher mass rate, especially if components containing SiO₂ are incorporated into the coating, and this is beneficial for increasing dielectric strength. Dielectric strength up to 2500 V can be reached, depending on the coating specification and the alloy. As an example, a PEO coating can replace the commonly used electric insulation painting material to make sensors, which not only simplifies the sensor structure, but also increases the stiffness reliability and accuracy.

5.4.5 Thermal protection properties

Thermal barrier coating requires a property combination of low thermal conductivity, good oxidation resistance and thermal shock resistance. PEO coatings are becoming attractive for the thermal protection (Curran and Clyne, 2005; Curran *et al.*, 2007) of metals working in high temperature environments. Recent investigations by Curran *et al.* (Curran and Clyne, 2005) on the thermal physical properties of PEO coatings have proved that thermal conductivity as low as 1 W m⁻¹ K⁻¹ can be achieved, which paves the way for thermal barrier applications. Although the phase compositions of the coatings formed on aluminium and magnesium substrates are different, there is no appreciable difference in their low thermal conductivities, which is mainly attributed to the special microstructure of fine grain size together with a significant proportion of amorphous phase. Comparatively, the mullite-rich PEO coating grown on aluminium alloys in silicate-rich electrolytes gives a slightly lower thermal conductivity of 0.5 W m⁻¹ K⁻¹ (Curran *et al.*, 2007).

High thermal shock resistance of the coatings is very important for a long lifetime of metallic components serving under high temperature conditions. After thermal shocking for 25 cycles at 500°C and 700°C of PEO coatings on Ti6Al4V (Wang *et al.*, 2006b) and for 40 cycles at 450°C of PEO coatings on pure aluminium (Shen *et al.*, 2008), the coatings did not show any spallation except for some minor microcracks, indicating good thermal shock performance and adhesion to the substrate. The porosity in the coating may pose beneficial effects: (i) the pores can help microcracks to propagate in more directions, thereby inhibiting very large crack formation; (ii) pores lead to a low stiffness, which will reduce the magnitude of thermally-induced stresses and improve the resistance to spallation during temperature changes.

Although there exist many pores in the coatings (porosity reaches up to 20%, as will be discussed in Section 5.4.1), only a very small number of pores locate in the compact inner layer without interconnection, which can serve as an effective inhibiting layer for active oxygen penetration at high temperature. The coating formed on Ti6Al4V demonstrates good anti-oxidation properties after oxidation for 80h at 700°C. The weight gain is about 0.98 mg/cm², which is much lower than that of the Ti6Al4V substrate (20 mg/cm²) (Wang *et al.*, 2006b). The similar experiments conducted by Yao *et al.* (2007) on Ti6Al4V are in good agreement with these results. PEO is an alternative method of improving anti-oxidation of TiAl alloy and isothermal oxidation tests indicate that the oxidation resistance is improved by three times (Li *et al.*, 2007).

Therefore, PEO coatings formed on metal substrates exhibit a low thermal conductivity, good thermal shocking and oxidation resistance properties, which gives them great potential for thermal barrier coating applications at high temperatures. The high heat resistance of the PEO coatings may be valuable in manufacturing protective barrier coatings for spacecraft and missiles.

5.4.6 Optical properties

The colour of PEO coatings can be changed over a wide range, depending on the process conditions such as substrate metal types, electrolyte composition and concentration, and electrical, and temperature parameters. Among them, alloying elements in the substrate and the composition and concentration of electrolyte play a crucial role for the formation of a specific colour. Some colouring additives such as KMnO₄, FeSO₄, Cr₂O₃ and NH₄VO₃ are also being developed to offer unique colours, which provide a wide range for decorative architecture or optical applications in aerospace.

Black absorptive coatings formed in eco-friendly electrolytes containing blackening additives finds a great potential on Al alloys as thermal control

layers applied to aerospace components (e.g. in satellite). PEO coatings with vanadium oxide predominating on the surface have been obtained on aluminium alloys in phosphate–vanadate (Gordienko *et al.*, 1993) and silicate–vanadate (Li *et al.*, 2007) electrolyte. It is thought that this V_2O_3 layer results in the black appearance observed. Compared with conventional blackening processes using Ni-P coating, sulphuric acid anodizing coating or spraying black paints, PEO can be applied to more alloy types and the properties of the coatings are satisfactory with low reflectance values (<0.1%) and good environmental stability.

The porous feature of the PEO coating is beneficial for infrared reflection applications, Jin *et al.* (2009) have reported that a porous and rough PEO ceramic coating formed on LD31 Al alloy is capable of reflecting active or passive infrared waves. The porous and rough surface influences the infrared reflection efficiency and significantly decreases the reflection of infrared waves from 780 nm to 3000 nm.

5.4.7 Biomedical properties

Titanium and its alloys (e.g. Ti6Al4V) have been widely used for orthopedic and dental implants due to their good biocompatibility, excellent corrosion resistance and high strength-to-weight ratio; however, their bio-inert nature restricts their wider clinical applications. PEO can form TiO_2 -based bioactive coatings on titanium substrates by incorporating Ca and P into the coating, firstly developed by Ishizawa and Ogino (1995a,b, 1999). To prepare the bioactive coatings, electrolytes containing calcium salts such as calcium acetate, calcium glycerophosphate and calcium dihydrogen phosphate have been explored in the PEO process (Li *et al.*, 2004; Zhu *et al.*, 2001, 2002; Song *et al.*, 2004). To increase the Ca content in the coating, Frauchiger *et al.* used a new electrolyte containing Ca-EDTA chelate complex to prepare them (Frauchiger *et al.*, 2004).

Recent investigations indicate that the formation of bioactive components in the coatings partially depends on the applied voltage. High voltage induces a high spark discharge intensity, which is beneficial for the crystalline transformation of as-produced amorphous components. Therefore, at high voltages, titania-based duplex coatings with high crystalline components of TiO_2 , $CaTiO_3$, $Ca_2P_2O_7$ and $Ca_3(PO_4)_2$ (Han *et al.*, 2003; Song *et al.*, 2004; Huang *et al.*, 2005) or TiO_2 and HA (Sun *et al.*, 2007; Kim *et al.*, 2007; Nie *et al.*, 2001) are easily produced, which have high bioactivity; however, when treated at low voltages (Zhu *et al.*, 2001; Wei *et al.*, 2007b), the coatings are composed mainly of TiO_2 phases with a small amount of amorphous composition, which indicates a weak or even no apatite-forming ability (Ishizawa and Ogino, 1995b; Han *et al.*, 2003; Wei *et al.*, 2007b).

To improve the bioactivity of TiO_2 -based coatings, post-treatment methods

such as sol-gel (Li *et al.*, 2005), hydrothermal treatment (Ishizawa and Ogino, 1995b, 1999; Baszkiewicz *et al.*, 2005), heat treatment (Yang *et al.*, 2004; Das *et al.*, 2007) and chemical treatment (Wei *et al.*, 2007b) have been developed. Hydrothermal treatment and heat treatment are limited due to a significant decrease in the bond strength of the coatings. Alternatively, a novel UV-irradiating method (Han *et al.*, 2008) has significantly promoted the bonelike apatite-forming ability of the original PEO coating, without obvious change in surface roughness, morphology, grain size and phase component. The enhanced bioactivity and cell response of the UV-irradiated coatings result from increasing Ti-OH groups formed by the reaction of absorbed water and oxygen vacancies caused by the UV-irradiation.

To stimulate bone formation and enhance osteointegration, PEO has also been applied to porous titanium surfaces (Sun *et al.*, 2008), which is beneficial for bone ingrowth into the porous structure, thus achieving a strong chemical bonding at the bone/implant interface. Strontium (Sr) may indirectly inhibit the resorption of the calcified matrix by stabilizing hydroxyapatite (HA) crystals, and therefore Sr-doped hydroxyapatite (Sr-HA) film has been prepared on titanium substrates (Nan *et al.*, 2009).

5.4.8 Catalytic properties

Titanium dioxide and manganese oxide films have been gaining much attention as photocatalysts offering practical benefits. Titanium, owing to its good mechanical, chemical and thermal properties, is usually used as the metal carrier. Design of special electrolytes has enabled PEO to form films containing titanium dioxide (Shin *et al.*, 2006, 2003) or manganese oxide (Rudnev *et al.*, 2005) on the Ti metal carrier, providing a low-cost method of fabricating photo-catalytic films compared with sol-gel processes, colloid baking, chemical vapor deposition, evaporation and various reactive sputtering depositions.

To obtain high activity, the micropore size and the content of anatase and rutile TiO₂ phases in the film must be tailored by optimizing electrical and electrolyte parameters (Wu *et al.*, 2003). The manganese-containing layers obtained possess catalytic activity in the CO→CO₂ oxidation reaction in the temperature range of 250–350°C. The catalytic activity depends on the concentration and surface distribution of manganese, as well as on the morphology of the layers (Rudnev *et al.*, 2005).

Enhanced anatase crystallinity in the film induced by the addition of F⁻ into the Na₃PO₄ electrolyte has shown improved visible light absorption properties and superior photocatalytic activity compared with undoped TiO₂ film, which was mainly attributed to the new state below the conduction band and the enhancement of anatase crystallinity caused by the F⁻ ions (Li *et al.*, 2006).

5.5 New process exploration

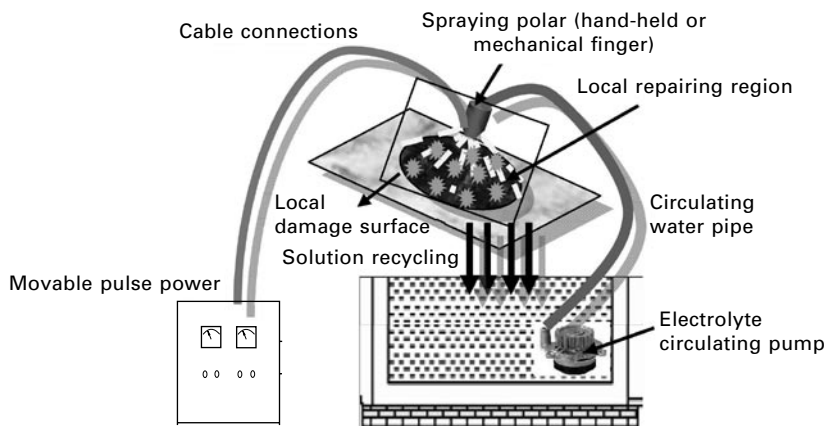
5.5.1 Combined processes with PEO for enhanced properties

The pores existing on the PEO coating surface pose a negative effect on the corrosion and wear properties. However, the coatings can be used as pre-treated subsurface layers to mechanically support surface layers produced by other processes. This will form duplex surface systems with combined property improvements, and can extend application areas. Taking advantage of the beneficial surface-connected pores, a wide variety of compounds, including paints, lubricants, sol–gels and polymers (such as PTFE) can be impregnated into the porous PEO layer to achieve duplex coatings for enhanced corrosion and friction-reduction properties. Porosity in the porous PEO layer can effectively improve adhesion of the top layer to the subsurface layer.

PEO coatings including alumina, MgO or Al_2TiO_5 on light alloys often exhibit relatively high friction coefficients against many counterface materials. Duplex treatments, combining a load-supporting PEO ceramic inner layer with a low friction or wear-resistant outer layer such as diamond-like carbon (DLC) (Liang *et al.*, 2007b; Nie *et al.*, 2000a), electroless Ni-P (Liu and Gao, 2006), spraying graphite (Wang *et al.*, 2005c), TiN, Cr(N) (Awad and Qian, 2006; Nie *et al.*, 2000b; Ceschini *et al.*, 2008) have been extensively investigated to extend light alloys (such as Al, Mg or Ti) to tribological applications under medium-to-high contact stresses. Duplex PEO/DLC (graphite, TiN, Cr(N)) coatings on soft light alloy substrate exhibit better tribological performance than the top low-friction layer or bottom PEO monolayer. This is because the PEO sublayer provides improved load support to the top low friction layer, and the latter can reduce the shear stress of the former because of reduced friction force. This duplex approach presents a promising technique for the surface engineering of light alloys for load-bearing tribological applications.

5.5.2 Flexible spraying process

Normally, parts for PEO treatment must be immersed in an electrolyser, as shown in Fig. 5.1. However, it is not feasible to immerse very large and heavy parts into an electrolyser. Sometimes only a local region on a larger part needs to be PEO treated. Here, the proposed novel mini PEO power source associated with a movable spraying polar provides an alternative way to address the above problem. Figure 5.13 schematically shows the new PEO equipment with a spraying polar for field repairing, which consists mainly of a mini volume bi-polar pulse source suitable for easy movement, a spraying polar easily held by hand or mechanical fixation, and an electrolyte circulating system. The mini bi-polar pulse source outputs the energy for



5.13 Schematic for plasma electrolytic oxidation equipment with spraying polar for field repairing.

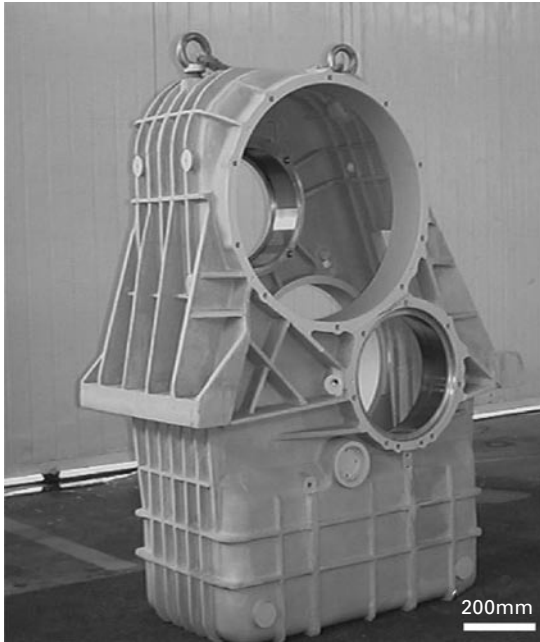
spark discharge. The spraying polar is connected to the part and enables us to restrict the electrical field to the area to be treated on the large part. This allows production of spark discharge only in the required area, achieved by controlling the size and shape of the spraying polar. This system offers the possibility of field repairing instead of replacing the worn parts. Therefore, it is very attractive for light alloy parts, rebuilding the damaged area and putting them back into service.

It is also interesting that the mini bi-polar pulse source with spraying polar system can be adapted to coat very large parts with sizes larger than the immersing electrolyser. In this case, the size of spraying polar must be enlarged according to the output power in order to meet high production efficiency, because the spraying polar needs to scan the parts surface for large area coating. In this way, the maximum surface coating area will not be limited by the output power of the processing equipment as in conventional immersions oxidation (currently less than 4 m^2). However, the process must be carefully controlled due to the high voltage used.

Figure 5.14 shows an example of PEO treated large parts in immersing oxidation mode using a 220 kW bi-polar pulse power source with a large chilling system. The coating (thickness of $18 \text{ } \mu\text{m}$ formed on a ZL204 aluminium alloy reduction gear box in a phosphate solution) can endure salt spray for more than 1000 hours with no sign of corrosion attack. However, for larger area coating fabrication, a bi-polar pulse source with a spraying polar system could be an alternative candidate.

5.5.3 Internal surface oxidation process

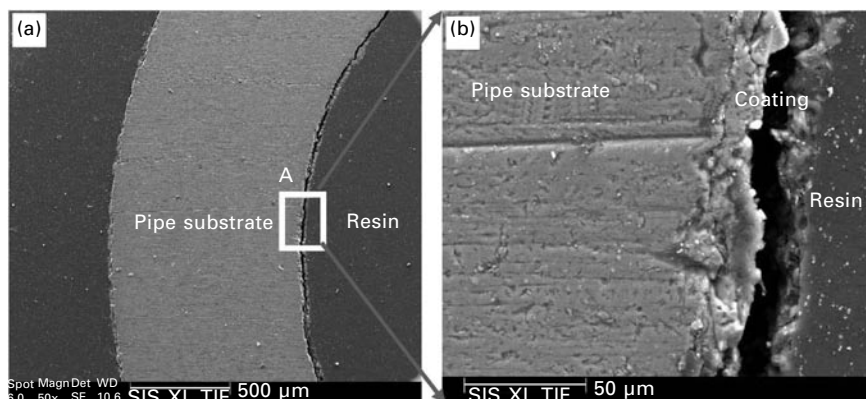
Metal pipes for transporting circulating water are commonly subjected to severe corrosion or erosion, which limits their application in the nuclear



5.14 Plasma electrolytic oxidation treated ZL204 aluminium alloy large reduction gear-box for corrosion resistance application.

and marine industries. PEO is being explored to coat the internal surfaces of light alloy or Zr alloy pipes. The main design challenge in processing internal pipe surfaces is to maintain the stable plasma with release of vapour from the pipe. This needs a specially-designed central auxiliary electrode to drill axially through the pipe and drive the electrolyte flow in the pipe for releasing the vapour. In this way, it enables one to eliminate the shielding effect of the electric field and obtain axially uniform coating in the inner surface of the pipes. The process has been extended to combine hot-dipping aluminium for achieving ceramic coating on the inner surface of 1045 (0.45%C) carbon steel pipes (Gu *et al.*, 2007a,b), with the purpose of improving their corrosion- and wear-resistance properties.

Figure 5.15 shows cross-section morphologies of the inner wall of an aluminium pipe with inner diameter $\phi 3.0$ mm coated by PEO using a central auxiliary electrode. It can be seen that the coating, of $10\ \mu\text{m}$ thickness and mainly composed of Al_2O_3 , is relatively dense and uniform, so will provide good corrosion and erosion protection. As another example, duplex coatings combining PEO impregnated with PTFE have been produced by Gnedenkov *et al.* (2003) to decrease water-scale deposition on the inner wall of heat-exchanger titanium pipes used in ships. The as-deposited PEO coating acts as a sublayer to improve the adhesion of polymer to the pipe substrate. The



5.15 Cross-section morphologies for the coated inner wall of aluminium pipe with inner diameter $\varnothing 3.0$ mm by plasma electrolytic oxidation using the central auxiliary electrode. (a) Cross-section of coated pipe inner wall, (b) magnified view of area A in (a).

duplex coating reduces the rate of salt deposition by approximately 10% owing to its specific semiconducting and electrochemical properties; this prolongs the serving lifetime and reduces the energy consumption.

5.5.4 Pre-shot peening process for improving fatigue

Currently, PEO coatings are attracting increasing interest for many applications in aircraft parts, due to their combination of excellent corrosion resistance and wear resistance. However, an issue laying ahead of engineers is the possibility that the PEO coatings will negatively affect the fatigue life of coated samples and if so, how the fatigue performance of coated samples can be improved.

Yerokhin *et al.* (2004) studied the influence of PEO coatings, on the fatigue performance of AZ21 Mg alloy, using two different thicknesses of 7 and 15 μm . They reported that the PEO coatings reduced the bending fatigue limit of the Mg alloy by not more than 10%, which was substantially lower than the influence of conventional anodizing. Lonyuk *et al.* (2007) made a comparative study on the axial fatigue strength of 7475-T6 aluminium alloy coated with hard anodic oxide and PEO coatings. While a 60 μm hard anodic coating reduced the fatigue strength of the alloy by 75%, a 65 μm PEO coating reduced the fatigue strength by only 58%. Rajasekaran *et al.* (2008a,b) compared the plain fatigue and fretting fatigue performance of PEO and hard anodizing treated Al–Mg–Si alloy. The plain fatigue and fretting fatigue lives of both coated samples were inferior to those of uncoated specimens. As the anodized layer had pre-existing through-thickness cracks and strong adhesion to the substrate, cracks propagated from the hard anodic

coating through the interface into the substrate easily: hard anodizing coated samples exhibited inferior fatigue properties compared with PEO coated samples.

The inferior fatigue performance of PEO-coated specimens compared with that of the substrate is mainly attributed to the tensile residual stresses present in the substrate, which lead to an early crack initiation in the substrate adjacent to the coating. The porous outer layer of the PEO coating and the uneven substrate–coating interface, which may lead to early crack initiation in the coating surface and interface respectively, also have detrimental influences on the fatigue performance of coated samples. While the inferior fatigue lives of hard anodic specimens were attributed to stress concentration at the microcracks present in the oxide layer, the superior fatigue lives of PEO samples were attributed to the presence of compressive residual stress within the oxide layer.

Considering the fact that crack initiation is a surface phenomenon controlled by residual stress levels near the surface, compressive residual stresses can increase fatigue life. One effective way to introduce surface compressive residual stresses is by shot peening. Asquith *et al.* (2006) demonstrated that combined shot peening and PEO treatment increased the bending fatigue limit of 2024 Al alloy by about 85% when compared to plain PEO treated material. Therefore, shot peening can improve the fatigue performance of PEO coated samples.

5.6 Future trends

Plasma electrolytic oxidation (PEO) is a very attractive, cost-effective, environmentally friendly surface engineering technique for light alloys. A variety of oxide ceramic coatings with different properties can be produced by PEO, which can effectively improve the tribological and corrosion properties of light alloys such as Ti and Al alloys. In particular, PEO is a unique and irreplaceable technique to fabricate functional coatings for specific applications.

Currently, PEO processes are in a transition phase from research to commercial applications, mainly focused on the corrosion- and wear-protection of light alloys. It is necessary to further study the fundamentals of the PEO technique to advance scientific understanding and to explore new functional PEO coatings for high-tech applications.

5.7 Acknowledgements

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5.8 References

- Ambat R, Aung N N and Zhou W (2000), 'Evaluation of microstructural effects on corrosion behaviour of AZ91D magnesium alloy', *Corros Sci*, 42, 1433–1455.
- Arrabal R, Matykina E, Skeldon P and Thompson E (2008a), 'Incorporation of zirconia particles into coatings formed on magnesium by plasma electrolytic oxidation', *J Mater Sci*, 43, 1532–1538.
- Arrabal R, Matykina E, Viejo F, Skeldon P, Thompson G E and Merino M C (2008b), 'AC plasma electrolytic oxidation of magnesium with zirconia nanoparticles', *Appl Surf Sci*, 254, 6937–6942.
- Arrabal R, Matykina E, Skeldon P and Thompson G E (2009), 'Coating formation by plasma electrolytic oxidation on ZC71/SiC/12p-T6 magnesium metal matrix composite', *Appl Surf Sci*, 255, 5071–5078.
- Asquith D T, Yerokhin A L, Yates J R and Matthews A (2006), 'Effect of combined shot-peening and PEO treatment on fatigue life of 2024 Al alloy', *Thin Solid Films*, 515, 1187–1191.
- Atroshchenko E S, Chufistov O E, Kazantsev I A and Kamyshanskii S I (2000), 'Formation of structure and properties of coatings developed by microarc oxidizing on parts fabricated from aluminum alloys', *Metal Science and Heat Treatment*, 42(9–10), 411–415.
- Awad S H and Qian H C (2006), 'Deposition of duplex $\text{Al}_2\text{O}_3/\text{TiN}$ coatings on aluminum alloys for tribological applications using a combined microplasma oxidation (MPO) and arc ion plating (AIP)', *Wear*, 260, 215–222.
- Barchiche C E, Rocca E and Hazan J (2008), 'Corrosion behaviour of Sn-containing oxide layer on AZ91D alloy formed by plasma electrolytic oxidation', *Surf Coat Technol*, 202, 4145–4152.
- Baszkievicz J, Krupa D, Mizera J, Sobczak J W and Bilin A (2005), 'Corrosion resistance of the surface layers formed on titanium by plasma electrolytic oxidation and hydrothermal treatment', *Vacuum*, 78, 143–147.
- Belov N A, Zolotarevsky V S and Shatrov A S (2002), 'Construction material based on aluminium and method for producing parts from said material', *WO 02/22902*, publ. 21.03.02.
- Brown S D, Kuna K J and Van T B (1971), 'Anodic spark deposition from aqueous solution of NaAlO_2 and Na_2SiO_3 ', *J Am Ceram Soc*, 54(8), 384–390.
- Ceschini L, Lanzoni E, Martini C, Prandstraller D and Sambogna G (2008), 'Comparison of dry sliding friction and wear of Ti6Al4V alloy treated by plasma electrolytic oxidation and PVD coating', *Wear*, 264, 86–95.
- Chigrinova N M, Chigrinova V E and Kukharev A A (2001), 'Formation of coatings by anodic microarc oxidation and their operation in thermally-stressed assemblies', *Powder Metallurgy and Metal Ceramics*, 40(5–6), 213–220.
- Cui S H, Han J M, Du Y P and Li W J (2007), 'Corrosion resistance and wear resistance of plasma electrolytic oxidation coatings on metal matrix composites', *Surf Coat Technol*, 201, 5306–5309.
- Curran J A and Clyne T W (2005), 'The thermal conductivity of plasma electrolytic oxide coatings on aluminium and magnesium', *Surf Coat Technol*, 199, 177–183.

- Curran J A and Clyne T W (2006), 'Porosity in plasma electrolytic oxide coatings', *Acta Materialia*, 54, 1985–1993.
- Curran J A, Kalkanc H, Magurova Y and Clyne T W (2007), 'Mullite-rich plasma electrolytic oxide coatings for thermal barrier applications', *Surf Coat Technol*, 201, 8683–8687.
- Das K, Bose S and Bandyopadhyay A (2007), 'Surface modifications and cell-materials interactions with anodized Ti', *Acta Biomater*, 3, 573–585.
- Districh K H, Krysmann W and Kurze P (1984), 'Structure and properties of ANOF layers', *Cryst Res Technol*, 19(1), 93–99.
- Duan H P, Yan C W and Wang F H (2007), 'Growth process of plasma electrolytic oxidation films formed on magnesium alloy AZ91D in silicate solution', *Electrochimica Acta*, 52, 5002–5009.
- Frauchiger V M, Schlottig F, Gasser B and Textor M (2004), 'Anodic plasma–chemical treatment of CP titanium surfaces for biomedical applications', *Biomaterials*, 25, 593–606.
- Gerasimov M V, Nikolaev V A and Shcherbakov A N (1994), 'Microplasma oxidation of metals and alloys', *Metallurgist*, 38(7–8), 179.
- Ghasemi A, Raja V S, Blawert C, Dietzel W and Kainer K U (2008), 'Study of the structure and corrosion behavior of PEO coatings on AM50 magnesium alloy by electrochemical impedance spectroscopy', *Surf Coat Technol*, 202, 3513–3518.
- Gnednikov S V, Gordienko P S, Sinebryukhov S L, Kovryanov A N, Khrisanova O A, Cherednichenko A I, Korkosh S V and Khromushkin K D (2000), 'Antiscuff coatings obtained by microarc oxidation of titanium alloys', *Russ J Appl Chem*, 73, 6–9.
- Gnednikov S V, Khrisanova O A, Zavidnaya A G, Sinebryukhov S L, Gordienko P S, Iwatsubo S and Matsui A (2001a), 'Composition and adhesion of protective coatings on aluminum', *Surf Coat Technol*, 145, 146–151.
- Gnednikov S V, Sinebryukhov S L, Minaev A N, Kovryanov A N, Mashtalyar D V and Gordienko P S (2003), 'Composite layers as means of lowering the intensity of scale deposition on elements of power units of ships', *Russian Journal of Applied Chemistry*, 76(8), 1205–1210.
- Gnednikov S V, Vovna V I, Gordienko P S, Sinebryukhov S L, Cherednichenko A I and Shchukarev A V (2001b), 'Chemical Composition of Antifriction Micro-arc Oxide Coatings on Titanium Alloy BT16', *Prot Met*, 37, 168–172.
- Gordienko P S, Rudnev V S, Orlova I I, Kurnosova A G, Zavidnaya A G, Rudnev A S and Tyurin V I (1993), 'Vanadium-containing anode-oxide films on aluminium alloys', *Zashchita Metallov*, 5, 739–742.
- Gu W C, Lv G H, Chen H, Chen G L, Feng W R and Yang S Z (2007a), 'PEO protective coatings on inner surface of tubes', *Surf Coat Technol*, 201, 6619–6622.
- Gu W C, Lv G H, Chen H, Chen G L, Feng W R, Zhang G L and Yang S Z (2007b), 'Preparation of ceramic coatings on inner surface of steel tubes using a combined technique of hot-dipping and plasma electrolytic oxidation', *J Alloy Compd*, 430, 308–312.
- Guo H F, An M Z, Xu S and Huo H B (2005), 'Formation of oxygen bubbles and its influence on current efficiency in micro-arc oxidation process of AZ91D magnesium alloy', *Thin Solid Films*, 485, 53–58.
- Guan Y J, Xia Y and Xu F T (2008a), 'Interface fracture property of PEO ceramic coatings on aluminum alloy', *Surf Coat Technol*, 202, 4204–4209.
- Guan Y J, Yuan X and Guang L (2008b), 'Growth mechanism and corrosion behavior

- of ceramic coatings on aluminum produced by autocontrol AC pulse PEO', *Surf Coat Technol*, 202, 4602–4612.
- Günterschultze A and Betz H (1934), 'Die electronenstromung in isolatoren bei extremen feldstarken', *Z Phys*, 91, 70–96.
- Han I, Choi J H, Zhao B H, Baik H K and Lee I S (2007), 'Changes in anodized titanium surface morphology by virtue of different unipolar DC pulse waveform', *Surf Coat Tech*, 201, 5533–5536.
- Han Y, Chen D H, Sun J F, Zhang Y M and Xu K W (2008), 'UV-enhanced bioactivity and cell response of micro-arc oxidized titania coatings', *Acta Biomaterialia*, 4, 1518–1529.
- Han Y, Hong S H and Xu K W (2003), 'Structure and *in vitro* bioactivity of titania-based coatings by micro-arc oxidation', *Surf Coat Technol*, 168, 249–258.
- He J, Cai Q Z, Luo H H, Yu L and Wei B K (2009), 'Influence of silicon on growth process of plasma electrolytic oxidation coating on Al-Si alloy', *J Alloys Compd*, 471, 395–399, doi:10.1016/j.jallcom.2008.03.114.
- Hirohata Y, Nakamura T, Aihara Y and Hino T (1999), 'Dependence of surface oxidation on hydrogen absorption and desorption behaviors of Ti6Al4V alloy', *J Nucl Mater*, 266–269, 831–836.
- Huang P, Xu K W and Han Y (2003), 'Character and Mechanism of the Film by Micro-arc Oxidation on Titanium Alloy', *Rare Metal Mat Eng*, 32, 272–275 (in Chinese).
- Huang P, Xu K W and Han Y (2005), 'Preparation and apatite layer formation by plasma electrolytic oxidation on titanium for biomedical application', *Mater Lett*, 59, 185–189.
- Huang Y F, Xu Y and Li G X (2000), 'Research advances on the surface treatment of aluminum and its alloys', *Plating and Finishing*, 22(1), 16–19 (in Chinese).
- Ikonopisov S, Girginor A and Machkova A (1977a), 'Post-breakdown anodization of aluminium', *Electrochem Acta*, 22(1), 1283–1286.
- Ikonopisov S, Girginov A and Machkova A (1977b), 'Theory of electrical breakdown during formation of barrier anodic films', *Electrochem Acta*, 22(10), 1077–1082.
- Ishizawa H and Ogino M (1995a), 'Formation and characterization of anodic titanium oxide coatings containing Ca and P', *J Biomed Mater Res*, 29, 65–72.
- Ishizawa H and Ogino M (1995b), 'Characterization of thin hydroxyapatite layers formed on anodic titanium oxide coatings containing Ca and P by hydrothermal treatment', *J Biomed Mater Res*, 29, 1071–1079.
- Ishizawa H and Ogino M (1999), 'Hydrothermal deposition of hydroxyapatite on anodic titanium oxide coatings containing Ca and P', *J Mater Sci*, 34, 5893–5898.
- Jaspard-Mécuson F, Czerwicz T, Henrion G, Belmonte T, Dujardin L, Viola A and Beauvir A (2007), 'Tailored aluminium oxide layers by bipolar current adjustment in the plasma electrolytic oxidation (PEO) process', *Surf Coat Technol*, 201, 8677–8682.
- Jin F, Paul K C, Xu G D, Zhao J, Tang D L and Tong H H (2006), 'Structure and mechanical properties of magnesium alloy treated by micro-arc discharge oxidation using direct current and high-frequency bipolar pulsing modes', *Mat Sci Eng A*, 435–436, 123–126.
- Jin F Y, Wang K, Zhu M, Shen L R, Li J, Hong H H and Chu P K (2009), 'Infrared reflection by alumina films produced on aluminum alloy by plasma electrolytic oxidation', *Mat Chem Phys*, 114, 398–401.
- Khan R H U, Yerokhin A L, Pilkington T, Leyland A and Matthews A (2005), 'Residual stresses in plasma electrolytic oxidation coatings on Al alloy produced by pulsed unipolar current', *Surf Coat Technol*, 200, 1580–1586.

- Kim M S, Ryu J J and Sung Y M (2007), 'One-step approach for nanocrystalline hydroxyapatite coating on titanium via micro-arc oxidation', *Electrochem Commun*, 9, 1886–1891.
- Krishna L R, Purnima A S and Sundararajan G (2006), 'A comparative study of tribological behavior of microarc oxidation and hard-anodized coatings', *Wear*, 261, 1095–1101.
- Krishna L R, Somaraju K R C and Sundararajan G (2003), 'The tribological performance of ultra-hard ceramic composite coatings obtained through microarc oxidation', *Surf Coat Technol*, 163–164, 484–490.
- Krysmann W, Kurze P and Districh K H (1984), 'Process characteristics and parameters of anodic oxidation by spark deposition (ANOF)', *Cryst Res Technol*, 19(7), 973–979.
- Krysmann W, Kurze P, Districh K H and Schneider H G (1971), 'Process characteristics and parameters of anode oxidation by spark discharge (ANOF)', *Corros Sci*, 11, 411–417.
- Kuhn A (2003), 'Plasma anodizing of magnesium alloys', *Met Finish*, 101, 44–50.
- Kurze P, Krysmann W and Schneider H G (1986a), 'Application field of ANOF layers and composites', *Cryst Res Technol*, 21(12), 1603–1609.
- Kurze P, Krysmann W and Schreckenbach J (1987), 'Colored ANOF layers on aluminium crystal', *Cryst Res Technol*, 22(1), 53–58.
- Kurze P, Schreckenbach J, Schwarz T H and Krysmann W (1986b), 'Coating by anodic oxidation with spark discharge (ANOF)', *Metallberflaeche*, 40(12), 539–540.
- Kuskov V N, Kuskov Y N, Kovenskii I M and Matveev N I (1990), 'Phase composition and microhardness of coatings produced by microarc oxidation', *Physics and Chemistry of Materials Treatment* (English translation of *Fizika i Khimiya Obrabotki Materialov*), 24(6), 619–621.
- Lee J M, Kang S B and Han J M (2008), 'Dry sliding wear of MAO-coated A356/20 vol.% SiCp composites in the temperature range 25–180°C', *Wear*, 264, 75–85.
- Li J F, Wan L and Feng J Y (2006), 'Study on the preparation of titania films for photocatalytic application by micro-arc oxidation', *Solar Energy Materials & Solar Cells*, 90, 2449–2455.
- Li J M, Cai H and Jiang B L (2007), 'Growth mechanism of black ceramic layers formed by microarc oxidation', *Surf Coat Technol*, 201, 8702–8708.
- Li L H, Kim H W, Lee S H, Kong Y M and Kim H E (2005), 'Biocompatibility of titanium implants modified by microarc oxidation and hydroxyapatite coating', *J Biomed Mater Res A*, 73, 48–54.
- Li L H, Kong Y M and Kim H W (2004), 'Improved biological performance of Ti implants due to surface modification by micro-arc oxidation', *Biomaterials*, 25, 2867–2875.
- Li X J, Wu X L, Xue W B, Cheng G A, Zheng R T and Cheng Y J (2007), 'Structures and properties of ceramic films on TiAl intermetallic compound fabricated by microarc oxidation', *Surf Coat Technol*, 201, 5556–5559.
- Liang J, Hu L T and Hao J C (2007a), 'Improvement of corrosion properties of microarc oxidation coating on magnesium alloy by optimizing current density parameters', *Appl Surf Sci*, 253, 6939–6945.
- Liang J, Wang P, Hu L T and Hao J C (2007b), 'Tribological properties of duplex MAO/DLC coatings on magnesium alloy using combined microarc oxidation and filtered cathodic arc deposition', *Mat Sci Eng A*, 454–455, 164–169.
- Liu Z M and Gao W (2006), 'A novel process of electroless Ni-P plating with plasma electrolytic oxidation pretreatment', *Appl Surf Sci*, 253, 2988–2991.
- Lonyuk B, Apachitei I and Duszczek J (2007), 'The effect of oxide coatings on fatigue

- properties of 7475-T6 aluminium alloy', *Surf Coat Technol*, 201, 8688–8694.
- Lu F H, Wu C T and Hung C Y (2002), 'Barium titanate films synthesized by an anodic oxidation-based electrochemical method', *Surf Coat Technol*, 153, 276–283.
- Luo H H, Cai Q Z, Wei B K, Yu B, He J and Li D J (2009), 'Study on the microstructure and corrosion resistance of ZrO₂-containing ceramic coatings formed on magnesium alloy by plasma electrolytic oxidation', *J Alloys Compd*, 474, 551–556.
- Lv G H, Gu W C, Chen H, Feng W R, Khosa M L, Li L, Niu E W, Zhang G L and Yang S Z (2006), 'Characteristics of ceramic coatings on aluminum formed by plasma electrolytic oxidation in silicate and phosphate electrolyte', *Appl Surf Sci*, 253, 2947–2952.
- Magurova Y V and Timoshenko A V (1995a), 'The effect of a cathodic component on AC microplasma oxidation of aluminum alloys', *Prot Met*, 31(4), 377–380.
- Magurova Y V and Timoshenko A V (1995b), 'The effect of a cathodic component on AC microplasma oxidation of aluminum alloys', *Zashchita Metallov*, 31, 414–418.
- Matykina E, Arrabal R, Skeldon P and Thompson G E (2009), 'Transmission electron microscopy of coatings formed by plasma electrolytic oxidation of titanium', *Acta Biomater*, 5, 1356–1366.
- McNiell W, Gruss L L (1966), *US Patent*, 3293158.
- McNiell W, Nordbloom G F (1958), *US Patent*, 2854390.
- Mécuson F, Czerwiec T, Belmonte T, Dujardin L, Viola A and Henrion G (2005), 'Diagnostics of an electrolytic microarc process for aluminium alloy oxidation', *Surf Coat Technol*, 200, 804–808.
- Mécuson F, Czerwiec T, Henrion G, Belmonte T, Dujardin L, Viola A and Beauvir J (2007), 'Tailored aluminium oxide layers by bipolar current adjustment in the Plasma Electrolytic Oxidation (PEO) process', *Surf Coat Technol*, 201, 8677–9682.
- Monfort F, Matykina E, Berkani A, Skeldon P, Thompson G E, Habazaki H and Shimizu K (2007), 'Species separation during coating growth on aluminium by spark anodizing', *Surf Coat Technol*, 201, 8671–8676.
- Mu W Y and Han Y (2008), 'Characterization and properties of the MgF₂/ZrO₂ composite coatings on magnesium prepared by micro-arc oxidation', *Surf Coat Technol*, 202, 4278–4284.
- Nan K H, Wu T, Chen J H, Jiang S, Huang Y and Pei G X (2009), 'Strontium doped hydroxyapatite film formed by micro-arc oxidation', *Mater Sci Eng*, 35, 871–878.
- Nie X, Hao Q K and Wei J M (1996), 'A novel modification technique for metal surface', *J. Wuhan Univ. Technol*, 11(1), 28–35.
- Nie X, Leyland A, Matthews A, Jiang J C and Meletis E I (2001), 'Effects of solution pH and electrical parameters on hydroxyapatite coatings deposited by a plasma-assisted electrophoresis technique', *J Biomed Mater Res*, 57, 612–618.
- Nie X, Leyland A and Matthews A (2000b), 'Low temperature deposition of Cr(N)/TiO₂ coatings using a duplex process of unbalanced magnetron sputtering and micro-arc oxidation', *Surf Coat Technol*, 133–134, 331–337.
- Nie X, Meletis E I, Jiang J C, Leyland A, Yerokhin A L and Matthews A (2002), 'Abrasive wear/corrosion properties and TEM analysis of Al₂O₃ coatings fabricated using plasma electrolysis', *Surf Coat Technol*, 149, 245–251.
- Nie X, Wilson A, Leyland A and Matthews A (2000a), 'Deposition of duplex Al₂O₃ DLC coatings on Al alloys for tribological applications using a combined micro-arc oxidation and plasma-immersion ion implantation technique', *Surf Coat Technol*, 121, 506–513.

- Patel J L and Saka N (2001), 'Microplasmic coatings', *Am Ceram Soc Bull*, 80(4), 27–29.
- Picas J A, Forn A, Rupérez E, Baile M T and Martín E (2007), 'Anodizing of aluminium matrix composite A6061/(Al₂O₃)_p for wear and corrosion resistance improvement', *Plasma Process Polym*, 4(S1), S579–S583.
- Popova N E, Popova S S and Povolotskii E G (1999), *Proceedings of the All- Russian Conf 'Electrochemistry of Membranes and Processes in Thin Ion-conducting Films on Electrodes'*, ECHM-99 Q June 24–26, 1999, SG TU, Saratov, 1999, p. 68 (in Russian).
- Rajasekaran B, Raman S G S, Joshi S V and Sundararajan G (2008b), 'Effect of microarc oxidised layer thickness on plain fatigue and fretting fatigue behaviour of Al-Mg-Si alloy', *Int J Fatigue*, 30, 1259–1266.
- Rajasekaran B, Rama S G S, Krishna L R, Joshi S V and Sundararajan G (2008a), 'Influence of microarc oxidation and hard anodizing on plain fatigue and fretting fatigue behaviour of Al-Mg-Si alloy', *Surf Coat Technol*, 202, 1462–1269.
- Rudnev V S, Vasilyeva M S, Kondrikov N B and Tyrina L M (2005), 'Plasma-electrolytic formation, composition and catalytic activity of manganese oxide containing structures on titanium', *Appl Surf Sci*, 252, 1211–1220.
- Rudnev V S, Yarovaya T P and Konshin V V (1998), 'Microplasma oxidation of an aluminum alloy in aqueous solutions containing sodium cyclohexaphosphate and nitrates of lanthanum and europium', *Russ J Electrochem*, 34(6), 510–516.
- Rudnev V S, Yarovaya T P, Boguta D L, Tyrina L M, Nedozorov P M and Gordienko P S (2001), 'Anodic spark deposition of P, Me(II) or Me(III) containing coatings on aluminum and titanium alloys in electrolytes with polyphosphate complexes', *J Electroanal Chem*, 497(1–2), 150–158.
- Shahid M (1997), 'Mechanism of film growth during anodizing of Al8090/SiC metal matrix composites in sulphuric acid electrolyte', *J Mater Sci*, 32, 3775–3781.
- Shatrov A S (2001a), 'Engraved shaft and method for manufacturing thereof', *WO 01/30572*, publ. 03.05.01.
- Shatrov A S (2001b), 'Head of a golf club made of light alloys and method for the production thereof', *WO 01/72384*, publ. 04.10.01.
- Shen D J, Wang Y L, Nash P and Xing G Z (2008), 'Microstructure, temperature estimation and thermal shock resistance of PEO ceramic coatings on aluminum', *J Mat Proc Technol*, 205, 477–481.
- Shi Z, Song G and Atrens A (2006), 'Influence of anodising current on the corrosion resistance of anodised AZ91D magnesium alloy', *Corros Sci*, 48, 1939–1959.
- Shin X H, Jiang Z H, Liu H L, Li X D and Hu X G (2003), 'TiO₂ ceramic films prepared by micro-plasma oxidation method for photodegradation of rhodamine B', *Mater Chem Phys*, 80, 39–43.
- Shin Y K, Chae W S, Song Y W and Sung Y M (2006), 'Formation of titania photocatalyst films by microarc oxidation of Ti and Ti–6Al–4V alloys', *Electrochem Commun*, 8, 465–470.
- Snizhko L O, Yerokhin A L, Pilkington A, Gurevina N L, Misnyankin D O, Leyland A and Matthews A (2004), 'Anodic processes in plasma electrolytic oxidation of aluminium in alkaline solutions', *Electrochimica Acta*, 49, 2085–2095.
- Song W H, Jun Y K, Han Y and Hong S H (2004), 'Biomimetic apatite coatings on micro-arc oxidized titania', *Biomaterials*, 25, 3341–3349.
- Sun J F, Han Y and Cui K (2008), 'Microstructure and apatite-forming ability of the MAO-treated porous titanium', *Surf Coat Technol*, 202, 4248–4256.

- Sun J F, Han Y and Huang X (2007), 'Hydroxyapatite coatings prepared by micro-arc oxidation in Ca and P containing electrolyte', *Surf Coat Technol*, 201, 5655–5658.
- The T H, Berkani A, Mato S, Skeldon P, Thompson G E, Habazaki H and Shimizu K (2003), 'Initial stages of plasma electrolytic oxidation of titanium', *Corros Sci*, 45, 2757–2768.
- Timoshenko A V and Magurova Y V (2000), 'Application of oxide coatings to metals in electrolyte solutions by microplasma methods', *Rev Metal Madrid*, 36(5), 323–330.
- Timoshenko A V and Magurova Y V (2005), 'Investigation of plasma electrolytic oxidation processes of magnesium alloy MA2-1 under pulse polarisation modes', *Surf Coat Technol*, 199, 135–140.
- Van T B, Brown S D and Wirtz G P (1977), 'Mechanism of anodic spark deposition', *J Am Ceram Soc*, 56(6), 563–566.
- Verdier S, Boinet M, Maximovitch S and Dalard F (2005), 'Formation, structure and composition of anodic films on AM60 magnesium alloy obtained by DC plasma anodising', *Corros Sci*, 47, 1429–1444.
- Vijh A K (1971), 'Sparking voltage and side reactions during anodization of valve metals in terms of electron tunneling', *Corros Sci*, 11, 411–417.
- Voevodin A A, Yerokhin A L, Lyubimov V V, Donley M and Zabinski J S (1996), 'Characterization of wear protective Al-Si-O coatings formed on Al-based alloys by micro-arc discharge treatment', *Surf Coat Technol*, 86–87, 516–521.
- Volynets V D, Gordienko P S, Efimenko A V and Semenova T L (1991), 'Electrochemical nature of the thermally stimulated currents of MOM structures', *Soviet Electrochemistry* (English Translation of *Elektro-Khimiia*), 26, 1371–1376.
- Wang Y K, Sheng L, Xiong R Z and Li B S (1999), 'Study of ceramic coatings formed by microarc oxidation on Al matrix composite surface', *Surf Eng*, 15(2), 109–114.
- Wang Y M, Jia D C, Guo L X, Lei T Q and Jiang B L (2005a), 'Effect of discharge pulsating on microarc oxidation coatings formed on Ti6Al4V alloy', *Mater Chem Phys*, 90, 128–133.
- Wang Y M, Jiang B L, Lei T Q and Guo L X (2005b), 'Microarc oxidation and spraying graphite duplex coating formed on titanium alloy for antifriction purpose', *Appl Surf Sci*, 246(1–3), 214–221.
- Wang Y M, Jiang B L, Lei T Q and Guo L X (2006a), 'Microarc oxidation coatings formed on Ti6Al4V in Na₂SiO₃ system solution: microstructure, mechanical and tribological properties', *Surf Coat Technol*, 201, 82–89.
- Wang Y M, Lei T Q, Guo L X, Zhou Y, Jia D C and Ouyang J H (2006b), 'Thermal shock and oxidation resistance property of microarc oxidation coating formed on Ti6Al4V alloy', *The 5th China International Conference on High-performance Ceramics*, 2006, Changsha.
- Wang Y M, Lei T Q, Jiang B L and Guo L X (2004), 'Growth, microstructure and mechanical properties of microarc oxidation coatings on titanium alloy in phosphate-containing solution', *Appl Surf Sci*, 233, 258–267.
- Wang X M, Zhu L Q, Li W P, Liu H C and Li Y H (2009), 'Effects of half-wave and full-wave power source on the anodic oxidation process on AZ91D magnesium alloy', *Appl Surf Sci*, 255, 5721–5728.
- Wang Y Q, Wu K and Zheng M Y (2006c), 'Effects of reinforcement phases in magnesium matrix composites on microarc discharge behavior and characteristics of microarc oxidation coatings', *Surf Coat Technol*, 201, 353–360.
- Wang Y Q, Zheng M Y and Wu K (2005c), 'Microarc oxidation coating formed on

- SiCw/AZ91 magnesium matrix composite and its corrosion resistance', *Mater Lett*, 59, 1727–1731.
- Wei C B, Tian X B, Yang S Q, Wang X B, Fu K Y and Chu P K (2007a), 'Anode current effects in plasma electrolytic oxidation', *Surf Coat Technol*, 201, 5021–5024.
- Wei D Q, Zhou Y, Jia D C and Wang Y M (2007b), 'Characteristic and *in vitro* bioactivity of a microarc-oxidized TiO₂-based coating after chemical treatment', *Acta Biomater*, 3, 817–827.
- Wirtz G P, Brown S D and Kriven W M (1991), 'Ceramic Coatings by Anodic Spark Deposition', *Materials and Manufacturing Processes*, 6(1), 87–115.
- Wu C T and Lu F H (2001), 'Electrochemical deposition of barium titanate films using a wide electrolytic voltage range', *Thin Solid Film*, 398–399, 621–625.
- Wu X H, Jiang Z H, Liu H L, Li X D and Hu X G (2003), 'TiO₂ ceramic films prepared by micro-plasma oxidation method for photodegradation of rhodamine B', *Mater Chem Phys*, 80, 39–43.
- Wu H H, Wang J B, Long B Y, Long B H, Jin Z S, Wang N D, Yu F R and Bi D M (2005), 'Ultra-hard ceramic coatings fabricated through microarc oxidation on aluminium alloy', *Appl Surf Sci*, 252, 1545–1552.
- Wu K, Wang Y Q and Zheng M Y (2007), 'Effects of microarc oxidation surface treatment on the mechanical properties of Mg alloy and Mg matrix composites', *Mat Sci Eng A*, 447, 227–232.
- Wu X H, Ding X B, Qin W, He W D and Jiang Z H (2006), 'Enhanced photo-catalytic activity of TiO₂ films with doped La prepared by micro-plasma oxidation method', *Journal of Hazardous Materials B*, 137, 192–197.
- Xin S G, Jiang Z H, Wang F P, Wu X H, Zhao L C and Shimizu T (2001), 'Effect of current density on Al alloy microplasma oxidation', *J Mater Sci Technol*, 17(6), 657–660.
- Xue W B, Wu X L, Li X J and Tian H (2006), 'Anti-corrosion film on 2024/SiC aluminum matrix composite fabricated by microarc oxidation in silicate electrolyte', *J Alloys Compd*, 425, 302–306.
- Xue W B (2006), 'Features of film growth during plasma anodizing of Al 2024/SiC metal matrix composite', *Appl Surf Sci*, 252, 6195–6200.
- Xue W B, Wang C, Tian H and Lai Y C (2007), 'Corrosion behaviors and galvanic studies of microarc oxidation films on Al-Zn-Mg-Cu alloy', *Surf Coat Technol*, 201, 8695–8701.
- Yang B C, Uchida M, Kim H M, Zhang X D and Kokubo T (2004), 'Preparation of bioactive titanium metal via anodic oxidation treatment', *Biomaterials*, 25, 1003–1010.
- Yao Z P, Jiang Y L, Jia F Z, Jiang Z H and Wang F P (2008), 'Growth characteristics of plasma electrolytic oxidation ceramic coatings on Ti-6Al-4V alloy', *Appl Surf Sci*, 254, 4084–4091.
- Yao Z P, Jiang Z H, Wang F P and Hao G D (2007), 'Oxidation behavior of ceramic coatings on Ti-6Al-4V by micro-plasma oxidation', *J Mat Proc Technol*, 190, 117–122.
- Yerokhin A L, Lyubimov V V and Ashitkov R V (1998b), 'Phase formation in ceramic coatings during plasma electrolytic oxidation of aluminium alloys', *Ceram Int*, 24(1), 1–6.
- Yerokhin A L, Nie X, Leyland A and Matthews A (2000), 'Characterisation of oxide films produced by plasma electrolytic oxidation of a Ti-6Al-4V alloy', *Surf Coat Technol*, 130, 195–206.
- Yerokhin A L, Nie X, Leyland A, Matthews A and Dowey S G (1999), 'Plasma electrolysis for surface engineering', *Surf Coat Technol*, 122, 73–93.

- Yerokhin A L, Shatrov T A, Samsonov V, Shashkov P, Leyland A and Matthews A (2004), 'Fatigue properties of Keronite coatings on a magnesium alloy', *Surf Coat Technol*, 182, 78–84.
- Yerokhin A L, Shatrov T A, Samsonov V, Shashkov P, Pilkington A, Leyland A and Matthews A (2005), 'Oxide ceramic coatings on aluminium alloys produced by a pulsed bipolar plasma electrolytic oxidation process', *Surf Coat Technol*, 199, 150–157.
- Yerokhin A L, Snizhko L O, Gurevina L, Leyland A, Pilkington A and Matthews A (2003), 'Discharge characterization in plasma electrolytic oxidation of aluminium', *J Phys, D: Appl Phys*, 36, 2110–2120.
- Yerokhin A L, Voevodin A A, Lyubimov V V, Zabinski J and Donley M (1998a), 'Plasma electrolytic fabrication of oxide ceramic surface layers for tribotechnical purposes on aluminium alloys', *Surf Coat Technol*, 110(3), 140–146.
- Zhang R F, Wang F Y, Hu C Y, Li W K, Xiang J H, Duo S W, Li M S and He X M (2007), 'Research progress in sealing treatment of anodic coatings formed on magnesium alloys', *J Mat Eng*, 11, 82–86.
- Zhao H, Chen J and Liu Z (2005), 'Microstructure and mechanical properties of ceramic coating on AM50 magnesium alloy by microarc oxidation', *Materials Science Forum*, 88–489, 693–696.
- Zhu X L, Kim K H and Jeong Y S (2001), 'Anodic oxide films containing Ca and P of titanium biomaterial', *Biomaterials*, 22, 2199–2206.
- Zhu X L, Ong LG, Kim S Y and Kim K H (2002), 'Surface characteristics and structure of anodic oxide films containing Ca and P on titanium implant material', *J Biomed Mater Res*, 60, 333–338.

Plasma electrolytic oxidation treatment of magnesium alloys

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Abstract: Plasma electrolytic oxidation (PEO) is an attractive surface engineering process for magnesium alloys. During PEO, the surface of a magnesium alloy is converted into a hard ceramic coating, in an electrolytic bath, using high energy electric discharges. This can offer improved wear and corrosion resistance to various magnesium components, thus expanding their fields of application. In this chapter, various aspects of PEO of magnesium alloys, such as the basics, processes, properties and applications, are discussed and the current status of the PEO of magnesium alloys is overviewed.

Key words: magnesium alloys, plasma electrolytic oxidation, microstructure, property.

6.1 Introduction

Anodizing is an electrolytic process for producing a thick, stable oxide film on metals and alloys that can mitigate the substrate corrosion or be used as a base for paint adhesion or dyeing. It is a well-known industrial technology for surface protection of light metals, especially aluminium, successfully used for many decades. However, the anodic behaviour of magnesium and magnesium alloys is strongly influenced by the voltage applied. Generally, different passive and active states influencing the coating formation are found, dependent on applied voltage, and the alloy and electrolyte compositions. However, due to the specific characteristics of magnesium alloys (see Chapter 1), the low voltage anodizing of these alloys was never successful enough to provide sufficient resistance to wear and corrosion. Currently, most of the anodizing processes use spark discharges to convert the magnesium surface into a ceramic oxide.

The core part of the anodizing process is the formation of an anodized layer that is normally about 5–30 μm thick, hard, dense, electrically insulating and wear resistant. The layers contain pores whose dimensions and distribution are a function of the electrolyte properties, temperature, anodizing current density and voltage. Depending on the aggressiveness of the environment, an anodized coating can also be additionally sealed and/or painted for optimal protection. Although the initial investment for

an anodizing treatment is relatively low, the ongoing costs of anodizing processes are rather high. Therefore, the use of this technique for surface protection of Mg alloys is limited in comparison to conversion coatings, e.g. for applications in the automotive industry (Hillis, 2001). Nevertheless, applied to many niche products, the coatings have already proven how beneficial they can be under wear and corrosive conditions. Ongoing research will most likely lead to cheaper processes, thus providing more competitive anodizing solutions.

Looking at the electrochemical conversion treatments available for Mg alloys, there are two different groups existing, which can be distinguished by the processing voltage as the driving force for the surface conversion process. The first group operates below the breakdown voltage – i.e. conventional anodizing (see Chapter 4), using the voltage mainly to accelerate and enhance the natural passive film formation in the specific electrolytes. The second group operates above the breakdown voltages, using mainly discharges at the electrolyte/metal interface to enhance film formation, and modify the composition, phases and density of the thick oxide films. The high energy in the discharges is able to melt substrate and passive films and convert them to hard ceramic types of coatings by incorporation of components from the electrolyte. The boundaries between the processes are not fixed, as the start of the appearance of micro-discharges, often denoted as breakdown potential, varies with the type and composition of the substrate alloy, electrolyte concentration and composition, and most importantly the type of power (pulse, AC, DC). A typical breakdown potential for PEO processing of magnesium alloys lies in the range between 100 and 200 V, and the final operating voltages are in the range of 300 to 600 V; thus much higher voltages than in conventional anodizing are normally used.

6.2 Plasma electrolytic oxidation (PEO) treatments of magnesium (Mg) alloys

In a PEO treatment, the applied voltage exceeds the dielectric breakdown potential of the growing oxide film and micro-discharges occur. These discharges are an essential part of the process responsible for incorporation of electrolyte compounds into the growing film and sintering it to a densified ceramic-like coating. As a result, mechanical properties, e.g. hardness and wear, are enhanced but unfortunately, discharge channels remain, thus causing an overall porous microstructure. Therefore, in aggressive environments, sealing is still required to obtain good corrosion resistance. The process is known under various synonyms, such as plasma electrolytic oxidation (PEO), micro arc oxidation (MAO), anodic spark deposition (ASD), plasma chemical oxidation (PCO), and plasma anodic oxidation (PAO), just to name a few. Discussion on the general features of PEO and its application to Ti and Al

alloys can be found in the preceding chapter (5). It is currently the most frequently used PEO technique for magnesium alloys that will be introduced in this chapter in more details.

6.2.1 Principles and process

The formation and evolution of the coating on magnesium alloy substrates during the PEO process in alkaline electrolytes can be described in four stages. The first stage is the dissolution of the magnesium alloy substrate, which then results in the formation of a passive film on the surface – comprising $\text{Mg}(\text{OH})_2$ and MgO . Depending on the electrolyte used, other compounds can be incorporated into the passive film as well.



Mizutani *et al.* (2003) have observed $\text{Mg}(\text{OH})_2$ and MgO on anodized coatings on magnesium alloys formed at 60 V under non-sparking conditions.

The second stage is marked by the beginning of sparks on the surface due to the breakdown of the passive film, hence termed the breakdown voltage. The breakdown voltage is characteristic for a given electrolyte system, depending on its composition and conductivity. Upon breakdown of the passive film on the surface, a vigorous gas evolution can be noticed. The following reactions occur at the anode surface:



The sparking characteristics and their intensity vary from electrolyte to electrolyte and they are also dependent on the processing parameters, *viz.* applied current density, frequency, etc. At the beginning of the second stage, the sparks are very fine and normally possess a very short lifetime.

With increase in voltage and time, and thus with the growth of the oxide layer on the surface, the sparks grow in size – which is described as the third stage. The increase in voltage during the first three stages in PEO processing is generally quite rapid.

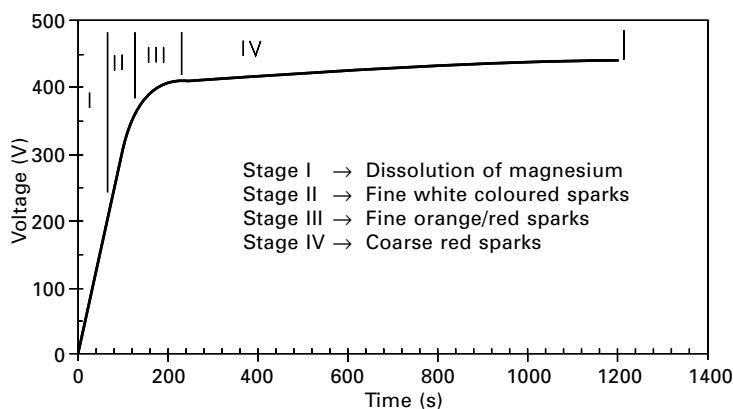
During the last stage, where the increase in voltage with time is very marginal, the sparks grow much bigger in size and have a much longer life time compared to the earlier stages. The final PEO layer is compounded with MgO , and other phases, *viz.* magnesium silicate, magnesium phosphate, magnesium fluoride, etc., depending on the ingredients of the electrolyte. A

typical voltage vs. time plot obtained from PEO processing of a magnesium alloy in a silicate-based electrolyte indicating the different stages of PEO – highlighting the characteristics of the sparks – is presented in Fig. 6.1 (Bala Srinivasan *et al.*, 2009).

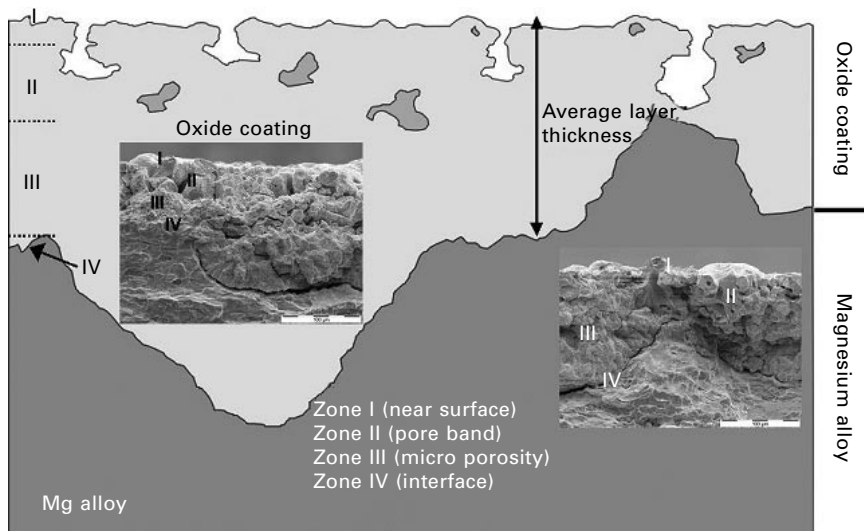
6.3 Microstructure of PEO-treated Mg alloys

6.3.1 Microstructure

The microstructural features of PEO coatings are dependent on the processing conditions, and the thickness of the coatings can range from 5 μm to 200 μm . The coatings have a jagged/wavy interface in most cases, which makes them an integral part of the substrate. Characteristically, all PEO coatings have a very thin barrier, with a thickness ranging from a few nm to a maximum of 2 μm . The core ceramic oxide layer is found above the barrier layer, growing in thickness with prolonged PEO processing. As the layer grows by the continuous discharge process, there are pores being formed and incorporated into the coating. Blawert *et al.* (2005) have described the microstructural features of a 120 μm thick PEO layer obtained from a silicate-based electrolyte as follows: The coating can be divided into four distinct regions, *viz.* (i) a thin inner barrier layer of < 1 μm , (ii) a relatively compact intermediate layer just next to the barrier layer with a lower number of pores and cavities, (iii) a region of pore bands with visible craters and pore channels and (iv) the outermost porous layer with craters on top. The above features are schematically represented in Fig. 6.2. This build-up of a PEO coating is more or less typical for many PEO coatings produced using Si-based electrolytes.



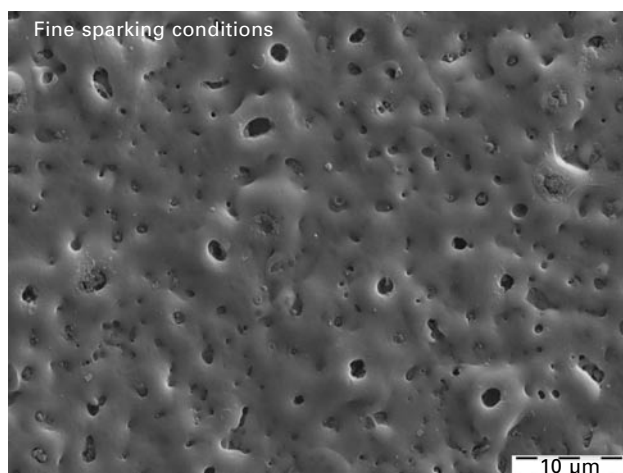
6.1 Schematic voltage vs. time plot and representation of different stages of PEO coating in a silicate electrolyte (Bala Srinivasan *et al.*, 2009a).



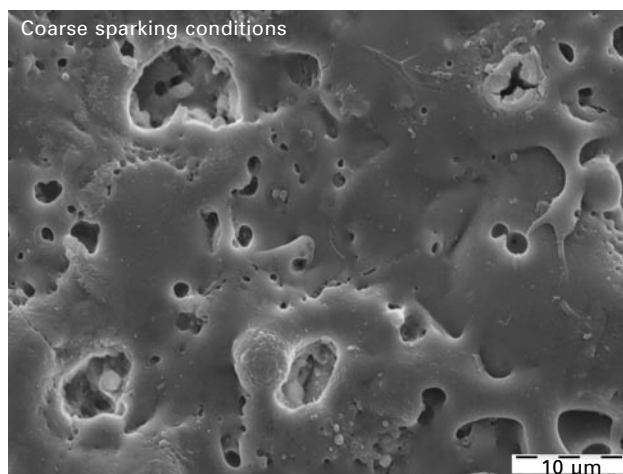
6.2 Schematic representation of cross-section of PEO coatings on magnesium alloys (typical features of the layer obtained by SEM micrographs are inserted) (Blawert *et al.*, 2005).

The porosity in PEO coatings is a function of discharge intensity and processing duration. Pores of sizes (diameters) ranging from as low as $0.5\ \mu\text{m}$ to as high as $50\ \mu\text{m}$ have been observed for various types of PEO coatings on magnesium alloys. The scanning electron micrograph of a typical PEO coating of $5\text{--}8\ \mu\text{m}$ thickness obtained from a silicate electrolyte at low processing voltages, *viz.* 380 V under conditions of fine discharges shown in Fig. 6.3a reveals fine and uniformly distributed pores on the surface of an AM50 magnesium alloy. On the other hand, the surface morphology of a $12\text{--}15\ \mu\text{m}$ thick coating in Fig. 6.3b shows large coarse oxide deposits with large pores on the surface. The cross-sectional features of the PEO coatings differ greatly depending on the electrolyte and also on the processing conditions. Coatings from silicate-based electrolytes (Si-PEO) are, in general, reported to be more compact than those produced in phosphate electrolytes (P-PEO). Typical scanning electron micrographs of Si-PEO and P-PEO coatings from the work of Liang *et al.* (2007) are shown in Fig. 6.4. Arrabal *et al.* (2008a) and Liang *et al.* (2009) have observed similar features in P-PEO and Si-PEO coatings produced by them.

Current density is one of the critical parameters for the growth of PEO coatings, which to a large extent decides the microstructural features of these layers (such as porosity and other defects) and thus their hardness, tribological and corrosion properties. Wu *et al.* (2007a) studied the effect of current density on the corrosion behaviour of PEO coatings on ZK60 magnesium alloy. Coatings were produced in an alkaline solution containing silicate. It



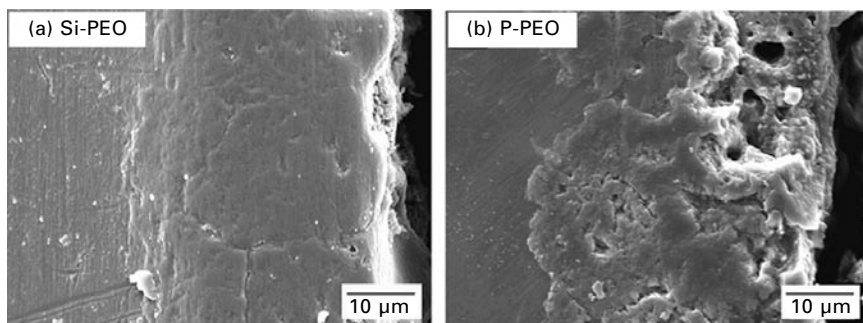
(a)



(b)

6.3 Scanning electron micrographs showing the surface morphology of PEO coatings obtained at two different stages of processing (Bala Srinivasan *et al.*, 2009a).

was reported that a high current density was helpful for the quick growth of the oxide layer, but resulted in a coarse microstructure and poor corrosion resistance. Within the current density range studied ($5\text{--}50\text{ mA}\cdot\text{cm}^{-2}$), $20\text{ mA}\cdot\text{cm}^{-2}$ was reported as the optimum condition. Scanning electron micrographs of PEO coatings on AM50 magnesium alloy, produced at $15\text{ mA}\cdot\text{cm}^{-2}$ and $150\text{ mA}\cdot\text{cm}^{-2}$ in 15 minutes in a silicate based electrolyte are shown in Figures 6.5a and 6.5b (Bala Srinivasan *et al.*, 2009). Even though the coating obtained at a low current density was thin, it was relatively compact, with low defect levels compared to the one produced at a high current density



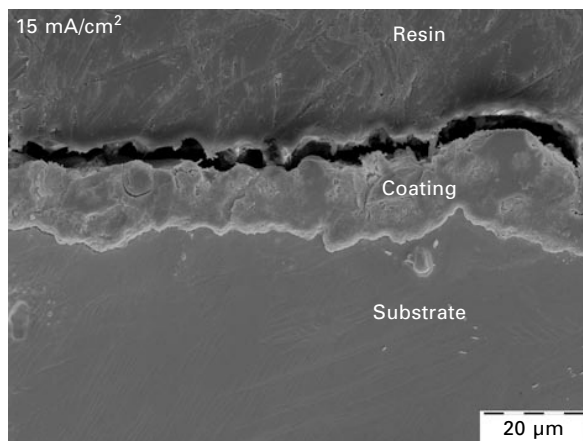
6.4 Scanning electron micrographs showing the cross-sections of Si-PEO and P-PEO coatings (Liang *et al.*, 2007).

level. High-voltage discharge conditions and the associated higher energy input levels were responsible for higher thickness and porosities/cracks as well. Thicker coatings produced at higher current density levels had larger pore sizes, pore channels and cracks, as seen in Fig. 6.5b.

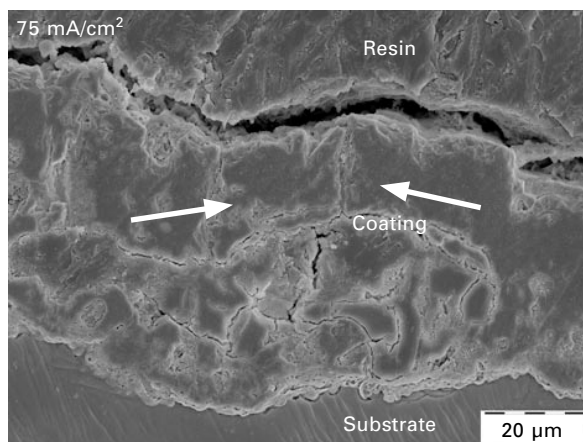
Liang *et al.* (2007a) reported the benefits of modifying the current density wave forms in order to realize smooth and compact coatings in a silicate-based electrolyte. The employment of stepped and freely decaying current density with time, as against a constant one, was reported to be helpful in realizing optimal energy intensity during the PEO process, resulting in coatings with better microstructural features. Even though the effect of frequency on the microstructural features of PEO coatings has not been fully understood, Lv *et al.* (2008) have claimed that the coatings formed at a frequency of 800 Hz using a pulsed DC power source had fine pores and a dense structure compared with those obtained at 100 Hz in a fluoride–phosphate electrolyte.

6.3.2 Phase composition

The phase composition of the PEO coating is mainly influenced by the electrolyte composition, and the energy intensity during the discharge is also considered to play a role. Coatings produced on an AZ91D alloy using an aluminate–fluoride electrolyte were found to be constituted with MgAl_2O_4 and Al_2Mg . A large number of research publications on PEO using silicate-based electrolytes have shown the formation of Mg_2SiO_4 as the major phase (Liang *et al.*, 2007a; Bala Srinivasan *et al.*, 2009, 2009a). In addition, the coatings from silicate-based electrolytes were reported to also contain MgO , MgAl_2O_4 and MgF_2 , depending on the alloy, processing conditions and additives employed. Liang *et al.* (2007a) reported the presence of only MgO in the coatings obtained from a phosphate-based electrolyte. However, a few other publications have documented the presence of $\text{Mg}_3(\text{PO}_4)_2$, as well, along with MgO in coatings from similar electrolytes (Liang *et al.*,



(a)



(b)

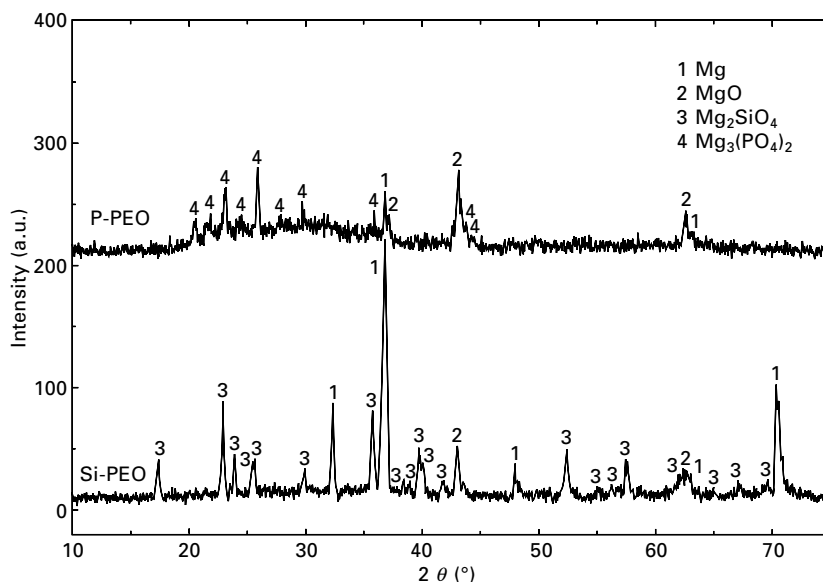
6.5 Effect of current density on the coating thickness of AM50 magnesium alloy (in a silicate based electrolyte) – arrows show pore channels (Bala Srinivasan *et al.*, 2009).

2009, Arrabal *et al.*, 2008a). A typical XRD profile showing the results of phase composition analysis performed on silicate- and phosphate-based PEO coatings on AM50 magnesium alloy by Liang *et al.* (2009) is presented in Fig. 6.6.

6.4 Properties of PEO-treated Mg alloys

6.4.1 Mechanical properties

The hardness values of PEO coatings can be in the range of 350 HV to 700 HV, depending on the composition, thickness and morphology of the



6.6 XRD patterns showing the phase composition of PEO coatings on AM50 magnesium alloy obtained from a silicate (Si-PEO) and a phosphate (P-PEO) based electrolyte (Liang *et al.*, 2009).

coatings. Addition of fluoride and tungstate to silicate-based electrolytes have been reported to result in higher hardness (Ding *et al.*, 2007; Liang *et al.*, 2005a). However reliable hardness values representing only the coating and not a combination of coating and substrate are difficult to obtain due to the high surface roughness and porosity preventing the use of nano and micro hardness testing.

Wu *et al.* (2007b) have reported a decrease in tensile strength and ductility (percentage elongation) for the AZ91 magnesium alloy and magnesium metal matrix composites after PEO treatment. Coatings produced with higher current density (120 mA/cm²) were found to show slightly inferior mechanical properties than those obtained at a lower current density (60 mA/cm²). The flaws, in the form of pores and the micro cracks, in the coatings were attributed to be the reasons for cracking at low stress levels. Bala Srinivasan *et al.* (2008) have also observed similar behaviour for the PEO-coated AM50 alloy in slow strain rate tensile tests performed in air.

Fatigue performance reduction in anodized metals is normally caused by several factors, including oxidation-induced surface tensile stress and structural defects in the oxide layer (e.g. pores and micro cracks). In the case of magnesium, the combination of these factors appears to be particularly disadvantageous, since magnesia has both high specific heat of formation and a substantial lattice misfit with the metal. Although the residual surface stress could be reduced by adjustment of the film structure and chemical

composition, no adequate conventional anodizing techniques have so far been found to minimize the risk of premature fatigue failure of magnesium alloys. The fatigue strength of the base metal can be reduced during hard anodizing, especially in thicker films, and the produced ceramic layer can be brittle and not adequate for certain applications (Gray and Luan, 2002). However, the plasma electrolytic oxidation (PEO) technique could be an approach to reduce this risk (Yerokhin *et al.*, 1999, 2004).

Compilation of the research work on coated magnesium has suggested that the majority of the coatings have a seriously adverse effect on fatigue strength, to as much as 40% (Blawert *et al.*, 2006). However, Ferguson *et al.* claim that the Anomag process produces smoother layers, thus offering better fatigue behaviour. Extensive testing of coated samples showed that the anodizing process did not significantly affect the mechanical properties of die cast magnesium alloys (Ferguson *et al.*, 2001). Also Kurze *et al.* demonstrated that the alloy AZ91 coated with 20 μm Magoxid-Coat did not suffer from an influence of the coating on the fatigue strength in comparison to the pure alloy. The tests were performed according to DIN 50100 (Kurze and Banerjee, 1996). Further, Yerokhin *et al.* (2004) reported a substantially improved fatigue behaviour of Keronite-coated magnesium alloys, which showed no more than a 10% drop in the endurance limit. The improved Keronite process was claimed to have provided dense and uniform oxide ceramic layers with fine-grained microstructures, which were said to be more favourable for components experiencing fatigue loading.

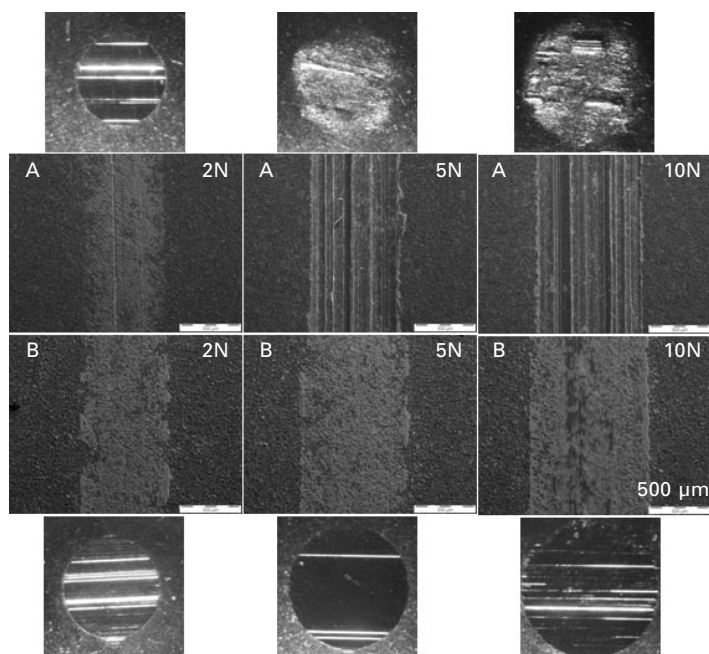
6.4.2 Tribological characteristics

The PEO coatings produced on magnesium alloy substrates are hard and hence can offer good wear resistance. The commercially available Keronite process claims a superior resistance against the CS17 abrasion wheel. Also, it is claimed that this coating is resistant to galling (<http://www.keronite.com>). However, there are no detailed reports available on the wear mechanisms of these coatings patented by Keronite.

Published information on the tribological behaviour of PEO coatings is limited. Goretta *et al.* (2007) reported the solid-particle erosion of an anodized WE43A magnesium alloy. The PEO layer of 12 μm thickness was found to have been removed quickly by the impact (at 20° and 90°) of irregular alumina particles of nominal diameters of 63 μm and 143 μm , travelling at 120 m/s. Jin *et al.* (2006) studied the wear behaviour of PEO coatings produced using DC and bipolar power sources on AZ91 magnesium alloy. The coatings obtained from both systems were reported to consist mainly of MgO and the wear resistance of the coating obtained using the bipolar power source was better. Higher thickness, hardness and better compactness were responsible for the better wear behaviour of the bipolar coatings.

Bala Srinivasan *et al.* (2009c) performed dry reciprocating ball-on-disc wear tests at ambient conditions ($25 \pm 2^\circ\text{C}$, $30 \pm 2\%$ RH) at three different load levels, 2 N, 5 N and 10 N, with an oscillating amplitude of 10 mm and at a sliding velocity of $5 \text{ mm}\cdot\text{s}^{-1}$ for a sliding distance of 12 m. Specimens with two different thickness levels were investigated ($A = 10 \mu\text{m}$, $B = 20 \mu\text{m}$) and an AISI 52100 steel ball was used as the counter part. The wear tracks produced on the PEO-coated magnesium alloy specimens (Fig. 6.7) revealed that coating A did not survive the test under 5 and 10 N. Heavy scoring marks on the surface, characteristic of adhesive/abrasive wear, are clearly seen in A-5N and A-10N micrographs. On the other hand, coating B, with a higher thickness, could resist adhesive and abrasive wear damage. The optical macrographs of the steel balls, used as the counter material, presented alongside the wear tracks suggest that the main wear was transferred from the magnesium substrate to the steel ball. It was clearly evidenced that the thickness of the PEO coating decided the load bearing capacity and thus played a role in preventing the adhesive/abrasive wear of the magnesium alloy substrate.

Liang *et al.* (2007) assessed the wear resistance of PEO coatings against a



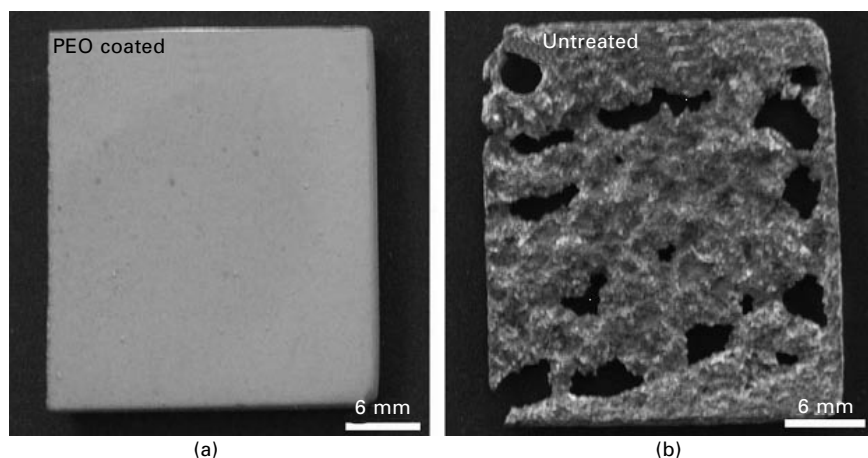
6.7 SEM micrographs of the wear tracks on PEO coated magnesium alloy specimens and optical macrographs of the corresponding counter face ball showing the extent of wear damage (Bala Srinivasan *et al.*, 2009c).

3 mm diameter Si_3N_4 ball in a ball-on-disc oscillating adhesive wear test. The friction coefficient values observed for the PEO/ Si_3N_4 sliding couples were in the range of 0.6–0.8 as against 0.25–0.30 for the magnesium substrate/ Si_3N_4 couple. The wear resistance of the Si-PEO coating was superior to that of the P-PEO coating, which was attributed to the higher hardness of the former.

6.4.3 Corrosion behaviour

PEO coatings can readily offer good protection to magnesium alloys in mild environments and/or for short durations. The corrosion resistance of PEO coatings in aggressive environments and for long-term exposures is dictated by many factors, including the coating composition, thickness, and defect levels. As is well known, these coatings are porous in nature, and the extent of porosity and other defects such as cracks can influence the corrosion behaviour. Particularly, galvanic attack cannot be prevented without additional sealing. The corrosion performance of the PEO coatings has been studied extensively by many researchers, an overview of which has been given by Blawert *et al.* (2006).

The corrosion resistance of a Si-PEO coating on AZ31B alloy to 3.5% NaCl solution was reported by Guo *et al.* (2006). Optical macrographs (Fig. 6.8) of the specimens exposed to the corrosive environment for 120 hours clearly suggest the improved resistance offered by the PEO coating. Similarly, Cai *et al.* (2006) studied the corrosion resistance of silicate and phosphate based PEO coatings in 5% NaCl solution by immersion and salt-spray tests,



6.8 Surface appearance of PEO coated and untreated AZ31 B magnesium alloy specimens after 120 hours of exposure to 3.5% NaCl solution (Guo *et al.*, 2006).

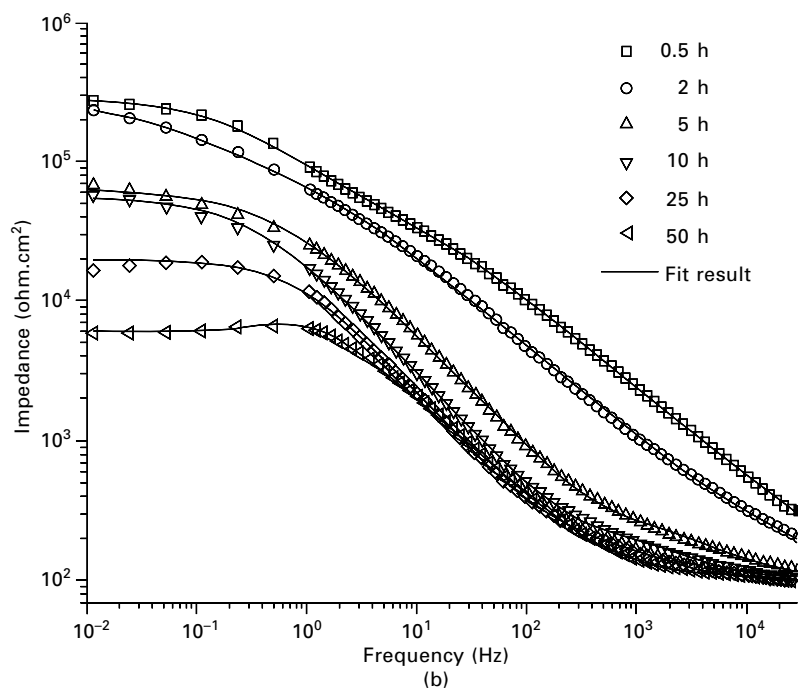
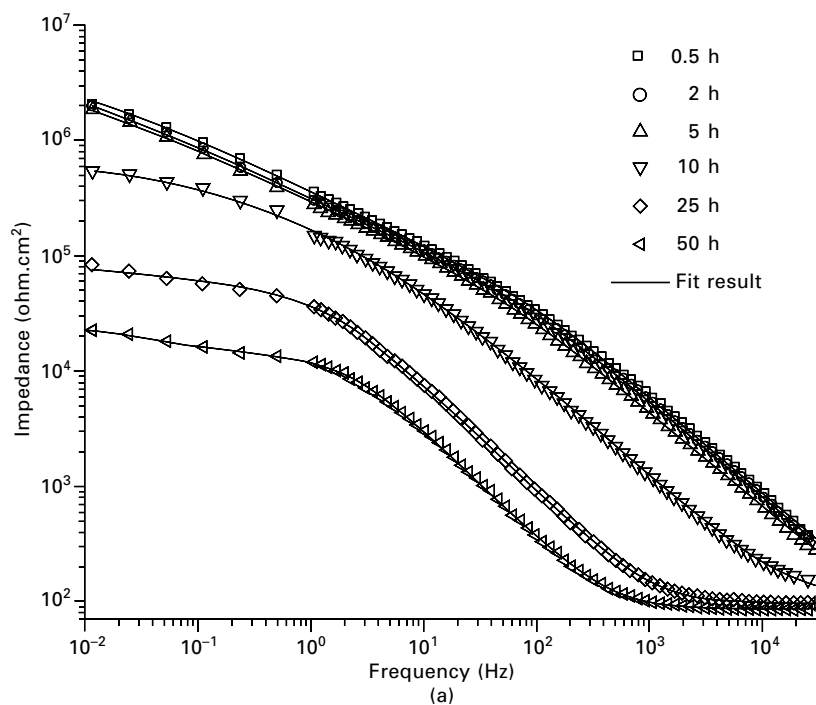
and reported the superior performance of Si-PEO coating. Magoxid-coatings were reported to withstand salt spray tests in accordance with DIN EN ISO 9227 for 80–100 hours (<http://www.aimt-group.com>), and Keronite and Anomag coatings have been claimed to withstand 1000 hours of salt spray tests in accordance with ASTM B117 (<http://www.keronite.com>).

Bala Srinivasan *et al.* (2009a) showed the beneficial influence of higher thickness coatings on the corrosion behaviour of PEO-coated AM50 magnesium alloy. The superior corrosion resistance of the silicate based PEO coatings over the phosphate coatings was demonstrated by Liang *et al.* (2007), based on short-term polarization tests. An extension of this work addressing the long-term corrosion performance of PEO coatings revealed that the Si-PEO coating outperformed the P-PEO coating (Liang *et al.*, 2009). Impedance tests performed for 50 hours demonstrated the better stability of Si-PEO coating than the P-PEO coating in 0.1 M NaCl solution, which was attributed to the phase composition, compactness/porosity level and the better substrate-coating interface of the Si-PEO coating (Fig. 6.9).

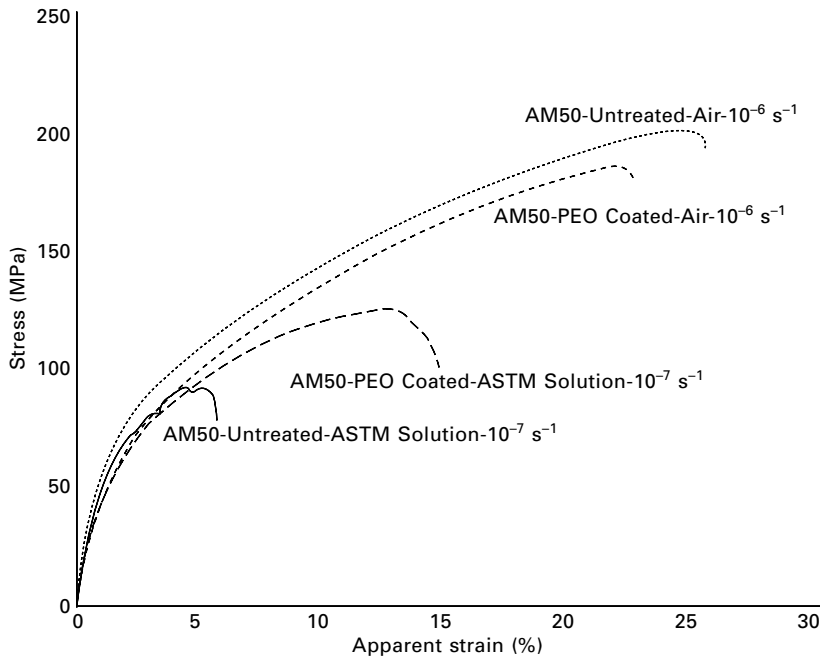
Information on the environmentally-assisted cracking behaviour of PEO-coated magnesium alloys is limited. Bala Srinivasan *et al.* (2008, 2008a) have assessed the tensile and stress corrosion cracking (SCC) of a cast AM50 alloy with and without a silicate-based PEO coating, by performing slow strain-rate tensile (SSRT) tests in air and in ASTM D1384 solution. The mechanical properties (SSRT tests in air) of this PEO-coated alloy were found to be slightly lower than those of the untreated alloy. Even though the general corrosion resistance of the PEO-coated alloy was superior, the PEO coating could not eliminate the stress corrosion cracking susceptibility of the alloy in the tests performed at strain rates of 10^{-6} and 10^{-7} s^{-1} . However, the coating could delay the failure under both conditions. The stress vs. strain plots obtained from the SSRT tests in air and in the ASTM solution are shown in Fig. 6.10. The cracking of the PEO coating due to the straining in the SSRT tests and the subsequent seepage of electrolyte onto the substrate were responsible for causing the transgranular fracture. Very similar SCC behaviour was observed in the case of PEO-coated wrought AZ61 alloy in the SSRT tests in ASTM D1384 solution (Bala Srinivasan *et al.*, 2008b).

6.5 Recent developments in PEO treatments of Mg alloys

Recently, numerous new developments have taken place to obtain high-performance PEO coatings on Mg alloys. These were aimed at not only improving the tribological and corrosion behaviour of magnesium alloy, but also reducing the cost of processing and increasing productivity to suit wider industrial applications.



6.9 Bode plots from the electrochemical impedance tests of (a) Si-PEO and (b) P-PEO coatings in 0.1 M NaCl solution (Liang *et al.*, 2009).



6.10 Slow strain rate tensile behaviour of untreated and PEO coated AM50 magnesium alloy in air and in ASTM solution at two different strain rates (Bala Srinivasan *et al.*, 2008).

6.5.1 Process optimization

The PEO technology has been under continuous development, including the employment of different power sources, use of auxiliary gas, and application of ultrasonic power, to achieve coatings with better integrity and properties.

Jin *et al.* (2006) have used two different modes of power sources, *viz.* DC and bipolar pulsing (BP), for PEO coating of AZ91 D alloy in a silicate-based electrolyte. In the BP mode, the rectangular pulse that was applied with a frequency of 800 Hz had four stages: 250 μs for the positive pulse, 500 μs for the negative pulse, 400 μs between the positive pulse and the next negative pulse, and 100 μs between the negative pulse and the following positive pulse. To maintain a stable average electric density, the voltage was varied between 120 and 198 V in the DC mode, and 180 and 470V for the positive voltage in the BP mode, whereas the negative voltage was maintained at 50V during the process. It was claimed that the oxidation rate was quicker with the BP mode and the films formed had a dense and compact structure. Higher hardness and better wear resistance were observed for the coatings produced in the BP mode.

Similarly, Lv *et al.* (2008) have reported the development of thin coatings with very fine pore sizes and dense structures on ZM5 magnesium alloy in

fluoride+phosphate electrolyte at high frequency (800 Hz). Although the coatings produced at this high frequency were thin, they had less surface roughness and better corrosion resistance than those obtained at 100 Hz.

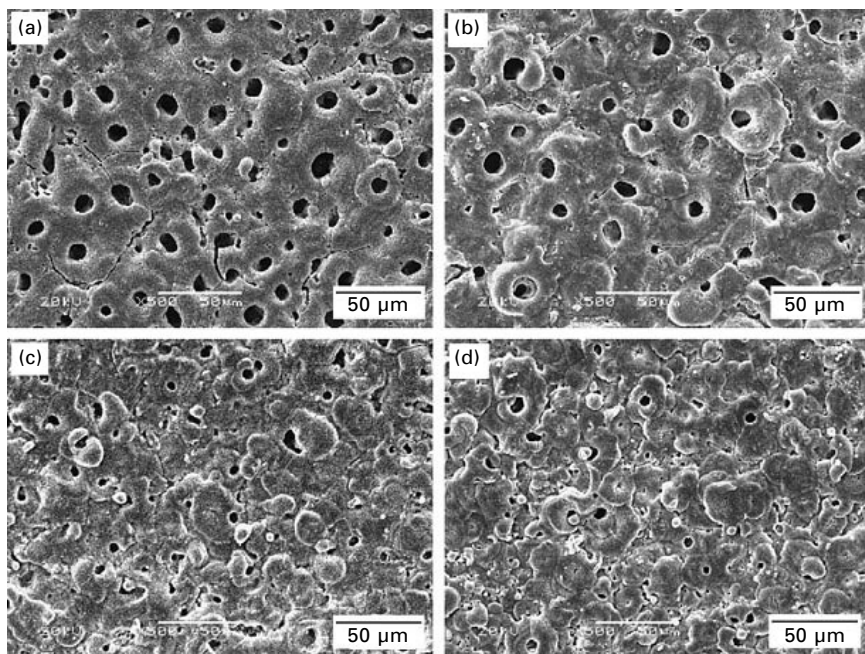
The influence of ultrasonic power on the structure and properties of PEO anodized coatings formed on AZ31B magnesium alloy was investigated by Guo *et al.* (2004). The application of ultrasonic power at a constant frequency of 25 Hz at 400 W was found to enhance the growth rate of anodic coatings. Nevertheless, the authors reported the formation of a thin coating with a lower power level (280 W), and it appears that there is a minimum threshold ultrasound power that is required to enhance the growth rate. There was, however, no effect of ultrasound on the phase composition of the coatings obtained under all the conditions (with and without ultrasound at two power levels). Some patented processes seem to use this technique for an improved growth rate and better compactness of coatings. In addition, employment of an auxiliary air stream to the electrolyte used for PEO processing of magnesium alloys is practised by Keronite (www.keronite.com).

6.5.2 Additives in the treatment solutions

The role of additives in the electrolyte on the microstructure and properties of PEO coatings has been studied extensively. The addition of potassium fluoride to a silicate-based solution was reported to reduce the conductivity of the electrolyte and decrease the working voltage range. Further, it was helpful in getting a compact coating, thus resulting in better hardness and wear resistance, and this was attributed to the spark discharge characteristics and phase composition of the coatings (Liang *et al.*, 2005a).

The effect of an addition of sodium tungstate (Na_2WO_4) to a silicate-based electrolyte was studied by Ding (2007). The breakdown voltage was significantly reduced due to the increase in conductivity of electrolyte in the presence of 6 g.L^{-1} of Na_2WO_4 . Although the XRD spectra did not show the incorporation of any additional phases other than MgO , MgAl_2O_4 and Mg_2SiO_4 , the authors claimed the presence of WO_3 and metallic W in the coatings through XPS analysis. The incorporation of these phases, along with the increase of Mg_2SiO_4 , was considered to be responsible for the increase in hardness and wear resistance of the resultant PEO coatings.

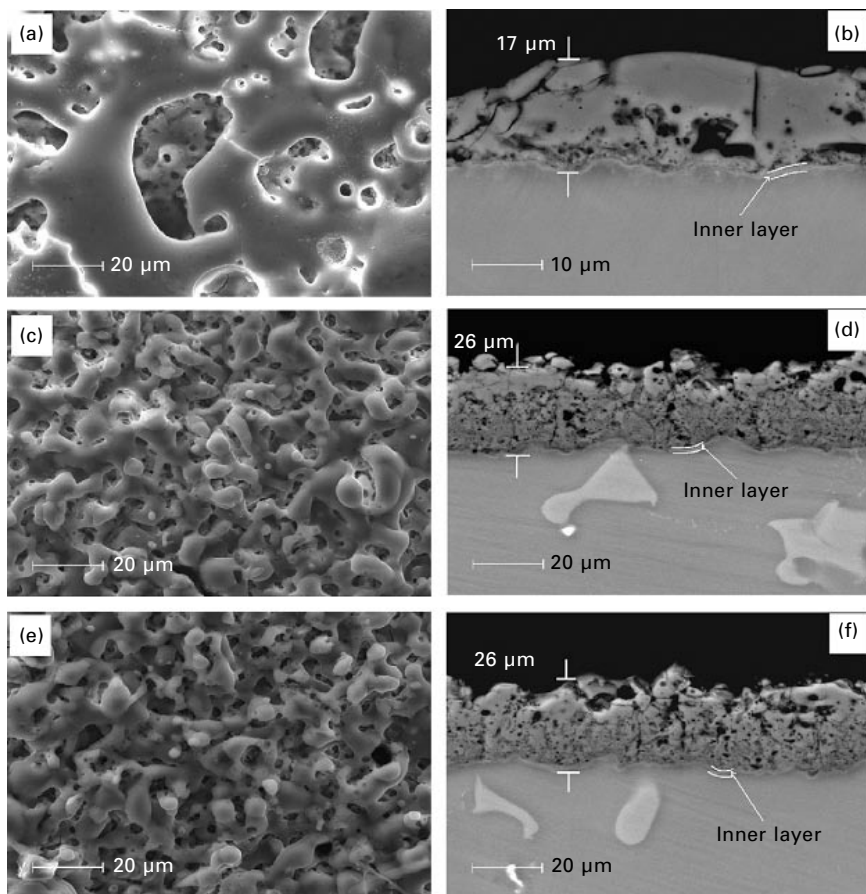
The addition of NaAlO_2 to a phosphate-based electrolyte was reported to result in coatings with fine pore sizes (Fig. 6.11). While the coating produced with the conventional phosphate electrolyte was constituted with only MgO , the formation of MgAl_2O_4 spinel was facilitated with the introduction of NaAlO_2 into the electrolyte. The conductivity of the electrolyte was reported to increase with increase in NaAlO_2 concentration, thus resulting in lower breakdown voltages. Due to finer discharges, the coatings produced with 8% NaAlO_2 were smoother. Furthermore, a better corrosion resistance was



6.11 Surface morphology of microarc oxidation coatings formed on Mg alloy in $\text{Na}_3\text{PO}_4\text{-KOH}$ electrolytes containing different concentrations of NaAlO_2 : (a) without NaAlO_2 ; (b) 1.0 g/L NaAlO_2 ; (c) 4.0 g/L NaAlO_2 ; (d) 8.0 g/L NaAlO_2 (Liang *et al.*, 2005).

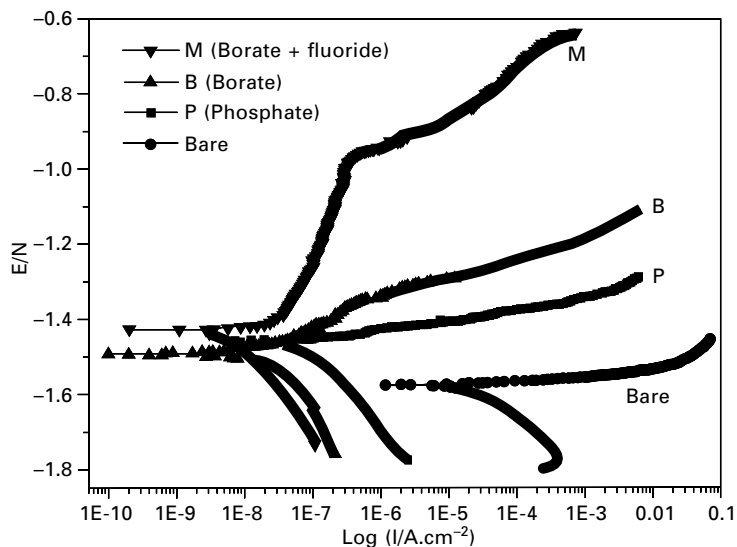
attributed to the higher volume fraction of MgAl_2O_4 and reduced structural imperfections in the coating (Liang *et al.*, 2005).

Addition of CrO_3 to the silicate-based electrolyte was examined by Blawert *et al.* (2007). The CrO_3 in the electrolyte was reported to reduce the coating thickness and also the amount of Forsterite (Mg_2SiO_4) in the coating. Further, the incorporation of chromium species into the layer did not yield any better inhibition capabilities. Duan *et al.* (2007) studied the influence of sodium borate in a silicate-based electrolyte, individually and in combination with potassium fluoride. The coatings produced were compared with those from an electrolyte containing phosphate and silicate. The morphology and cross-section of the coatings shown in Fig. 6.12 suggest that those produced with borate and fluoride additions were better in terms of pore size and thickness. The corrosion behaviour of the coatings was evaluated in 3.5% NaCl solution by potentiodynamic polarization studies. The coatings (designated as P – phosphate/silicate, B – borate, M – borate + fluoride) were found to show an increase in corrosion resistance in that order (Fig. 6.13). The better behaviour of the borate + fluoride coating was attributed to higher thickness, more uniform structure and the more compact inner barrier layer of the coating.



6.12 Morphologies of PEO films on magnesium alloy AZ91D, respectively, treated in solutions containing (a) phosphate, (c) borate and (e) both borate and fluoride. (b), (d) and (f) represent the respective cross-sections. (Duan *et al.*, 2007).

Luo *et al.* (2009) studied Si-PEO coatings obtained from the following electrolytes: (i) $\text{Zr}(\text{NO}_3)_4\text{-KOH}$, (ii) $\text{ZrOCl}_2\text{-KOH}$ and (iii) $\text{K}_2\text{ZrF}_6\text{-Na}_2\text{SiO}_3\text{-KOH}$. The phase composition of the coatings from electrolytes (i) and (ii) contained ZrO_2 and Zr, and that obtained from (iii) MgO , SiO_2 , MgF_2 and Mg_2SiO_4 . The improvement in the corrosion resistance at 20°C and 60°C was attributed to the presence of these phases and a more compact/thicker coating. Coatings containing crystalline TiO_2 on AM60B magnesium alloy were produced by the addition of titania-sol to a phosphate-based electrolyte by Liang *et al.* (2007c). Addition of 4% of titania-sol was found to evolve fine sized pores, in a coating consisting of MgO , MgAl_2O_4 , TiO_2 (rutile) and TiO_2 (anatase). Polarization studies showed a two-fold improvement in



6.13 Potentiodynamic polarization behaviour of PEO films (obtained with different additives) on AZ91D magnesium alloy in 3.5% NaCl (Duan *et al.*, 2007).

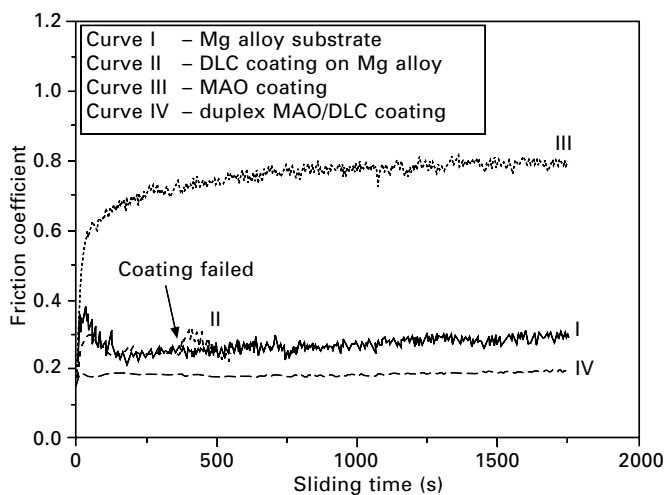
the corrosion resistance for the coatings containing TiO_2 when compared to the phosphate PEO coating.

6.5.3 Duplex coatings

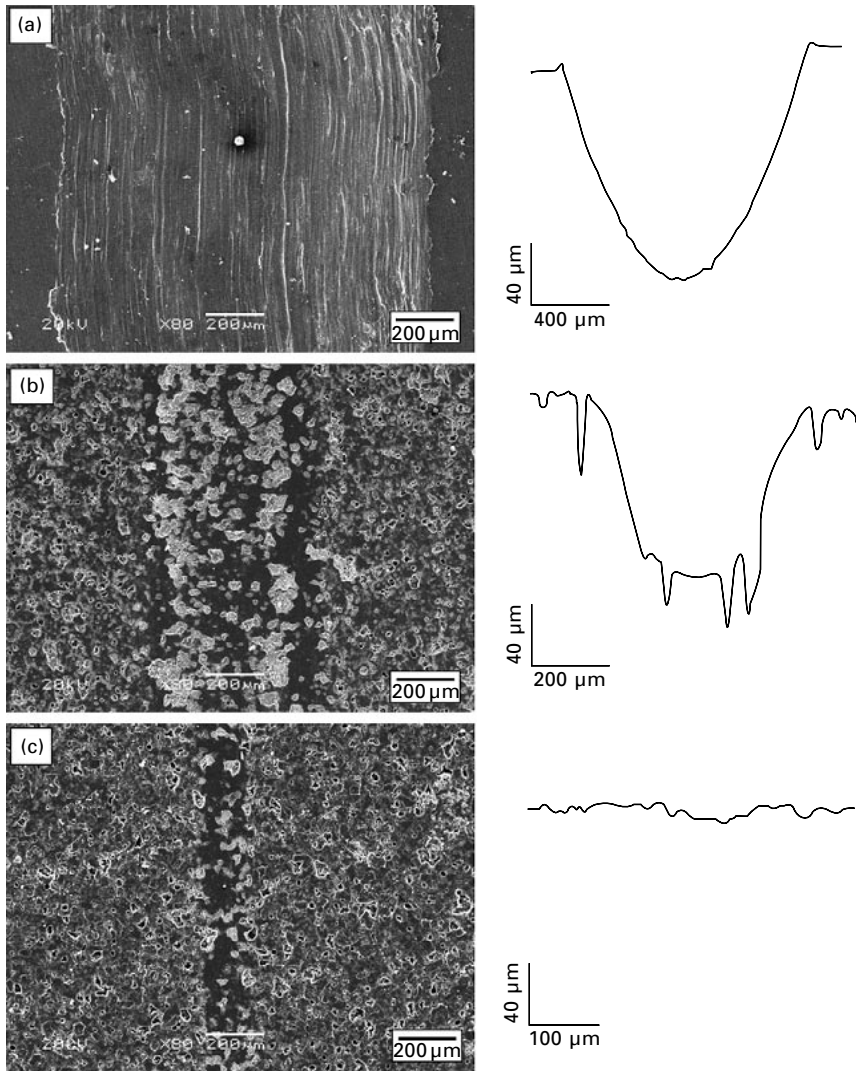
Although PEO coatings offer reasonably good corrosion and wear resistance to magnesium alloys, for critical applications with stringent requirements, a better tailoring of the surface is necessary. Galvanic attack in combination with more noble metals is a special concern. The long-term electrochemical and salt spray-test results available in the literature suggest that degradation of the coating is governed by the phase composition, thickness and the degree of porosity in the coating. In this context, it would be beneficial to apply an overlay coat on the PEO coated surface to seal the pores, in order to realize even better corrosion resistance. This can be accomplished in many ways, and in the last couple of years researchers have attempted electroless plating, physical vapour deposition and polymer coatings on PEO-coated magnesium surfaces.

Liu and Gao (2006) have attempted an electroless nickel (EN) plating process on a PEO-treated magnesium substrate. Salt fog spray and potentiodynamic polarization testing demonstrated that the PEO treatment produces a dense, well adhered oxide coating on the AZ91 Mg alloy. The adhesion of the EN coating (measured as critical load) was 10.8 N and that of the PEO-EN layer was 14.6 N. The presence of the PEO coating on the magnesium substrate

acted as an effective barrier and catalytic layer, and also provided high-density nucleation sites for the subsequent EN coating, which significantly reduced the porosity of the nickel coating and benefited the adhesion strength as well. Potentiodynamic polarization studies on the PEO-EN duplex coating in 3.5% NaCl solution showed a 2–3 fold improvement in corrosion resistance compared to the monolayer EN or PEO coatings. Considering the hardness of the magnesium substrate, it would be difficult to achieve better wear properties by depositing hard coatings such as TiN, TiC, etc. on these substrates directly, as the hardness mismatch between the substrate and PVD coatings might result in crumbling of the thin/hard layers. It would be worthwhile to improve the hardness of the magnesium alloy surface by some means and then provide the overlay hard coatings by PVD. For this, the PEO coatings should be very attractive. Tribological behaviour of duplex PEO/DLC coatings on a magnesium alloy was characterized by Liang *et al.* (2007b) and was compared with that of the monolayer DLC or PEO coatings and the untreated substrate as well. Dry, sliding wear studies showed a very high friction coefficient for the PEO coated substrate/Si₃N₄ (ball) couple. The DLC coating, even though it showed a low friction coefficient, was found to crumble under similar testing conditions (load: 2N, sliding speed: 0.1 m/s, sliding amplitude: 5 mm, ambient temperature/humidity). The duplex coated substrate, when slid against this ceramic ball, registered friction coefficient values of less than 0.2 throughout the test duration. The friction coefficient vs. sliding time plots documented in that investigation are shown in Fig. 6.14 and the SEM micrographs of the worn tracks and the respective wear depth profiles are presented in Fig. 6.15.



6.14 Dry sliding behaviour of Mg alloy substrate, polished MAO coating, DLC monolayer and duplex MAO/DLC coating against Si₃N₄ ball (Liang *et al.*, 2007c).



6.15 SEM micrographs and surface profiles of the wear tracks after sliding tests: (a) Mg alloy substrate, (b) MAO coating, and (c) duplex MAO/DLC coating (Liang *et al.*, 2007c).

Tan *et al.* (2005) deposited multi-layer sol-gel coatings on anodized magnesium substrates. The sol-gel layers were applied by spraying and, by changing the number of passes that the spray gun made over the substrate, the coating thickness was varied. One-layer and two-layer coatings were produced and cured (UV-curing followed by thermal cure at 150°C) before the electrochemical characterization. The mechanism of corrosion protection was through the sealing of pores in the anodized layer, which also acted

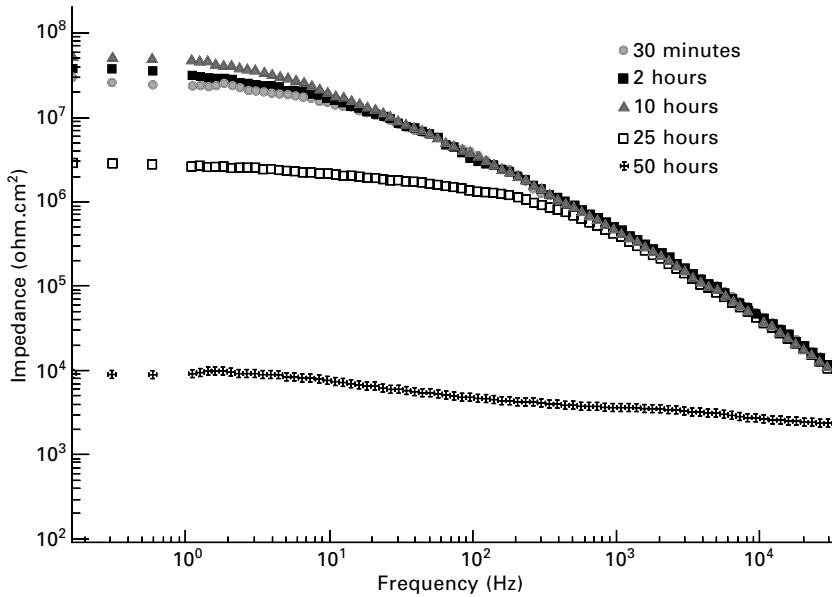
as an excellent barrier for the sol-gel layers. Since defects and porosity in the coatings are the main causes of degradation, application of such layers minimizes the diffusion of electrolyte through the coating towards the interface of the substrate, thereby controlling the corrosion damage.

Duan *et al.* (2006) applied a thin, organic coating layer, of the order of 3–5 μm , on PEO coated magnesium substrates by a controlled multi-immersion technique under low-pressure conditions. These coatings, termed ‘composite coatings’ by the authors, were characterized for their microstructural features and electrochemical behaviour. SEM observations revealed that the sealing agent was integrated with PEO film by physical interlocking, thereby covering uniformly the surface, as well as penetrating into pores and micro-cracks of PEO film. Based on the results of chrono-potentiometric ($E \sim t$) and electrochemical impedance spectroscopy EIS measurements for long-time immersion in 3.5% NaCl solution, the authors concluded that, due to the blocking effect of the sealing agent in the pores and cracks of the PEO film, the composite coatings could effectively suppress the corrosion process by holding back the transfer or diffusion of electrolyte and corrosion products between the composite coatings and solution during immersion.

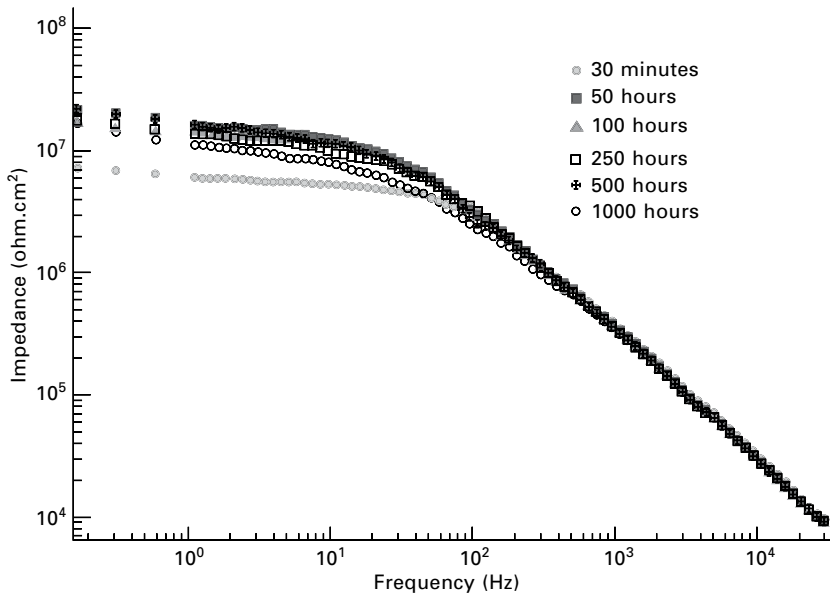
Bala Srinivasan *et al.* (2009b) have also reported a very similar enhancement of corrosion resistance of PEO + polymer duplex coatings on a wrought AZ31 magnesium alloy. While the polymer (poly(ether-imide), Ultem 1000[®]) coated and the merely-PEO treated magnesium alloy specimens lasted less than 50 hours in the EIS tests (0.1 M NaCl solution), the specimens with the duplex coating (PEO + polymer) successfully resisted 1000 hours without showing any degradation. The improved adhesion of the polymer coating in the presence of the PEO layer, and the effective sealing of the pores in the PEO coating with the polymer, were responsible for the enhanced corrosion resistance. The synergistically beneficial effect of the duplex coatings on the corrosion behaviour was also witnessed in the salt spray tests. The EIS plots obtained for the polymer-coated and the duplex (polymer+PEO) coated magnesium alloy substrates are shown in Figures 6.16 and 6.17, which clearly demonstrate the beneficial effect of PEO coating as an interlayer, promoting a better adhesion for the polymer.

6.5.4 Composite coatings

It is known that PEO coatings are harder than the magnesium substrate and can offer a superior wear resistance, as demonstrated by researchers. It is also believed that the introduction of secondary phases into the porous PEO coating may offer even better tribological characteristics. However, dry sliding wear tests have revealed that the friction coefficient values for PEO coating/steel and PEO coating/ceramic (Si_3N_4) couples are higher than that for couples of the parent magnesium substrates (Liang *et al.*, 2007; Bala



6.16 EIS spectra of the polymer-coated AZ31 magnesium alloy in 0.1 M NaCl solution after different durations of exposure (Bala Srinivasan *et al.*, 2009b).



6.17 EIS spectra of the magnesium alloy with the duplex coating (PEO + polymer) in 0.1 M NaCl solution after different durations of exposure (Bala Srinivasan *et al.*, 2009b).

Srinivasan *et al.*, 2009a). It would be beneficial if the friction coefficient could be reduced by some means. There is not much literature on composite PEO coatings. Mu and Han (2008) developed composite coatings comprising MgF_2 and ZrO_2 from a K_2ZrF_6 based electrolyte with some additives. The processing voltage was found to be instrumental in governing the thickness and composition, and thus the micro hardness of the coatings. The coatings were found to consist of MgF_2 , tetragonal and monoclinic ZrO_2 , and MgO . The bond strength, hardness and corrosion resistance were found to be better for the coatings obtained with a higher processing voltage (550 V).

Arrabal *et al.* (2008) and Matykina *et al.* (2008) have experimented with the incorporation of particles of monoclinic zirconia during the PEO processing, and have investigated the mechanism of coating formation. The coatings obtained using a DC power source in alkaline silicate–phosphate electrolytes comprised MgO , Mg_2SiO_4 and $\text{Mg}_3(\text{PO}_4)_2$ phases, and zirconia particles were found to get incorporated preferentially into the inner regions and at the coating surface. Due to local heating at the micro discharge regions, these monoclinic zirconia particles were found to transform into tetragonal zirconia. Also, a $\text{Mg}_2\text{Zr}_5\text{O}_{12}$ phase was identified in the PEO coatings when zirconia incorporation was attempted in the phosphate-based electrolyte. These interesting findings with the nano-particle incorporations provide more avenues for further investigation and development of these coatings for commercial application.

6.6 Industrial PEO processes and applications

6.6.1 Industrial PEO processes

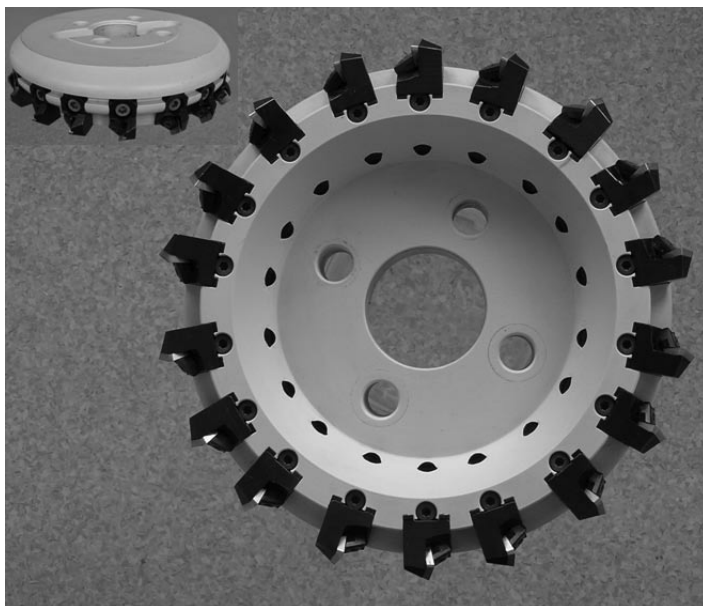
Parallel to extensive scientific research around the world, PEO coating technology is readily available on a commercial basis. Commercial processes such as Anomag, Keronite (<http://www.keronite.com>), Magoxid (<http://www.aimt-group.com>), Tagnite (<http://www.tagnite.com>), Algan 4 (<http://www.magnesium-technologies.com>) and others have been developed. Among them, only the Anomag process is claimed to work without discharges. At what voltages the newly-developed plasma gel anodizing process Algan 2M (<http://www.magnesium-technologies.com>) is working – with or without discharges – is an open question. Nevertheless, it seems as if all anodized coatings obtained from the new electrolytic plasma-based processes share quite similar corrosion performances, which are generally better than HAE or Dow 17 (see Chapter 4). Additionally, good sealing can further upgrade the corrosion prevention properties of all the anodized layers (Blawert *et al.*, 2006).

6.6.2 Applications

The main purpose of PEO oxide layers applied on magnesium components is to improve their wear and corrosion resistance. They are used alone, as a base for further build up of coating systems, e.g. promoting the adhesion of paint and powder coating systems to the magnesium substrate, or as a pre-treatment for adhesive bonding. One early example where a PEO coat was industrially used in combination with a paint finish is shown in Fig. 6.18.

Basically, all commercial magnesium alloys independent of their production process (cast or wrought) can be treated; thus, there is a large range of possible applications across all industrial sectors (automotive, consumer, aviation, medical, food, electronics, etc.) which use magnesium for weight reduction and have to fight poor wear and corrosion resistance. However, despite more favourable properties compared to conversion coatings, the disadvantage is clearly the higher cost involved with PEO, limiting the number of actual applications. Thus, main competitors of the PEO coatings are conversion coatings that are inexpensive and simple in comparison with PEO processes.

Nevertheless, quite a number of applications can be found by screening the homepages of AIMT, Keronite and Tagnite. A large variety of housings, casings and covers are treated in the automotive, aviation, space and consumer



6.18 PEO (Magoxide provided by AIMT) and paint-coated magnesium body of a high-speed milling cutter (Fette GmbH).

industry. Structural, load-bearing parts are found as well, including wheels, frames (bicycle, motorcycle) and levers, but also some more unexpected examples, e.g. eyewear, cookware, parts for textile machinery (e.g. bobbins) and packaging moulds.

Finally, one should keep in mind, that in spite of being more expensive than conversion coatings, the properties of PEO coatings regarding paint adhesion and the prevention of undermining of paint films are much superior. Thus, wherever magnesium is used in aggressive surroundings and needs to survive for a longer period, a PEO coating in combination with a suitable paint system can sometimes be the only solution to provide the required corrosion resistance.

6.7 Summary

Plasma electrolytic oxidation has become one of the most important surface engineering technologies for magnesium alloys. The PEO treatment utilizes micro-discharges to convert the surface of magnesium alloys into hard ceramic layers using mainly alkaline-based chromate-free solutions. This has the advantage that not only corrosion resistance but also the wear resistance can be improved. Furthermore, the coatings have good adhesion to the substrate, thermal stability, thermal shock resistance, heat resistance, high dielectric strength and good optical properties, which offer a wide range of property improvements for Mg alloys in their applications. The phase composition of the coating depends strongly on the electrolyte used and quite a large number of different treatment solutions are available for controlling the phase composition and thus adjusting particular properties.

In spite of those advantages, the corrosion resistance of PEO coatings alone is not sufficient under harsh conditions, or to prevent galvanic corrosion in contact with other metals. This is due to the inherent open porosity of the process, which requires sealing if long-term stability under the above conditions is required. However, this can be an advantage as well, because they offer good adhesion if used as a pre-treatment for paint and powder coatings, or for adhesive bonding. Especially, as a pre-treatment, PEO has mainly to compete with conversion coatings. Despite their higher cost, the better property profile of PEO coatings should be considered wherever a simple combination of conversion coating and top coat is not sufficient to obtain the required performance.

6.8 References

Arrabal R, Matykina E, Skeldon P, Thompson GE (2008), Incorporation of zirconia particles into coatings formed on magnesium by plasma electrolytic oxidation, *Journal of Materials Science*, 43, 1532–1538.

- Arrabal R, Matykina E, Viejo F, Skeldon P, Thompson GE (2008a), Corrosion resistance of WE43 and AZ91D magnesium alloys with phosphate PEO coatings, *Corrosion Science*, 50, 1744–1752.
- Bala Srinivasan P, Blawert C, Dietzel W (2008a), Effect of plasma electrolytic oxidation treatment on the corrosion and stress corrosion cracking behaviour of AM50 magnesium alloy, *Materials Science and Engineering*, A494, 401–406.
- Bala Srinivasan P, Blawert C, Dietzel W (2008b), Effect of plasma electrolytic oxidation coating on the stress corrosion cracking behaviour of wrought AZ61 magnesium alloy, *Corrosion Science*, 50, 2415–2418.
- Bala Srinivasan P, Blawert C, Dietzel W (2009c), Dry sliding wear behaviour of plasma electrolytic oxidation coated AZ91 cast magnesium alloy, *Wear*, 266, 1241–1247.
- Bala Srinivasan P, Blawert C, Dietzel W, Kainer KU (2008), Stress corrosion cracking behaviour of a surface-modified magnesium alloy, *Scripta Materialia*, 59, 43–46.
- Bala Srinivasan P, Blawert C, Störmer M, Dietzel W (2009a), Characterisation of tribological and corrosion behaviour of plasma electrolytic oxidation coated AM50 magnesium alloy, *Surface Engineering*, DOI 10.1179/174329409X379246.
- Bala Srinivasan P, Liang J, Blawert C, Störmer M, Dietzel W (2009), Effect of current density on the microstructure and corrosion behaviour of plasma electrolytic oxidation treated AM50 magnesium alloy, *Applied Surface Science*, 255, 4212–4218.
- Bala Srinivasan P, Scharnagl N, Blawert C, Dietzel W (2009b), Enhanced corrosion protection of AZ31 magnesium alloy by duplex plasma electrolytic oxidation and polymer coatings, *Surface Engineering*, doi: 10.1179/174329409X409314
- Blawert C, Dietzel W, Ghali E, Song G (2006), Anodizing treatments for magnesium alloys and their effect on corrosion resistance in various environments, *Advanced Engineering Materials*, 8(6), 511–533.
- Blawert C, Heitmann V, Dietzel W, Nykyforchyn HM, Klappkiv MD (2005), Influence of process parameters on the corrosion properties of electrolytic conversion plasma coated magnesium alloys, *Surface and Coatings Technology*, 200, 68–72.
- Blawert C, Heitmann V, Dietzel W, Nykyforchyn HM, Klappkiv MD (2007), Influence of electrolyte on corrosion properties of plasma electrolytic conversion coated magnesium alloys, *Surface and Coatings Technology*, 201, 8709–8714.
- Blawert C, Manova D, Störmer M, Gerlach JW, Dietzel W, Mändl S (2008), Correlation between texture and corrosion properties of magnesium coatings produced by PVD, *Surface and Coatings Technology*, 202, 2236–2240.
- Cai Q, Wang L, Wei B, Liu Q (2006), Electrochemical performance of microarc oxidation films formed on AZ91D magnesium alloy in silicate and phosphate electrolytes, *Surface and Coatings Technology*, 200, 3727–3733.
- Ding J, Liang J, Li TH, Hao J, Xue Q (2007), Effects of sodium tungstate on characteristics of microarc oxidation coatings formed on magnesium alloy in silicate–KOH electrolyte, *Transactions of Metals Society of China*, 17, 244–249.
- Duan H, Du K, Yan C, Wang F (2006), Electrochemical corrosion behavior of composite coatings of sealed MAO film on magnesium alloy AZ91D, *Electrochimica Acta*, 51, 2898–2908.
- Duan H, Yan C, Wang F (2007), Effect of electrolyte additives on performance of plasma electrolytic oxidation films formed on magnesium alloy AZ91D, *Electrochimica Acta*, 52 (2007) 3785–3793
- Ferguson WG, Liu W, Ross P, MacCulloch J (2001), Corrosion fatigue of high pressure die cast magnesium alloys, in Hryn J (Ed.), *Magnesium Technology*, The Minerals, Metals & Materials Society, 269–274.

- Goretta KC, Cunningham AJ, Chen N, Singh D, Routbort JL, Rateick Jr RG (2007), Solid-particle erosion of an anodized Mg alloy, *Wear*, 262, 1056–1060.
- Gray JE, Luan B (2002), Protective coatings on magnesium and its alloys – a critical review, *Journal of Alloys and Compounds*, 336, 88–113.
- Guo H, An M, Xu S, Huo H (2006), Microarc oxidation of corrosion resistant ceramic coating on a magnesium alloy, *Materials Letters*, 60, 1538–1541.
- Guo XW, Ding W, Lu C, Zhai CQ (2004), Influence of ultrasonic power on the structure and composition of anodizing coatings formed on Mg alloys, *Surface and Coatings Technology*, 183, 359–368.
- Hillis JE (2001), Magnesium Corrosion Performance in Automotive Applications – the Importance of Internal Quality and Surface Cleanliness, in Essadiqi E., Goodwin F.E., Elboudjaïni M. (eds), *Materials in the Automotive Industry, 40th Annual Conference of Metallurgists of CIM*, Montreal, Canadian Institute of Mining, Metallurgy and Petroleum, 3–26.
- Homepage AIMT AHC Oberflächentechnik GmbH at <http://www.aimt-group.com>
- Homepage Keronite International Ltd at <http://www.keronite.com>
- Homepage: Advanced Magnesium Technologies & Solutions (AMTS) at www.magnesium-technologies.com
- Homepage: Magn. Technol. Licensing Ltd. at <http://www.magnesium.co.nz>
- Homepage: Technology Applications Group, Inc. at <http://www.tagnite.com>
- Jin F, Chub PK, Xua G, Zhaoa G, Tang D, Tong H (2006), Structure and mechanical properties of magnesium alloy treated by micro-arc discharge oxidation using direct current and high-frequency bipolar pulsing modes, *Materials Science and Engineering*, A435–436, 123–126.
- Kurze P and Banerjee D (1996), Eine neue anodische Beschichtung zur Verbesserung der korrosionsbeständigkeit von Magnesiumwerkstoffen, *Gießerei-Praxis*, 11/12, 211–217.
- Liang J, Bala Srinivasan P, Blawert C, Störmer M, Dietzel W (2009), Electrochemical corrosion behaviour of plasma electrolytic oxidation coatings on AM50 magnesium alloy formed in silicate and phosphate based electrolytes, *Electrochimica Acta*, 54, 3842–3850.
- Liang J, Guo B, Tian J, Liu H, Zhou J, Liu W, Xu T (2005), Effects of NaAlO₂ on structure and corrosion resistance of microarc oxidation coatings formed on AM60B magnesium alloy in phosphate–KOH electrolyte, *Surface and Coatings Technology*, 199, 121–126.
- Liang J, Guo B, Tian J, Liu H, Zhou J, Xu T (2005a), Effect of potassium fluoride in electrolytic solution on the structure and properties of microarc oxidation coatings on magnesium alloy, *Applied Surface Science*, 252, 345–351.
- Liang J, Hu L, Hao J (2007c), Preparation and characterization of oxide films containing crystalline TiO₂ on magnesium alloy by plasma electrolytic oxidation, *Electrochimica Acta*, 52, 4836–4840.
- Liang J, Hu L, Hao J (2007), Characterization of microarc oxidation coatings formed on AM60B magnesium alloy in silicate and phosphate electrolytes, *Applied Surface Science*, 253, 4490–4496.
- Liang J, Hu L, Hao J (2007a), Improvement of corrosion properties of microarc oxidation coating on magnesium alloy by optimizing current density parameters, *Applied Surface Science*, 253, 6639–6645.
- Liang J, Wang P, Hu L, Hao J (2007b), Tribological properties of duplex MAO/DLC coatings on magnesium alloy using combined microarc oxidation and filtered cathodic arc deposition, *Materials Science and Engineering*, A454–455, 164–169.

- Liu Z and Gao W (2006), A novel process of electroless Ni-P plating with plasma electrolytic oxidation pretreatment, *Applied Surface Science*, 253, 2988–2991.
- Luo H, Cai Q, Wei B, Yu B, He J, Li D (2009), Study on the microstructure and corrosion resistance of ZrO₂-containing ceramic coatings formed on magnesium alloy by plasma electrolytic oxidation, *Journal of Alloys and Compounds*, doi:10.1016/j.jallcom.2008.06.151.
- Lv GH, Chen H, Gu WC, Li L, Niu EW, Zhang XH, Yang SZ (2008), Effects of current frequency on the structural characteristics and corrosion property of ceramic coatings formed on magnesium alloy by PEO technology, *Journal of Materials Processing Technology*, 208, 9–13.
- Matykina E, Arrabal R, Monfort F, Skeldon P, Thompson GE (2008), Incorporation of zirconia into coatings formed by DC plasma electrolytic oxidation of aluminium in nanoparticle suspensions, *Applied Surface Science*, 255, 2830–2839.
- Mizutani Y, Kim SJ, Ichino R, Okido M (2003), Anodizing of Mg alloys in alkaline solutions, *Surface and Coatings Technology*, 169–170, 143–146.
- Mu W, Han Y (2008), Characterization and properties of the MgF₂/ZrO₂ composite coatings on magnesium prepared by micro-arc oxidation, *Surface and Coatings Technology*, 202, 4278–4284.
- Tan ALK, Soutar AM, Annergren IF, Liu YN (2005), Multilayer sol–gel coatings for corrosion protection of magnesium, *Surface and Coatings Technology*, 198, 478–482.
- Wu H, Cheng Y, Li L, Chen Z, Wang H, Zhang Z (2007a), The anodization of ZK60 magnesium alloy in alkaline solution containing silicate and the corrosion properties of the anodized films, *Applied Surface Science*, 253, 9387–9394.
- Wu K, Wang YQ, Zheng MY (2007b), Effects of microarc oxidation surface treatment on the mechanical properties of Mg alloy and Mg matrix composites, *Materials Science and Engineering*, A447, 227–232.
- Yerokhin AL, Nie X, Leyland A, Matthews A (1999), Plasma electrolysis for surface engineering, *Surface Engineering*, 122, 73–93.
- Yerokhin AL, Shatrov A, Samsonov V, Shashkov P, Leyland A, Matthews A (2004), Fatigue properties of Keronite® coatings on a magnesium alloy, *Surface and Coatings Technology*, 182, 78–84.

Abstract: Thermal spray coatings have been widely applied to add functions such as wear resistance, corrosion resistance, bioactivity and dielectric properties to light metals. The characteristics of the deposition process, involving splat cooling and successive stacking of splats, create coatings of unique microstructure which are different from conventional materials. In this chapter the characteristics of the thermal spray processes, and factors influencing spray particle parameters are described. The metal alloy particle oxidation, splat formation (including solid–liquid two-phase droplet impact involved in cermet coating deposition) and features of the pores in the coating are reviewed. Additionally, characterization of the coating microstructure, the dominant effect of lamellar structure on coating properties, and reactions of spray particles with the light metal substrates are examined for control of cohesion, adhesion, and properties of the coatings.

Key words: thermal spraying, coating microstructure, splat formation, lamella bonding, coating adhesion.

7.1 Introduction

Thermal spray processes have been widely used in various industrial fields to enhance surface properties of various engineering parts. Light metals are generally soft, and their wear resistance is very poor. With Mg alloys, their high chemical activity makes them subject to corrosion (see Chapter 1). Through applying various coating materials to light metal surfaces by thermal spray processes, the wear resistance, thermal resistance and corrosion resistance of engineering parts made from light metals can be significantly improved.

Thermal spray coatings are formed by successive impact of a stream of spray droplets in fully molten or partially melted states, followed by flattening, rapid cooling and solidification. Heating and accelerating of the spray materials are necessary to create spray droplets. Chemical reactions, such as metal alloy oxidation during heating, may occur, which change chemical compositions and phases of the spray materials and may add additional functions to the coatings. The parameters of the droplets, including temperature, velocity and size, which are determined by spraying processes and conditions, influence interaction of the spray particles with the spray flame, coating deposition processes.

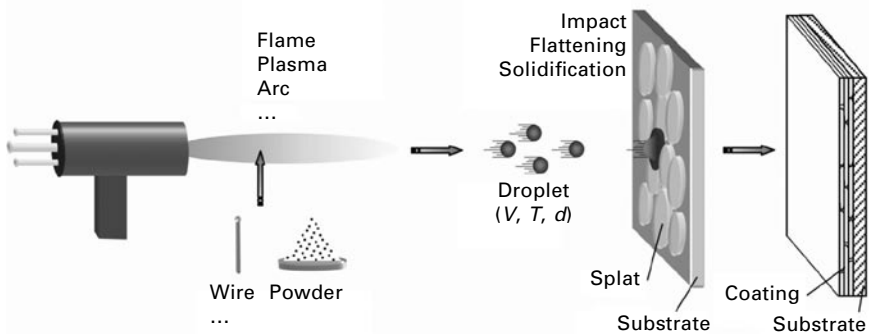
Splat formation is the fundamental process in thermal spray coating. The rapid quenching characteristics during splat formation upon impact

of molten spray droplets involved in coating deposition result in a quasi-stable fine microstructure in individual splats. The successive deposition of spray particles provides the coatings with a unique lamellar microstructure, different from that produced by other processes. Pores are always present in thermal spray coatings and their geometry presents two-dimensional characteristics that are different from the pores in bulk porous materials processed by conventional processes such as powder metallurgy. Therefore, the relationship between properties and microstructure for materials processed by conventional processes are not applicable to thermal spray coatings. Moreover, the presence of pores interconnected throughout the coating thickness makes the as-sprayed coating unable to fully protect the substrate from corrosion. Therefore, general features of the thermal spray process, physical phenomena of the interaction of spray particles with the spraying flame and droplet impact, coating microstructure features, microstructure/property relations, and coating/substrate adhesion are introduced in this chapter, based on state-of-the-art thermal spray coating developments that effectively achieve successful surface modification of light metals.

7.2 Characteristics of thermal spraying

7.2.1 The thermal spray concept

A thermal spray coating is formed by successive impact of molten droplets and/or semi-molten droplets at a certain velocity on a substrate, followed by lateral flattening, rapid solidification and cooling, as schematically depicted in Fig. 7.1. Three basic stages are involved in spray coating formation. Firstly, spray particles are created. Then, these spray particles are heated by a heat source or a power source, and accelerated by a gas or plasma jet, to generate a high-velocity droplet stream through acquiring sufficient



7.1 Schematic diagram of the concept of thermal spray coating formation.

kinetic energy (in the form of velocity) and thermal energy (in the form of high temperature) up to or over their melting points. During this stage, the chemical reaction between the droplet material and the flame atmosphere may lead to compositional change of the particles from their starting composition, and introduce new phases. Finally, the high velocity droplets successively impact on the well-prepared rough surface of the substrate to adhere to it through rapid cooling and solidification to form a coating. Additionally, substrate surface preparation and post-processing of the coating are also requirements.

Almost all materials, including metal alloys, ceramics, plastics, and composites of those materials can be deposited to form coatings by thermal spraying. Spraying materials can be employed in the form of powders, wire or rod. Powder materials are directly fed into a high temperature flame through a powder feeder to complete the first stage, while with wire or rod material, spray droplets are created by atomizing the melting tip as it is fed into the flame.

To completely or partially melt spray materials, various heat sources including gas flames, electrical arcs and plasma jets are employed. The heating ability of a heat source is limited by its maximum temperature, which determines the types of materials that can be applied with a specific spray process. Generally, thermal spray processes are classified and termed according to the heat source involved, as listed in Table 7.1. Flame spraying, plasma spraying and arc spraying are the three major types of spraying process. D-gun and HVOF are varieties of flame spraying, using specially designed flame guns. Cold spraying is an emerging coating technology in which solid particles at a high velocity and a temperature lower than their melting point, are used to deposit a coating through plastic deformation on impact; this is described in Chapter 8. In Table 7.1, typical maximum temperatures of the heat sources involved, and particle velocities obtainable are shown.

Table 7.1 Temperature of heat sources and particle velocity achievable for typical thermal spray methods

Thermal spray methods	Temperature of heat source (K)	Particle velocity (m/s)
Powder flame spray	~ 3500	30 ~ 50
Wire flame spray	~ 3500	100 ~ 200
Detonation gun (D-gun)	4200	500 ~ 700
High-Velocity Oxy-Fuel (HVOF)	~ 3500	300 ~ 700
Air Plasma spray	10 000 ~ 15 000	100 ~ 400
Arc spray	5000 ~ 6000	100 ~ 200
Cold spray	RT~900	300 ~ 1000

7.2.2 Features of thermal spraying

Thermal spray has the following general features when used for coating light metals:

- (i) Coating materials can be deposited on the surface of light metals and alloys to achieve various surface properties and functions, such as wear protection, thermal insulation, corrosion resistance, abrasion resistance, abrasiveness, electrical insulation, dimension restoration and, medical applications.
- (ii) The thermal effect on the substrate during coating deposition can be minimized through controlling the relative motion of the traversing torch over the substrate, and proper cooling. Thermal spraying is relatively cool and the temperature of the substrate is usually kept below 150°C. The coating can be applied on parts machined to final shape without deteriorating the substrate microstructure and properties, or causing deformation.
- (iii) Coatings can be deposited at a rapid deposition rate and thus a low processing cost. They can be applied flexibly on the whole surface or on a local area of the part. Coating thicknesses can be changed over a wide range, from several tens of micrometers to several millimeters.
- (iv) The surface of a thermal spray coating is rough. Post surface finishing may be necessary for some parts.
- (v) Spray coatings are not fully dense, with porosities up to 20% depending on spray conditions. The pores in the coatings can act as a reservoir for lubricating oils to improve tribological performance. On the other hand, post-spray sealing may be necessary to achieve full corrosion protection.
- (vi) The tensile bond strength of thermal spray coatings is relatively low, compared with coatings produced by other processes. The tensile adhesion for most thermal spray coatings is lower than about 70 MPa, although the adhesion of HVOF WC-Co coating may be higher. Thermal spray coatings are anisotropic, and their properties in the longitudinal direction are very different from those in the direction normal to the surface.
- (vii) This is a line-of-sight process and the coating can be deposited on the surface only where the torch or spray gun can 'see'. With complex shapes or contours, multiaxial manipulators or robots are required for uniform coatings. Spray deviation from normal to surface will compromise coating properties in terms of porosity, and reduced coating cohesion.

The first three characteristics are advantages of the thermal spray process, and the final four items are generally considered as disadvantages.

7.2.3 Spray materials for modification of light metal

Generally, materials stable at elevated temperature are suitable for thermal spray processing. Most metals, intermetallics, alloys, all forms of ceramics including oxides, borides, silicides etc., cermets and some polymers are sprayable by one or more of the thermal spray processes. The broad classes of thermal spray materials, classified according to their chemical nature, are shown in Table 7.2. Many new materials belonging to one of the above definitions are progressively being developed for different applications.

Some typical materials used recently for modification of Al-based alloy parts are listed in Table 7.3. A typical application is coating aluminum cylinder bores to reduce the weight of an engine. Another case is ceramic coatings to provide dielectric properties for semiconductor manufacture. A wide span of spray materials has been investigated for different applications. With titanium alloys, in addition to coatings for surface protection, many different bioactive materials including hydroxyapatite (HA), Ti, CaO–SiO₂ and bioinert ceramics such as Al₂O₃, ZrO₂, TiO₂ have been coated on implants (Liu *et al.*, 2004). With Mg alloys, corrosion protection through thermal spray coatings is challenging. Because the functions of coatings are essentially determined by the coating material, therefore the coating microstructure and properties can be considered in a similar way to other substrate materials, except for the adhesive strength of the coatings with specific light metals.

7.2.4 Thermal spray processes

Conventional flame spraying was first developed in 1910 (Davis, 2004) and is still widely used. Oxyacetylene torches are the most common heating source, using acetylene as the main fuel in combination with oxygen to generate the highest combustion temperature. Powders are introduced axially into the nozzle and are heated by the flame. The density of the coatings

Table 7.2 Typical spray materials classified according to the chemical nature of materials

Material types	Typical spray materials
Metals and alloys	aluminum, aluminum-zinc, copper, molybdenum, nickel-aluminum, nickel-chromium alloys (Ni-Cr, NiCrAl, NiCrAlY), NiCrBSi, carbon steel, stainless steel
Ceramics	Al ₂ O ₃ , TiO ₂ , Cr ₂ O ₃ , mullite, spinel, ZrO ₂ , YSZ (Y ₂ O ₃ -ZrO ₂), hydroxyapatite (HA, Ca ₁₀ (OH) ₄ (PO ₄) ₆)
Cermets	WC-Co, Cr ₃ C ₂ -NiCr
Composites and blends	Al/Si/polyester, Ni/graphite, bentonite/NiCrAl
Intermetallics	NiAl, Ni ₃ Al, NiAl ₃
Polymers	Polyester, polyamides, polyethylene

Table 7.3 Typical materials involved in surface modification of Al alloys by thermal spray process

Coating materials	Applications	References	Remarks
Carbon steel with wustite and magnetite, Composite of carbon tool steel and Mo, Corrosion resistant steel, Metal matrix composite	Cylinder bore walls	Barbezat (2005)	APS
Cast iron	Cylinder bore walls	Tsunekawa <i>et al.</i> (2008)	APS
Cast iron	Cylinder bore walls	Cook <i>et al.</i> (2003)	PTWA
Nano-crystalline composite Low carbon steel	Cylinder bore walls	Bobzin <i>et al.</i> (2006) Schlaefer <i>et al.</i> (2008)	PTWA
Al-12%Tin	Alloy engine bearing	Sturgeon <i>et al.</i> (2003)	HVOF
Cr ₃ C ₂ -NiCr	Wear and corrosion protection for aeronautical parts	Magnani <i>et al.</i> (2008)	HVOF
WC-Co, Fe-alloy, FeCrMo, Cr ₃ C ₂ -NiCr, NiCrBSi	Cylinder bore walls	Rauch <i>et al.</i> (2009)	HVOF
WC-CoCr	Wear and corrosion protection	Bolelli <i>et al.</i> (2009)	HVOF
Al ₂ O ₃	Dielectric coating for semiconductor production equipment	Gansert (2003) Kato <i>et al.</i> (2006) Kitamura <i>et al.</i> (2008)	APS

Note: APS, atmospheric plasma spraying; HVOF, high velocity oxy-fuel; PTWA, plasma transferred wire arc spraying.

achieved by powder flame spraying is low due to the low jet velocity and flame temperature.

With wire or rod flame spray, the melting tip is atomized by a high pressure and high velocity gas stream to form droplet jets towards the substrate. One significant advantage of wires and rods over powders is that the degree of melting is complete, producing a denser coating. In addition, the atomizing gas (often compressed air) at high velocity produces fine droplets, resulting in finer, smoother coatings.

Detonation guns (D-guns), introduced in the 1950s (Davis, 2004), generate higher thermal energy and kinetic energy jets by confining the combustion within a tube or barrel into which powders are introduced. The explosive mixture of fuel, oxygen and powders generates particle jets at velocities of 600 to over 700 m/s (Kawase *et al.*, 1988) upon ignition by a spark plug. Following purging and injection of the mixture and ignition, repeated

detonation at a frequency of 3 to 6 Hz leads to the formation of overlaying deposits. The high velocity particles produce dense coatings with high particle/substrate bonding. The process can be employed to deposit WC-Co cermet, $\text{Al}_2\text{O}_3/\text{TiO}_2$ oxide, and ceramic/alloy composite coatings.

High-velocity oxyfuel spray (HVOF) was commercialized in the early 1980s (Davis, 2004). Compared with intermittent detonation in the D-gun process, the combustion of oxygen and fuel confined in a barrel is continuous. The confined combustion can create gas jets of velocities in the range 1500 to over 2000 m/s (Wagner *et al.*, 1984; Li *et al.*, 1999a). Spray particles introduced into the HVOF flame in the barrel are effectively accelerated to high velocities, from 300 to 600 m/s (Wagner *et al.*, 1984; Kowalsky *et al.*, 1990; Wang *et al.*, 2005). Comparable dense coatings with excellent substrate/coating adhesion can be created in comparison with the D-gun (Kawase, 1993). HVOF has become the most popular process to deposit WC-Co and Cr_3C_2 -NiCr coatings. It is also employed to deposit alloys such as MCrAlY used in gas turbines (Chen *et al.*, 2008).

The electrical arc spray process uses a direct-current electric arc, struck between two consumable electrode wires, to melt the wires. A high-pressure gas jet is used to atomize the melts on the tips of the wires to create droplets with high velocity. The high spray-rate of arc spraying for different materials makes arc spraying the most cost-effective process. Arc spraying is limited to using conductive materials that can be formed into wires. The use of cored wires has extended materials to include cermet and other alloy materials (Xu *et al.*, 2004). The size and velocity of the droplets depend on the atomizing gas velocity. Increasing atomizing gas velocity results in the formation of fine droplets with high velocity. Thus, highly dense coatings are produced; otherwise, porous coatings are deposited. High-velocity arc spraying is a variety of arc spraying developed using a supersonic atomizing gas nozzle (Xu *et al.*, 2004; Liao *et al.*, 2005). To coat cylinder bore surfaces made of aluminum alloy, a single wire transferred arc spray process has been developed (Cook *et al.*, 2003.; Bobzin *et al.*, 2006; Schlaefer *et al.*, 2008) and various coating materials, including carbon steel and composites, have been investigated.

Plasma jets having a maximum temperature from 10 000 to 15 000°C are employed in plasma spraying (Boulos *et al.*, 1993), which is a versatile thermal spray process that can deposit any type of coating material. Therefore, thermal spray processes have been widely applied to deposit protective coatings for anti-wear and anti-corrosion, and functional coatings for surface engineering of lightweight metal alloys such as Al, Mg and Ti alloys. Due to the high-temperature gradients within the plasma jet generated by common plasma spray torches, the melting degree of powders fed radially into the plasma jet changes significantly with the particle trajectories across the jets (Fauchais *et al.*, 1989); this may result in a non-uniform coating microstructure. As

a result, with uncontrolled powder feeding conditions, even at high plasma power input the deposition efficiency cannot be increased by further increasing the plasma power input but must be improved by an increase of mean temperature of the spray particles (Bisson *et al.*, 2005).

It is ideal to axially feed the spray powders into the plasma jet for effective heating and acceleration. Plasma spray torches with axial powder feeds have been developed by many researchers over decades. Three-cathode designs (Maruo *et al.*, 1988) and hollow cathode designs (Kobayashi and Arata, 1988) were proposed for axial powder feeding. The process has been commercialized since the early 1990s. The first commercial axial-feed plasma spray gun designs, developed at the University of Vancouver in the early 1990s using a multiple radial cathode configuration, was marketed by Northwest Mettech Corporation (Hawthorne *et al.*, 1997). Advantages of the process are high powder feed rate and high deposition efficiency. It is reported that deposition efficiency of ceramics reaches 90%. A torch with a triple-electrode and an extended arc, developed by Sulzer-Metco Company, has realized comparable deposition efficiency (Barbezat and Landes, 2000). A plasma torch with a hollow cathode for the axial powder feed can melt spray materials such as Cu, Mo and Al_2O_3 even at power levels of 2 kW to 4 kW (Li and Sun, 2004a, 2004b), which is only one-tenth the power input of a conventional plasma spray torch.

Generally, thermal spraying is carried out at atmospheric pressure, while plasma spraying can be performed in an inert gas chamber at a reduced pressure. Thus, variations of plasma spraying have been developed including low pressure plasma spraying (also referred as vacuum plasma spraying) and shrouded plasma spraying (SPS) to prevent oxidation of metallic materials during spraying. As can be seen in Table 7.4, by using shrouded plasma spraying, the oxygen content in metal coatings can be greatly reduced, especially for those materials susceptible to oxidation, such as Ti.

To apply a coating to the inner surface of cylinder bores of Al alloys, a rotating type of extension plasma spray torch has been developed by the Sulzer-Metco Company (Barbezat, 2005). A wide range coating materials, including carbon steel, composites of carbon tool steel and Mo, corrosion

Table 7.4 The content of oxygen (wt%) in metal coatings sprayed using APS and SPS techniques (Tucker, 1974)

Materials	Powder	APS coating	SPS coating
Cu	0.126	0.302	0.092
Ni	0.172	0.456	0.151
W	0.027	0.274	0.030
Ti	0.655	>2.0	0.730
Mo	0.419	0.710	0.160

resistant steel, and metal matrix composites have been investigated (Barbezat, 2005).

7.3 Introduction to physics and chemistry of thermal spraying

Many parameters influence coating microstructure and properties, including substrate properties, coating material properties, heat source characteristics, and operating conditions of the spray torch. However, when a particular spray process for a certain material is selected, the droplet state parameters determine their deposition behavior and coating microstructure. The principle particle parameters are temperature (melting degree), velocity and size prior to impact on the substrate, in addition to the particle's chemistry. It is generally considered that higher particle velocity and temperature lead to the formation of a denser coating. Moreover, with YSZ ceramic material, it has been reported that the deposition efficiency is directly proportional to the mean surface temperature and that high temperature and high melting degree lead to high deposition efficiency of spray materials (Bisson *et al.*, 2005). However, with WC-Co cermet particles, excessive heating leads to decomposition of the wear-resistant carbide phase (Li *et al.*, 1996a). Therefore, it is necessary to understand the interaction between spray particles and heat source for the optimization of spray conditions in terms of heating and acceleration.

7.3.1 Particle acceleration

Basically, although the acceleration of a solid particle injected into a flame jet may result from several different forces (Lewis and Gauvin, 1973), the drag force (F_d) expressed in the following equation determines particle acceleration in thermal spray processes:

$$F_d = \frac{1}{2} c_d A \rho_g (v_g - v_p) |v_g - v_p| \quad [7.1]$$

Therefore, the local acceleration of solid particles in a spherical shape in the moving gas flame can be expressed as follows:

$$\frac{dv_p}{dx} = \frac{3C_d \rho_g}{4d_p \rho_p v_p} (v_g - v_p) |v_g - v_p| \quad [7.2]$$

Where, v_g and v_p are the gas velocity and particle velocity, respectively, d_p is particle diameter, ρ_g and ρ_p are the gas density and particle density, respectively, A is the cross-sectional area of particle, C_d is the drag coefficient.

The drag coefficient depends on the Reynolds number as expressed typically in the following equations.

$$C_d = 24/\text{Re} \quad \text{Re} < 0.2 \quad [7.3]$$

$$C_d = \frac{24}{\text{Re}} \left(1 + \frac{3}{16} \text{Re} \right) \quad 0.2 \leq \text{Re} \leq 2 \quad [7.4]$$

$$C_d = \frac{24}{\text{Re}} (1 + 0.11 \text{Re}^{0.81}) \quad 2 \leq \text{Re} \leq 21 \quad [7.5]$$

$$C_d = \frac{24}{\text{Re}} (1 + 0.189 \text{Re}^{0.623}) \quad 21 \leq \text{Re} \leq 200 \quad [7.6]$$

The Reynolds number is defined as follows:

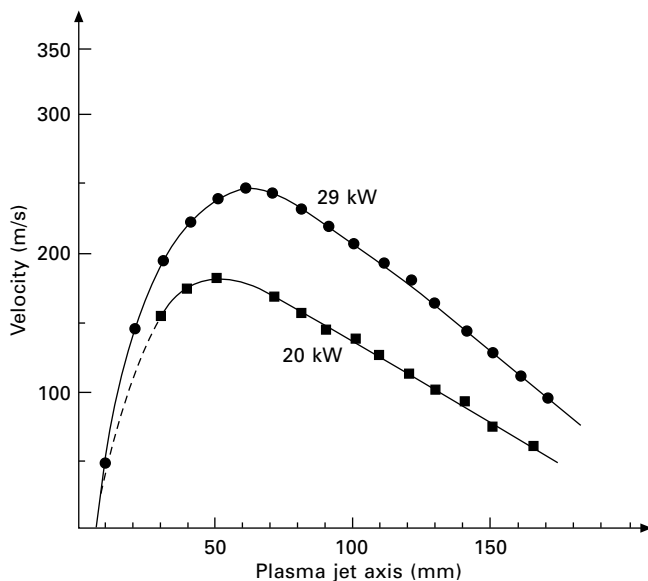
$$\text{Re} = \frac{\rho_g d_p (v_g - v_p)}{\eta_g} \quad [7.7]$$

where η_g is the dynamic viscosity of the gas.

Therefore, the acceleration of a spray particle depends on the particle velocity relative to the gas flame, the size and density of the particle, and the gas density and viscosity. The product of $d_p \rho_p$ can be considered as the inertia of a spray particle. The higher the gas velocity is and the lower the inertia of particle is, the higher the acceleration and subsequently the higher the particle velocity are.

Figure 7.2 shows the velocity change of an alumina particle of mean size 18 μm along the centerline of a plasma jet under various plasma generation conditions (Fauchais *et al.*, 1989). It can be seen that particle velocity increases rapidly at an early stage, due to higher gas velocity relative to the particle. At a spray distance of 40 mm to about 70 mm, the particle reaches the highest velocity and then starts to decrease, due to the action of the drag force in the opposite direction when the particle velocity becomes higher than the gas velocity. The different plasma generation conditions lead to different jet characteristics and thus different particle velocity histories, as illustrated in Fig. 7.2.

The spray particle stream consists of particles in different sizes. When spray particles are radially injected into the flame jet, as in most cases of practical plasma spraying, particle velocity is significantly influenced by the trajectories of the powders in the flame due to a significant gradient in the velocity field of the flame. Moreover, the trajectory of a spray particle is influenced by the injection velocity, i.e. the initial velocity at which the particle is injected into the flame. The injection velocity of the spray particle depends on the carrier gas flow rate, particle size, and particle feed rate. The penetration of injected particles into the flame jet is influenced by particle inertia. The higher the inertia a spray particle possesses, the easier it can penetrate into the flame jet. Due to the wide particle size distribution of practical spray powders, some particles travel along the centerline of the



7.2 Acceleration characteristics of spray particles along traveling direction with an indication of the effects of plasma arc power (Ar-H₂ plasma, alumina particles in a mean particle size of 18 μm) (Fauchais *et al.*, 1989).

flame jet, some take an intermediate position, and still others travel along the periphery of the jet. Attention should be paid to small particles of low inertia, especially less than 5 μm , because it is difficult to feed them into the flame jet. Further reading on particle acceleration is available in the literature (Boulos *et al.*, 1993; Fauchais *et al.*, 1989).

7.3.2 Heat transfer between gas flame and spray particle

The major mechanisms of heat transfer from the flame to the particles inside a flame are conduction, convection and radiation. The radiation of a flame is assumed to be comparable to the reradiation from a particle and therefore it is neglected (Boundin *et al.*, 1983). The other two mechanisms mainly contribute to the heating of the particles in thermal spraying, and are usually related by the Nusselt number (Nu).

$$Nu = \frac{hd_p}{\lambda_g} = 2 + 0.6 \text{Pr}^{1/3} \text{Re}^{1/2} \quad [7.8]$$

The Prandtl number (Pr) and Reynolds number are defined as:

$$\text{Pr} = c_p \eta_g / \lambda_g \quad [7.9]$$

$$\text{Re} = \frac{\rho_g V_p d_p}{\eta_g} \quad [7.10]$$

Spray particle heating can be considered in two distinctive cases: rapid heating with negligible temperature gradient inside the particle, and heating with a temperature gradient inside the particle. These cases can be divided according to Biot number (Dresvin, 1972).

$$\text{Bi} = \frac{h d_p}{2 \lambda_p} \quad [7.11]$$

For, $\text{Bi} < 0.01$, the temperature gradient within the particle during its heating can be neglected and the isothermal particle heating model is applicable. The heating rate of a spray particle of a high thermal conductivity in a flame can be expressed as follows:

$$\frac{dT_p}{dt} = \frac{6h}{\rho_p c_p d_p} (T_g - T_p)$$

or

$$\frac{dT_p}{dt} = \frac{6N_u \lambda_g}{\rho_p c_p d_p^2} (T_g - T_p) \quad [7.12]$$

where T_g and T_p are the gas and particle temperature, respectively, h is the heat transfer coefficient from flame jet to particle, c_p is the specific heat of the particle, λ_g is the thermal conductivity of the flame gas.

The influence of the main factors on particle heating can be considered with assistance of the equation [7.12]. It is evident that high gas temperature and high gas thermal conductivity result in rapid heating of the spray particle. Practically, addition of a fraction of H_2 gas into Ar plasma will increase the gas thermal conductivity and subsequently significantly improve heating of the spray powders (Bisson *et al.*, 2005). Moreover, the smaller the particle is, the faster the heating rate becomes. However, high velocity of small particles may lead to a significant reduction of dwelling time of the particles in the flame and consequently less heating time. Integration of the formula $\rho_p c_p d_p^2$ at the temperature range up to the melting point plus latent heat, represents the heat content of the spray particle heated to its melted state. A higher heat content means more difficulty for a spray particle to be melted, although the high thermal conductivity of spray particles benefits a rapid heating.

When $\text{Bi} > 0.01$, the temperature gradient in the spray particle cannot be neglected and an estimation of particle heating should be made by numerical simulation according to basic equations. Further references can be found in Pawlowski (1995) and Suryanarayanan (1993).

With spray materials of low thermal conductivity, heat conduction from the particle surface towards the inside controls its melting degree. In order to fully melt spray particles within a limited in-flight time, the particle size should not be too large. Therefore, oxide ceramic materials are usually used in a size range of less than about 50 μm (300 mesh) except for those with a hollow morphology for thermal barrier coating. Increasing the power input to the plasma flame increases its heating ability and increases flame velocity as well, which reduces dwelling time. Therefore, particle velocity and melting are compromised owing to simultaneous increase of particle velocity (reducing heating time) and heating ability when the plasma power input is increased. Moreover, the degree of melting is enhanced through manufactured to the hollow morphology due to the large surface area. Owing to the positive relationship between degree of melting of the particles and deposition efficiency, the heating of spray materials should be optimized. For further more detailed discussion of particle heating, please refer to Boulos *et al.* (1993) and Fauchais *et al.* (1989).

7.3.3 Oxidation and decomposition of spray materials

Oxidation of metal alloys

Most thermal spray coatings are deposited at ambient atmosphere. The flame traveling in the atmosphere inevitably pulls the oxygen in the air into the spray flame. Therefore, oxidation of in-flight alloy particles and also nitridization occur, which introduces metal oxides and nitrides into the coating. Barbezat (2005) reported that utilizing oxidation during the spraying of carbon steel to form *in-situ* wustite and magnetite phases as lubricants leads to the formation of a composite coating of excellent tribological performance for Al alloy cylinder bores. Table 7.4 shows the oxygen contents of atmospheric plasma-sprayed metal coatings compared with those of the starting powders (Tucker, 1974). It was found that the oxygen content of the coatings was increased compared with the powders, which results from oxidation of the metals during spraying. The level of oxygen in different coatings ranges from 0.27wt% to 0.71 wt%, except for the Ti coating which contains greater than 2wt% oxygen.

Generally, the oxidation of spray material occurs at two stages, *viz.* in-flight oxidation and post-flattening oxidation in which the solidified fresh metal surface at high temperature is exposed to the high temperature flame jet. In-flight oxidation is influenced by the oxygen content in the flame, particle temperature, melting degree, particle size and dwelling time of the spray droplet in the flame. The oxidation of in-flight particles occurs usually from their surface. However, it has been found that convection in a fully molten droplet occurs due to a significant difference between particle velocity and

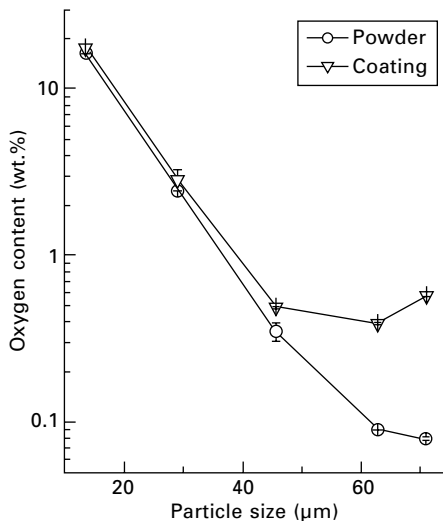
flame velocity, which pulls the surface oxide into the inside of the droplets (Espie *et al.*, 2001). This leads to more intensive oxidation of alloy powders. In spray processes using wires, such as arc spraying and wire flame spraying, the atomized alloy droplets in the fully molten state travel within the flame. The pulling of surface oxide towards the inside becomes strong. As a result, more oxygen in the form of oxide is included in coating.

Li and Li (2003) investigated the effect of particle size on the oxidation of NiCrAlY in-flight powder particles during HVOF by collecting powders passing through the flame and comparing the oxygen contents of the collected powders with those in the deposited coatings. As shown in Fig. 7.3, the oxygen content of the collected powders increased significantly with decrease of particle size, following an approximate exponential rule as follows

$$W_o = \frac{a}{d_p^b} \quad [7.13]$$

where W_o is oxygen content in the coating (wt%), a and b are constants, d_p is particle size (μm). With HVOF NiCrAlY coating under spray conditions reported in the literature, a and b are 144000 and 3.4, respectively.

From the results shown in Fig. 7.3, it is clear that even with NiCrAlY materials, the oxygen content of the coating deposited with particles of mean size of about $15 \mu\text{m}$ reached 16wt%. Moreover, at particle sizes of less than about $45 \mu\text{m}$, the oxygen content in the powder is the same as that



7.3 Effect of mean diameter of NiCrAlY spray powders on the oxygen content of the collected powders passing through HVOF flame, and the deposited coatings (Li and Li, 2003).

in the coating. This means that oxidation during in-flight is dominant and post-flattening oxidation contributes to the oxygen content less significantly. On the other hand, as particle size becomes larger than 45 μm , the oxygen content in the coating greatly deviated from that in the powder and ranged from 0.4wt% to 0.6wt%, which changed less despite particle size, although the oxygen content in the collected powders became less by a factor of about 10 than the coating in the case of a mean particle size of about 75 μm . This fact means that as particle size becomes larger than 45 μm , post-flattening oxidation becomes dominant. However, the different oxidation mechanisms contribute the oxygen content of coating at different levels. The post-flattening oxidation contributes oxygen content at a level of less than 1wt% and this is not significantly influenced by particle size. This fact accounts for the oxygen levels shown in Table 7.4. But the contribution of in-flight oxidation to the oxygen content of the coating much depends on particle size, as is revealed by the relation with particle size mentioned previously. Therefore, it is indicated that the oxygen content in the spray coating can be controlled by spray particle size. To minimize the oxygen content of thermally sprayed metallic coatings, metal powders larger than 45 μm are preferable. Therefore, the particle sizes of most commercial metallic powders supplied by various powder suppliers are in a range from 45 μm to 105 μm . Conversely, in order to increase oxygen content and oxide inclusion in the coating to produce metal-oxide composite coatings *in-situ*, small spray particles in the fully molten state are needed. In tests using high velocity arc spraying with a converging-diverging gas nozzle to increase the velocity of the atomizing gas, spray particles were atomized to small sizes with a higher velocity and a coating of a lower porosity was deposited; the oxide content reached over 20% (Liao *et al.*, 2005).

The oxidation not only changes the chemistry of the coating and introduces an oxide phase, but it also alters the coating performance. Surface oxides generally weaken the cohesion between splats. Although the introduction of oxides into alloy coatings affects adversely their corrosion resistance, especially high temperature corrosion, a certain amount of oxide phase may benefit their wear performance because the hardness of oxides is much higher than the corresponding alloy. Barbezat (2005) reported that wustite and magnetite phases included in a carbon steel coating resulting from oxidation during spraying act as lubricating phases that contribute significantly in improving wear performance of Al alloy cylinder bores.

Cast iron coatings containing the solid lubricant graphite are a promising candidate for wear resistant applications on aluminum alloy substrate. The graphite content of the cast iron coating may be largely reduced due to its oxidation and dissolution into the molten iron. Tsunekawa *et al.* (2008) showed that the graphite content in coatings deposited with annealed cast iron spray powders can be increased by increasing particle velocity, which is

controlled by adjusting the plasma gas composition and flow rate. Because high graphite content tends to decrease the coating/substrate adhesion and enhance the lubricating effect, they proposed to deposit cast iron coating with various graphite contents in the thickness direction so that the different coating microstructure requirements could be fulfilled.

However, with spraying of WC–Co, oxidation leads to the decarburization of the W_2C phase, (which results from thermal decomposition of WC phase), to metallic tungsten (Li *et al.*, 1996a).

Thermal decomposition during spraying of carbide-based cermet materials

WC–Co system and Cr_3C_2 –NiCr system carbide cermets constitute two main carbide material classes for thermal spraying to produce hard protective coatings on light metals. Two decades ago, those materials were mainly sprayed by plasma spraying and much effort have been made to limit decarburization through control of particle heating (Li *et al.*, 1996a; Lovelock, 1998). High temperature in the plasma jet leads to significant decarburization of WC during plasma spraying. The HVOF spray process has proved to be an effective process to deposit dense carbide cermet coatings of excellent wear performance due to low flame temperature and high particle velocity. Those coatings are widely applied to improve wear performance of light metals (Magnani *et al.*, 2008; Rauch *et al.*, 2009; Bolelli, 2009). Additionally, with the environmental necessity to replace hard chromium plating, HVOF deposition of WC–Co has become a promising alternative. Marple *et al.* (1999) reported that HVOF WC-based coatings, especially WC–CoCr coatings, exhibit higher wear resistance by a factor of over 10 and higher corrosion resistance than Cr plating.

One of the essential problems with deposition of carbide materials concerns the thermal and chemical stability of carbides during the interaction of spray particle with the high temperature flame and subsequent deposition process. Thermal decomposition of carbide, dissolution of carbide into molten binder and oxidation decarburization, and physical rebounding of large carbide particles on high velocity impact are the basic mechanisms involved in the thermal spraying of the cermet. Overheating of the powder is usually undesirable during thermal spraying using metal cemented carbide powders, because the decomposition of WC carbide occurs before deposition.

Many studies have been done concerning the decarburization of the WC–Co system through thermal and chemical processes (Vinayo *et al.*, 1985; Subrahmanyam, 1986; Li *et al.*, 1996a). The main factors which influence the microstructure of cermet coatings include spray processing methods, spray parameters, and the structure of the feedstocks. Among those factors, Li *et al.* (1996a, 2004b) showed that the structure of the starting powder

materials has a significant effect on the decarburization of carbides and the subsequently performance of the coating.

Li *et al.* (1996a) investigated the deposition behavior of WC–Co using four different commercial WC–Co powders manufactured by sinter-crushing (Type-1 and Type-2), agglomerate (Type-3) and clad (Type-4) methods. Except for Type-1 powder, in which the $\text{Co}_3\text{W}_3\text{C}$ is present as the binder phase instead of cobalt, the other three powders consist only of WC and Co phases. Moreover, the WC carbide particle sizes are all different in the four powders, as shown in Table 7.5. All four WC–Co coatings deposited by HVOF presented dense microstructures, as shown in Fig. 7.4. However, the XRD patterns of the four coatings showed significantly different results (see Fig. 7.5). With the Type-1 powder, the peak of tungsten appeared as the main peak, which indicates the subsequent decarburization during HVOF spraying. With the Type-4 coating, a substantial amount of amorphous phase was observed which resulted from the rebound of large WC carbide particles on impact. Based on those results, Li *et al.* (1996b) indicated that the binder phase which was in molten state prior to impact, deposited the WC–Co coating as an amorphous phase consisting of Co–W–C. With Type-1 powder, when the coating was deposited by plasma spraying in an Ar atmosphere, tungsten was not observed in the coating. This fact means that thermal decomposition of WC occurs only to W_2C without oxygen. Based on systematic investigation, Li *et al.* (1996a) suggested the following two steps for the chemical decarburization mechanism, i.e. the thermal decomposition mechanism of WC and oxidation decarburization of W_2C .

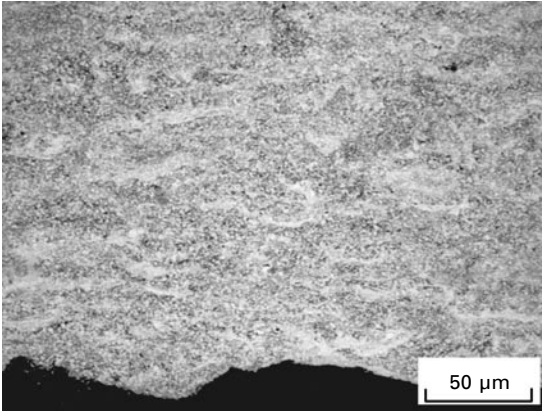


Therefore, as far as the thermal decomposition is suppressed through spray particle heating control, the decarburization to metallic tungsten can be suppressed. Even with HVOF, it is necessary to control heat input to the spray powder in order to limit powder heating. However, the density of the WC–Co coating is positively associated with the degree of melting of the spray powder. Therefore, proper heating to melt the binder phase is necessary in

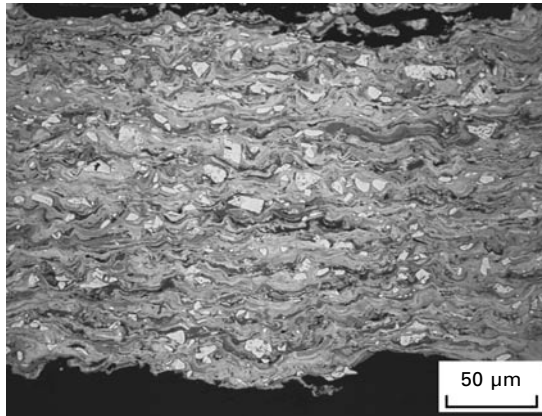
Table 7.5 Comparison of the mean particle size of WC carbides in the starting powders and those in HVOF coatings (Li *et al.*, 2004b)

Types of powder	Mean carbide size in powder (μm)	Mean carbide size in coating (μm)
Type-1	1.48 ± 0.45	1.34 ± 0.32
Type-2	2.35 ± 1	2.09 ± 0.53
Type-3	3.06 ± 1	2.84 ± 1.00
Type-4	17.5 ± 7.06	5.95 ± 2.00

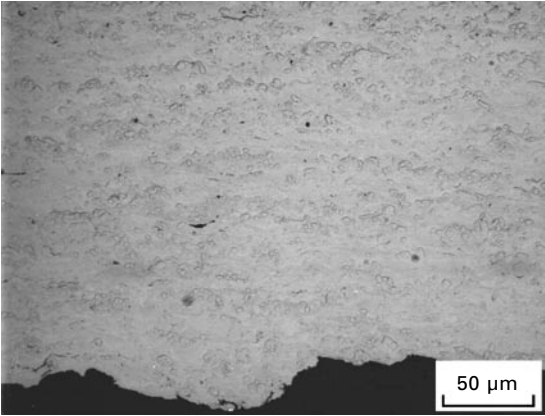
7.4 Typical microstructures of HVOF WC-Co coatings deposited by four different powders (After Li *et al.*, 1996a).



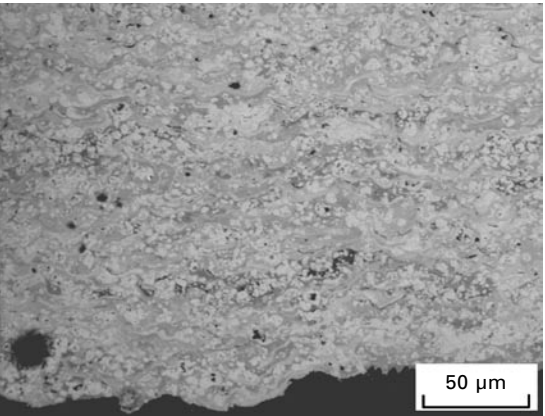
(a)



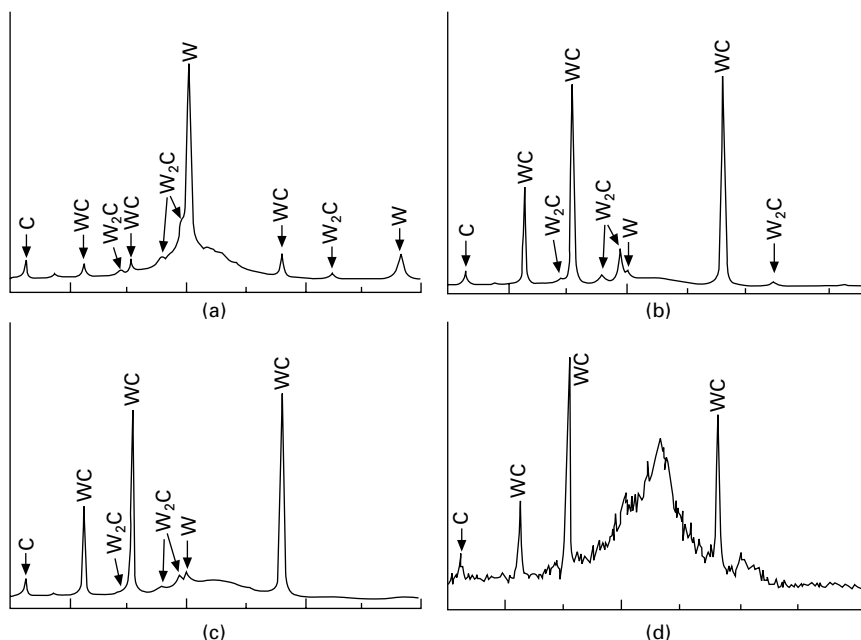
(b)



(c)



(d)



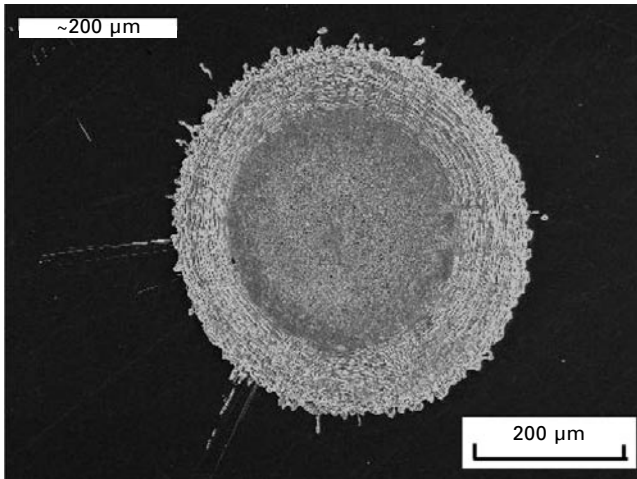
7.5 XRD patterns of four HVOF WC-Co coatings corresponding to the microstructures shown in Figure 7.4 (After Li *et al.*, 1996a).

order to reduce porosity and increase coating density. To effectively prevent the thermal decarburization, a WC-Co powder with WC carbide particles densely bonded by the metal binder phase rather than $\text{Co}_3\text{W}_3\text{C}$ complex carbides is more suitable.

With Cr_3C_2 -NiCr, the melting of Cr_3C_2 carbide leads to its decarburization to Cr_7C_3 . Therefore, under good heating conditions, Cr_7C_3 was observed around Cr_3C_2 particles (Ji *et al.*, 2006). The resolved carbon results in a saturated solution of carbon in a NiCr matrix and subsequently Cr_{23}C_6 particles are precipitated during the cooling and annealing process (Ji *et al.*, 2006). The precipitated carbides are dispersed in a NiCr matrix phase and increase the matrix phase hardness (Zimmermann and Kreye, 1996). It should be noted that during HVOF deposition of cermets using powders having large sizes of carbides, Li *et al.* (2002, 2004b) reported that the rebound of large carbide particles on impact will dominate the decarburization.

7.3.4 Flattening of molten spray particles and individual splat microstructure

When a spray droplet impacts on a substrate surface, ideally it will spread laterally to form a thin layer in a disk shape – the so-called splat (See Fig. 7.6).



7.6 Cu splat deposited on preheated flat stainless steel substrate surface (Li *et al.*, 2005).

The morphology of the splat will be influenced by the thermal reaction between the molten droplet and the cold substrate, and the geometry of the substrate surface, leading to splashing, which will be described later. The flattening to disk, cooling and solidification characteristics are dealt with in this section.

Flattening of liquid droplet in thermal spraying and splat size

Upon impact of the droplet on the substrate, cooling of the melt starts simultaneously with lateral spreading. With spray droplets of diameter from 20 μm to 100 μm, the spreading completes in less than 1 μs (Moreau *et al.*, 1992; Vardelle *et al.*, 1995). Complete solidification of splat will take several tens to several hundreds of microseconds. Therefore, it is considered that under general spray conditions the effect of splat cooling on its spreading can be neglected (Jones, 1971). As a result, the spreading process and the solidification process can be modeled as two separate processes.

The flattening ratio, which is defined as the ratio of the diameter of the ideal disk splat to the diameter of the spray droplet, is a parameter for characterizing splat size. It can be generally related to the Reynolds number (Re) of the droplet by the following equation (Li *et al.*, 2005a).

$$\xi = a(\text{Re})^b \quad [7.16]$$

where ξ is the flattening ratio, a and b are constants.

Madjeski (1976) derived a formula for the flattening degree as a function of Reynolds number, Weber number and solidification effect. The following

equation was obtained when the effects of both surface tension and solidification were neglected (Madejski, 1976).

$$\xi = 1.249 \text{ Re}^{0.2} \quad [7.17]$$

Following a theoretical treatment by Jones (1971), the following relation can be obtained for the flattening of molten spray droplet (Ohmori *et al.*, 1990a).

$$\xi = 1.06 \text{ Re}^{0.125} \quad [7.18]$$

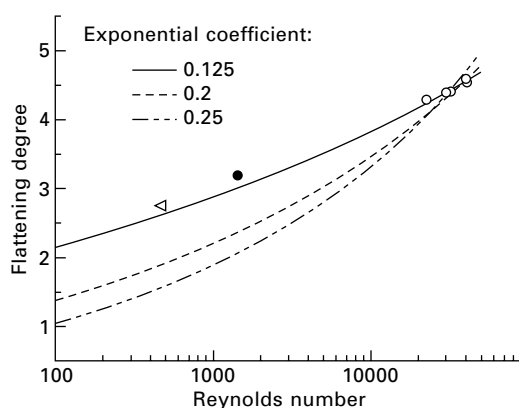
With recent experimental data on Cu droplets and splats, and those for Al_2O_3 and YSZ, using an exponential equation derived following the model suggested by Jones (1971) with a power coefficient of 0.125, Li *et al.* (2005a) obtained the following correlation equation:

$$\xi = 1.21 \text{ Re}^{0.125} \quad [7.19]$$

The above equation correlates with the experimental data reasonably well over a large range of Reynolds numbers from several hundreds to tens of thousands (see Fig. 7.7). The thickness of the splat and thus the splat size can be reasonably estimated by droplet parameters through Equation [7.19].

Microstructure features of splats in thermal spray coating

With splat cooling, the cooling rate of a flattened molten droplet is inversely proportional to splat thickness, with a power factor from one to two depending on the interface thermal contact conditions (Ruhl, 1967). The rapid cooling feature determines the microstructure of subsequent splat (Jones, 1973). When the cooling occurs at a relative low rate, which is controlled by heat



7.7 Effect of droplet Reynolds numbers on the flattening ratio of splat. Solid lines are theoretically correlated results using the Equation 7.19 with different exponential coefficients (Li *et al.*, 2005a).

transfer at the interface between droplet and the underlying substrate, it is termed Newton cooling, i.e. isothermal cooling, and the cooling rate is the lowest and can be expressed as follows (Jones 1973):

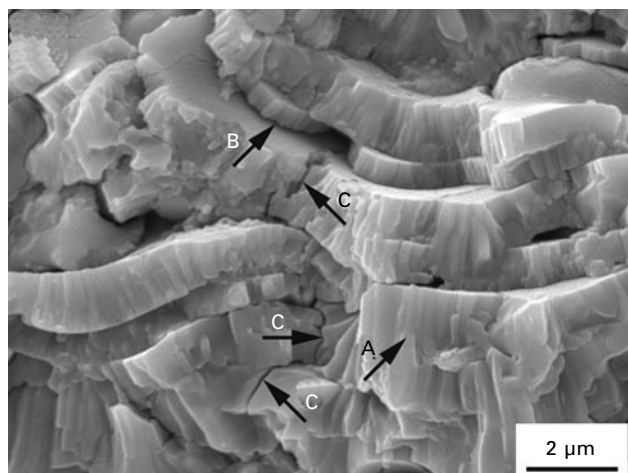
$$\frac{dT_p}{dt} = \frac{h(T_s - T_p)}{\delta \rho_p c_p} \quad [7.20]$$

where T_p is the temperature of liquid splat, T_s is the temperature of substrate surface, h is the heat transfer coefficient at the interface, δ is the thickness of splat.

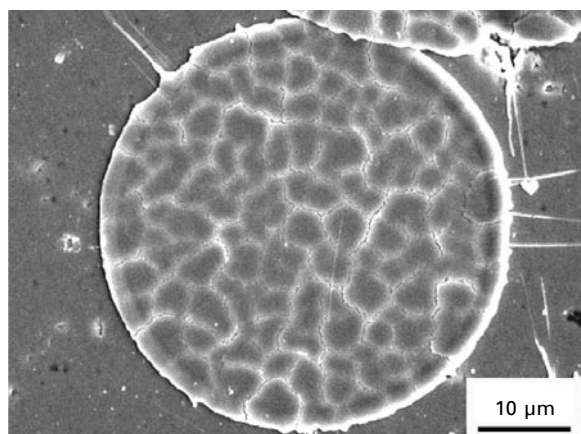
The cooling rate is inversely proportional to splat thickness. The estimation yields a cooling rate higher than 10^5 K/s using the heat transfer coefficient suggested by Jones (1973). With improvement of the interface heat transfer, the cooling rate will be further increased (Ruhl, 1967; Jones, 1973).

The rapid cooling features lead to the formation of splats with unique fine microstructures which are observed under splat quenching. The quasi-stable phases with fine microstructure are present in individual splats (McPherson, 1988). With carbon steel, the quenching effect results in the formation of a hard martensite phase. With alumina, droplet melt is solidified in the quasi-stable γ -phase instead of the α -phase of the starting powders (Vardelle and Besson, 1981). Consequently, the fraction of γ -phase in alumina splat is also used to estimate the degree of melting of the alumina spray droplet. TiO_2 coatings sprayed with TiO_2 feedstocks of rutile phase consist of a fraction of anatase and magneli phases (Ohmori *et al.*, 1991), which influences the electrical conductivity of these coatings. Due to heat transfer perpendicular to the splat/substrate interface, the columnar grain structure with a size of about or less than $1 \mu\text{m}$ is present in individual splats (see Fig. 7.8, Xing *et al.*, 2008a). With many materials, including alloy, cermet and ceramics such as self-fluxing alloy (Li *et al.*, 2004a), WC-Co (Li *et al.*, 1996b), HA (Liu *et al.*, 2004), rapid cooling leads to the formation of amorphous phases in the coating. Annealing of the meta-stable phases in the as-sprayed splat can be employed to adjust coating microstructure and properties. Li *et al.* (2004a) showed that, through controlling recrystallization to nanostructured phases, the hardness and wear performance of HVOF NiCrBSi coating can be improved. The amorphous matrix phase in HVOF WC-Co can be recrystallized to different complex carbides (Li *et al.*, 1996b).

Rapid cooling of splats induces very high quenching stress (Kuroda and Clyne, 1991). The quenching stress can be higher than the strength of the splat materials. With ductile material, it can be relieved through plastic deformation. The accumulation of quenching stress of splats in the coating, along with stress resulting from the thermal expansion mismatching between coating and substrate, leads to the evolution of residual stress in thermal spray coating. However, the stress in brittle ceramic splat can be relieved only



7.8 Morphology of cross-section of fractured plasma-sprayed YSZ coating exhibiting typical lamellar structure with columnar grains in individual lamellae (after Xing *et al.*, 2008a).



7.9 YSZ splat deposited on flat YSZ substrate. The substrate was preheated before splat deposition. The micro-crack networks are clearly seen (after Xing *et al.*, 2008b).

through cracking. As a result, a network of through-thickness microcracks is formed in plasma-sprayed ceramic splats, as illustrated for the YSZ splat in Fig. 7.9 (Xing *et al.*, 2008b). The microcrack network makes pores in a ceramic coating be interconnected through the whole thickness, leading to easy penetration of liquid or gaseous medium through the coating (Ohmori *et al.*, 1990b), causing gas leakage or corrosion the substrate.

Impact behavior of the solid–liquid two-phase droplets

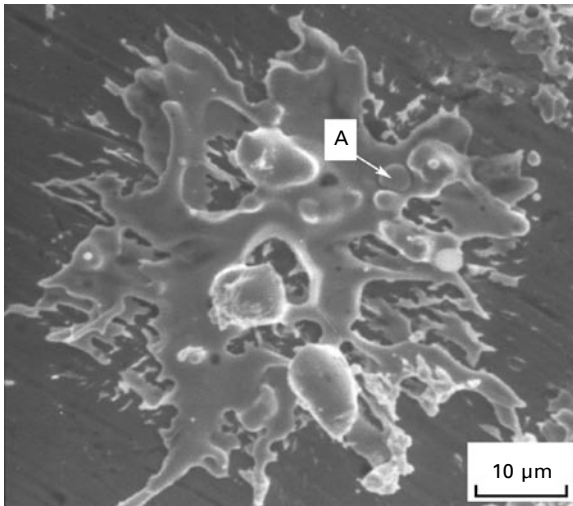
With cermet spray materials, consisting of hard ceramic particles and metallic binder, effort is generally made to retain the hard phase in the powder to deposit so that the compositions and microstructure of the composite deposit can be designed through powder design. WC–Co is a typical material of this kind. The WC carbide particles in the powder should be kept in a solid state if possible while the binder phase of Co needs to melt (Li *et al.*, 1996a; Chivavibul *et al.*, 2007). Li *et al.* (1995b, 2001, 2004b) put forward the concept of the impact of the solid–liquid two-phase particles where WC and Co are at solid and liquid state, respectively, prior to impact on the substrate. Li *et al.* (2004b) investigated the impact behavior of such particles. They found that, at a high velocity, such as under HVOF conditions, the large solid carbide particles tend to be either embossed or pushed out of the splat and subsequently rebound off the splat to produce a matrix-based splat (see Fig. 7.10). Based on their experimental results, they suggested that the splat formation by a solid–liquid two-phase droplet can be divided into the following three cases.

$$\text{Case I: } d_s \leq \delta_e \quad \delta = \delta_e \quad [7.21]$$

$$\text{Case II: } d_s > \delta_e \quad \delta = d_s \quad [7.22]$$

$$\text{Case III: } d_s = d_t \gg \delta_e \quad \delta = \delta_e \quad [7.23]$$

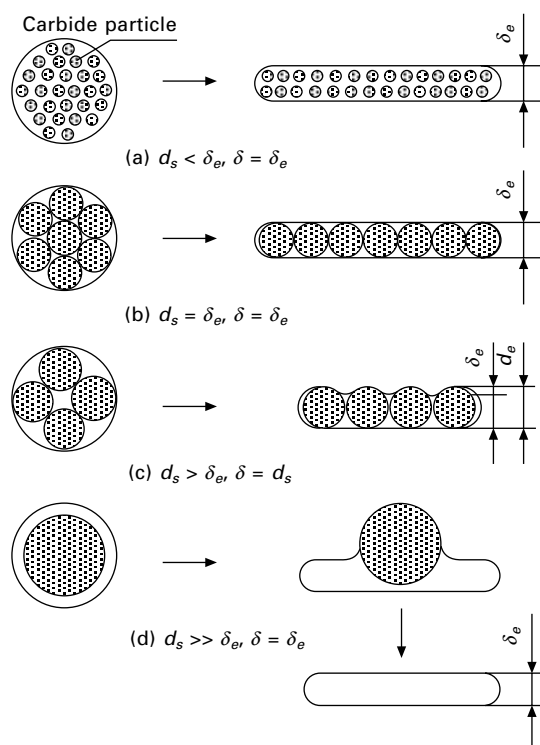
where d_s is the size of solid particle in the two-phase droplet, and δ_e is



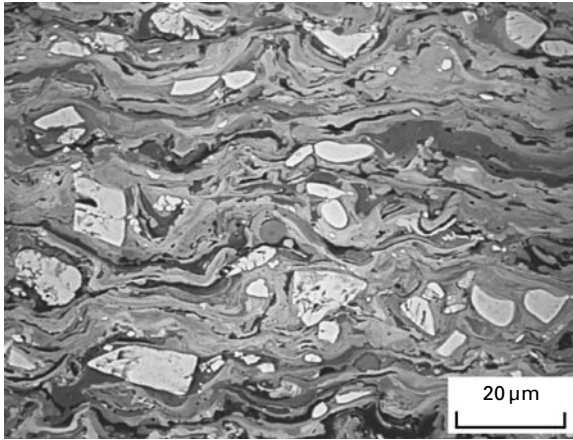
7.10 WC-Co splat deposited on flat stainless steel substrate showing large WC particles embossed out of liquid splat and rebounding off. (after Li *et al.*, 2004b).

the thickness of splat expected theoretically from droplet parameters by equation [7.19].

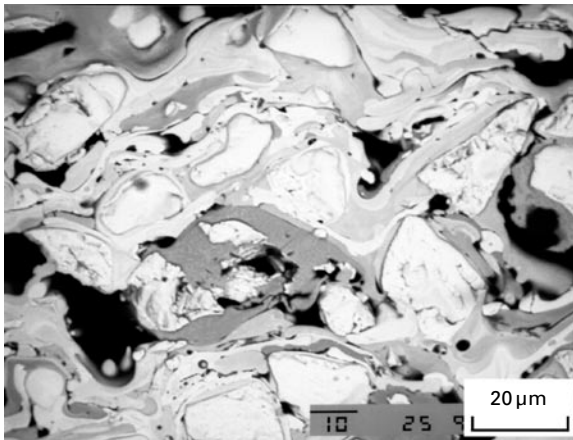
Such a model is expressed schematically in Fig. 7.11. Figures 7.11 (a) and (b) illustrate Case I, (c) and (d) illustrate Case II and Case III, respectively. Figure 7.11 (b) is a special case of Case I. In Fig. 7.11 (d), because the embossed solid particle rebounds off the splat, the final thickness of splat is determined by the liquid binder phase. The carbide particle size (d_t), causing the transition from Case-II to Case-III, depends on particle velocity. With decrease of particle velocity, d_t increases. As shown in Fig. 7.12, large WC particle clad with Co can be retained in the WC–Co coating deposited by low velocity plasma spraying while the mean size of WC particles in HVOF WC–Co coating was reduced to $5.95\text{ }\mu\text{m}$ from $17.5\text{ }\mu\text{m}$ in the starting powders (Li *et al.*, 2004b). Moreover, it was found that WC–Co coatings with small



7.11 Schematic diagram of two-phase droplet deposition: behavior of solid particles during deposition. As d_s is less than δ_e , two-phase droplet spreads in the same way as the liquid droplet on impact; as d_s is larger than δ_e , the splat thickness will be dominated by solid particle size; as d_s is remarkably larger than δ_e , the rebound off of solid particle occurs which depends on spray particle velocity (after Li *et al.*, 2004b).



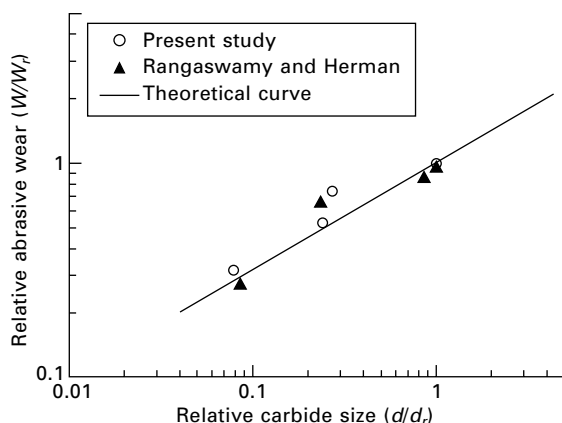
(a)



(b)

7.12 Comparison of microstructure of WC-Co coatings deposited by (a) HVOF and (b) plasma spraying, using WC clad by 18wt%Co. The average size of WC particles is 18 μm . Only a few large WC particles were deposited in the HVOF coating (after Li *et al.*, 2004b).

carbide particles exhibit better abrasive wear resistance under low-stress abrasive conditions (Fig. 7.13) (Rangaswamy and Herman, 1986; Li *et al.*, 2004b). At higher contact stress condition, spalling of deposited particles from the lamella interface may significantly influence wear behavior of WC–Co coatings (Stewart *et al.*, 1999). Therefore, reasonably small ceramic particles should be used to produce cermet powders for HVOF in order to increase the deposition efficiency of the ceramic constituent and improve wear performance.



7.13 Effect of carbide particle size on the wear weight loss of thermally sprayed WC coatings. Solid line is correlated by $W/W_i = a(d/d_f)^{1/2}$ (Li *et al.*, 2004b).

7.4 Microstructure and properties of thermal spray coatings

7.4.1 Porosity in thermal spray coating

Characterization of porosity

The pores are inherent to thermal spray coating. The volume fraction of the pores, often referred to as the porosity, is widely used as a typical structure parameter. Porosity is usually estimated by qualitative examination from a cross-sectional microstructure.

The porosity level in thermal spray coatings ranges from several percent up to 20%, depending on spray materials and spray conditions. Without any doubt, the porosity in the coating influences coating properties and performance in different manners, i.e. both positively and negatively based on the coating application. High porosity results in low thermal conductivity and consequently benefits the thermal barrier effect of a thermal barrier coating. Pores in the coatings can also serve to store lubricant oil to enhance tribological performance. On the other hand, the porosity generally reduces mechanical properties such as hardness, strength, and toughness compared with corresponding bulk materials (Pawlowski, 1995). Most pores are interconnected through the non-bonded lamellar interfaces, which permits corrosive solutions or gas species to penetrate through to the interface between substrate and coating (Arata *et al.*, 1988b). As a result, pores in the coating are harmful to corrosion or oxidation protection. Kuroda (1995) reported that no closed pores exist in plasma-sprayed ceramic coatings while closed pores exist in plasma-sprayed metal alloy coatings.

Generally, the porosity of thermal spray deposits is characterized qualitatively by microstructural observation, and quantitatively by MIP (mercury intrusion porosimetry) and deposit density determination. Direct examination of deposit microstructure from a cross-section, using optical microscopy or scanning electron microscopy, is usually used for qualitative comparison of porosity. With application of the digital imaging analysis technique, the porosity could be quantitatively measured from cross-sectional microstructure. However, because pull-out of loosely-bonded particles in the ceramic deposit, and smear-out of pores in ductile material coatings, may occur during grinding and polishing processes, such quantitative characterization may lead to a misleading results (Smith *et al.*, 1992). Therefore, to minimize the above mentioned effects, infiltration of resin into the voids of the deposits under an evacuated condition prior to cutting has been proposed (Karthikeyan *et al.*, 1996). Another problem with quantitative estimation of porosity using the cross-sectional microstructure is the limitation of such direct observation methods to reveal the voids in sub-micrometers (Ohmori and Li, 1991).

Using the mercury intrusion method (MIP), not only total porosity for open voids, but also distribution of void size could be evaluated quantitatively (Whitmore, 1981). The MIP measurement indicated that the voids in thermal spray deposits appeared as a bi-modal distribution (Vardelle and Besson, 1981). However, because the intrusion of mercury into voids in the deposits is controlled by the small dimensions of the channels interconnecting small and large voids, MIP can result in a misleading interpretation of the void distributions (McPherson, 1988; Kuroda, 1995). Kuroda (1995) examined the effect of sample preparation methods on the results of MIP measurements by covering the deposit surface with polyester to limit the deposit surface contacting with mercury using a plasma-sprayed Ni–Cr deposit. Compared to the ordinarily prepared sample, the plastic covered samples show almost no voids larger than 1 μm . However, the porosity volume of the voids of small size is almost the same despite the sample preparing methods. Therefore, it was suggested that the porosity volume of those voids larger than 1 μm is an artifact resulting from the surface roughness of the deposits. It is evident that the porosity fraction corresponding to small voids gives the measurement of the deposit porosity volume. This does not mean, however, that there are no voids larger than 1 μm in the deposits. Therefore, it was suggested that the deposits should be encapsulated or surface-polished to diminish the effect of sample preparation on the MIP result (Kuroda, 1995).

Control of coating porosity

The various applications of the coatings require different levels of porosity, from an optimized minimum level up to 50% in abradable coatings (Matejcek *et al.*, 2006). Coating porosity is generally controlled by spray conditions

and powder design. Porosity in a thermal spray coating decreases with increase of spray particle velocity and improvement of degree of particle melting (Turunen *et al.*, 2006). Therefore, the higher the velocity of spray particles and the more complete the melting of the spray powder particles, the lower the coating porosity becomes. The coatings deposited by high velocity processes, such as HVOF or D-gun, are generally dense compared with flame spray and plasma spray coatings (Tucker, 1982; Kulkarni *et al.*, 2004). Porosity of HVOF WC-Co coatings can be reduced to be less than 1% (Barbezat *et al.*, 1988). Based on easy characterization through image analysis of cross-sectional microstructure, the coating porosity is usually used as a popular microstructure parameter for spray condition optimization. It should be noted that the optimization of spray conditions leads mainly to a reduction of large size pores in the coating.

A coating porosity of up to 30% to 50% can be achieved by powder design (Matejcek *et al.*, 2006). By adding polymer or graphite into metallic or ceramic spray powders to form a composite powder or powder blend, as shown in Table 7.2, a composite coating can be obtained. The polymer or graphite included in the coating acts as a pore-former. Through post-spray heat treatment, those phases burn off, which increases the porosity of the coating. These coatings are typically applied to compressor or gas turbines as abrasion-resistant coatings.

Plasma-sprayed titanium coatings with a porous structure on titanium substrates have been used in tooth root, hip, knee and shoulder implants. The porous surface improves fixation via the growth of bone into the coating forming a mechanical interlock (Liu *et al.*, 2004). Porous Ti coatings can be deposited by vacuum plasma spraying through using large titanium powder particles of low velocity, limiting flattening. Recently, Sun *et al.* (2008) deposited a Ti-Mg composite coating through cold spraying, and a porous Ti coating with a porosity of 48.6% was obtained through post-spray vacuum sintering. Here, Mg acted as a pore former.

Thermal spray deposition of nanostructured ceramic coatings has been widely investigated (Lima and Marple, 2007). The nanostructured feedstock powders are usually made through agglomerating nanosized ceramic particles and present a porous structure. Through using partially melted powders and controlling melting degree, a fraction of feedstock powders in the porous nanostructure can be retained into the coating with the same porous structure as the feedstock. The deposit presents a bimodal microstructure, i.e. a conventional microstructure resulting from rapid solidification of the melted powder fraction and a nanostructure retained from the nonmelted powder fraction (Lima *et al.*, 2002). Therefore, coating porosity can be adjusted through degree of melting of the feedstock during spraying when agglomerated porous powders are employed as feedstocks.

Post-spray treatment for sealing pores for improvement of corrosion resistance of thermal spray coatings

The pores in the coatings influence their performance. In particular, thermal spray coatings with through-thickness interconnected pores are not able to inhibit corrosive liquid or gaseous medium from penetration to the interface between substrate and coating. As a result, all investigations indicate that the corrosion of Mg alloy cannot be effectively prevented through using thermal spray coatings in the as-sprayed state, and post-spray treatment is necessary to achieve effective protection (Yue *et al.*, 1999; Parco *et al.*, 2006, 2007; Pokhmurska *et al.*, 2008; Pardo *et al.*, 2009a, 2009b). Even with WC–Co (Parco *et al.*, 2006) on Mg alloy and WC–CoCr (Bolelli *et al.*, 2009) on Al alloy deposited by HVOF, the interconnecting pores from the coating surface to the interface between coating and substrate lead to corrosion of the substrate under a corrosive environment. Therefore, a post-spray pore sealing treatment becomes necessary for corrosion protection. Many different treatments, including laser remelting (Yue *et al.*, 1999), electron beam and infrared light beam irradiation (Pokhmurska *et al.*, 2008), cold-pressing (Pardo *et al.*, 2009a) and resin infiltrating (Parco *et al.*, 2006) are employed to densify thermal spray coating. During the remelting of Al-based light alloys by high energy density beams such as lasers, the pores easily form due to the low density of the melt. With laser remelting of Al-12.5wt.% Si eutectic alloy, Yue *et al.* (1999) reported that high laser power results in the formation of cracks and porosity, and high scanning velocity causes insufficient melting of the as-sprayed coating. After remelting treatment of spray coatings, due to the removal of interconnected pores, the corrosion behavior is dependent on the composition of the coatings (Pokhmurska *et al.*, 2008). By cold pressing of Al-SiCp composite coatings containing different SiCp contents sprayed on magnesium substrates at a pressure of 32 MPa (Pardo *et al.* 2009a, 2009b), the corrosion of coated magnesium alloy is determined by coating materials and the effect of substrate on the corrosion rate is not observed. Li *et al.* (2003a, 2003b) showed that by using epoxy adhesive resin to infiltrate plasma-sprayed ceramic coatings, not only are the pores sealed for improvement of corrosion resistance, but the coating adhesion and erosion resistance can be significantly improved owing to the improved bonding between lamellae and substrate/coating interface by the infiltrated adhesives. Therefore, it was evident that the sealing of HVOF WC-Co coating by epoxy sealant is effective to prevent corrosion of the coated Mg alloy (Parco *et al.*, 2006). Through coating composition design, laser remelting treatment of plasma-sprayed Ni-Ti, Ni-Al and Ti-Al composites leads to formation of intermetallic coatings on Ti and Mg alloy surface for the improvement of wear performance (Wilden and Frank, 2003).

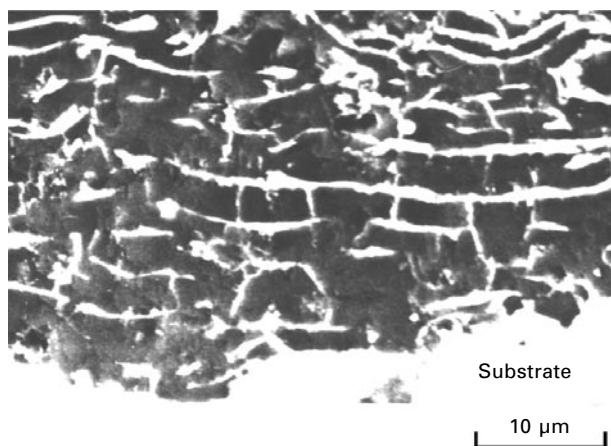
7.4.2 Lamellar structure of thermally sprayed ceramic coatings

Characterization of lamellar structure

A thermally sprayed deposit is formed by a stream of molten droplets impacting on the substrate followed by flattening, rapid cooling and solidification processes. Therefore, spray coating presents a lamellar structure, as shown by the cross-sectional morphology of a fractured YSZ coating shown in Fig. 7.9. McPherson and Shafer (1982) experimentally confirmed the existence of the non-bonded lamellar interface area in terms of a non-contact area through direct TEM observation of a plasma-sprayed Al_2O_3 deposit.

The limited interface contact between lamellae was visually revealed by electro-plating copper into a plasma-sprayed Al_2O_3 deposit, by Arata *et al.* (1988a), and Ohmori and Li (1991). The typical microstructure of copper-plated Al_2O_3 deposit is shown in Fig. 7.14, where the white strings in the microstructure are the copper, plated into ‘voids’ in the as-sprayed deposit. Those copper strings clearly reveal the void structure in the sprayed ceramic deposit, and indicate the existence of substantial non-bonded interface areas between lamellae. Those non-bonded areas constitute the 2-D ‘voids’ in the deposits mentioned earlier.

More recently, a universal visualization approach to the microstructure, by infiltration of oxide in which the metal element is exclusive into coating, assisted by a detecting technique for the infiltrated material, has been developed



7.14 Microstructure of Cu-plated plasma-sprayed Al_2O_3 coating. The white strings are copper plated in the coating, showing the distribution of the non-bonded interfaces (parallel direction to substrate interface) and vertical cracks in lamellae (perpendicular direction to lamella) (Ohmori and Li, 1991).

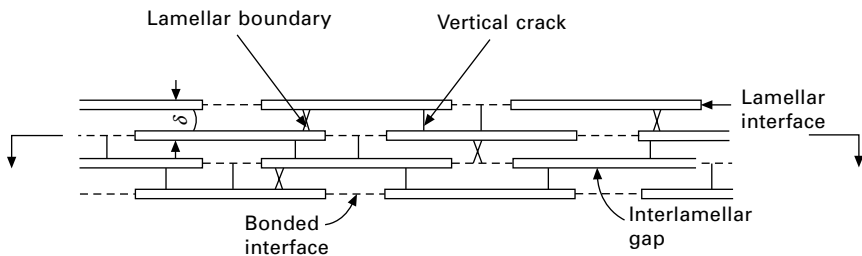
by Li and Wang (2004). In order to make a quantitative characterization, Li and Ohmori (2002) suggested the use of lamellar structure parameters to characterize the microstructure of coatings sprayed with completely molten droplets and composed of well flattened splats for an idealized layer structure model (Fig. 7.15) based on previous work (Arata *et al.*, 1988a; Ohmori *et al.*, 1991). The structural parameters introduced included mean lamellar thickness (δ), splat diameter (D), mean bonding ratio between lamellae (α), average width of the non-bonded lamellar interface gaps (β_i), size of the bonded region ($2a$), vertical crack density (ρ_c) and average width of crack (β_c) (Li and Wang, 2004).

Accordingly, the structure of plasma-sprayed Al_2O_3 deposits was intensively studied using the visualization methods described (Arata *et al.*, 1988a; Ohmori *et al.*, 1990; Ohmori and Li, 1991; Li *et al.*, 1995a; Li and Ohmori, 1996; Li and Wang, 2004; Wang *et al.*, 2005) with structural parameters, especially mean lamellar thickness, mean lamellar bonding ratio, vertical crack density, and gap width between non-bonded interface area.

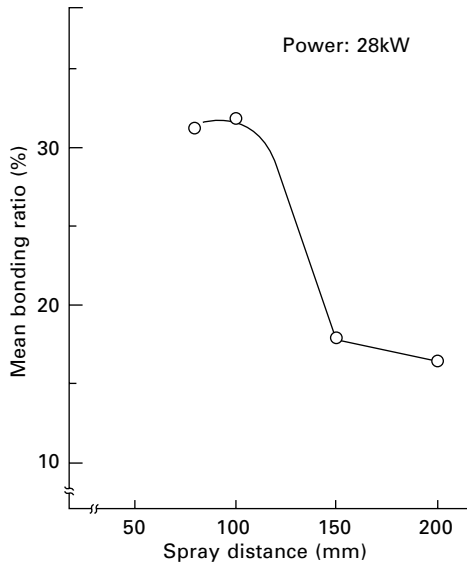
Effect of spray condition on the lamellar bonding ratio

The characterization revealed that the bonding ratio of lamellar interfaces in thermally sprayed coating is influenced by spray conditions such as spray method, spray distance and plasma arc power. A quantitative measurement of the bonding ratio for APS Al_2O_3 deposits showed that a rapid drop in the bonding ratio occurs when the spray distance is increased from 100 mm, to 150 mm as shown in Fig. 7.16 (Ohmori *et al.*, 1990a), while such a decrease occurs for YSZ when the spray distance is increased from 80 mm, to 100 mm owing to the higher melting point of YSZ (Wang and Li 2005).

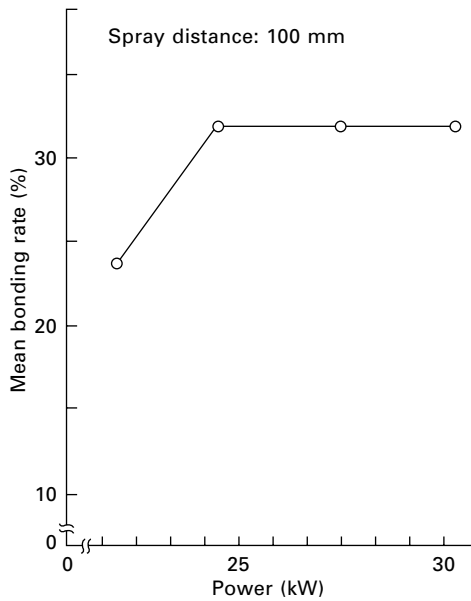
The effect of plasma power during plasma spraying reveals that the bonding ratio is rapidly saturated to about 32% with an increase in plasma power (Fig. 7.17) (Ohmori *et al.*, 1990a). This result implies that an increase in power during plasma spraying does not necessarily contribute to an increase



7.15 Schematic of the idealized lamellae structure of thermal spray coating, with an indication of lamellar interface bonding state in the cross-sectional view.



7.16 Effect of spray distance on the mean bonding ratio of plasma-sprayed Al₂O₃ coating (After Ohmori *et al.*, 1990).



7.17 Effect of plasma arc power on the mean bonding ratio of plasma-sprayed Al₂O₃ coating (After Ohmori *et al.*, 1990).

in interface bonding. A systematic investigation into the lamellar bonding revealed that a bonding ratio up to around 32% can be achieved for plasma-sprayed ceramic deposits. Accordingly, two-thirds of the interfaces between lamellae in the ceramic deposit are separated by inter-lamellar gaps of sub-micrometer dimensions.

Li and Ohmori (1996) reported that the interface bonding ratio of a D-gun Al_2O_3 coating was about 10%. An investigation into the effect of spray methods yielded a bonding ratio of 26% for vacuum plasma sprayed Al_2O_3 (Li *et al.*, 1995a). Although the Al_2O_3 particle velocity in D-gun spraying reaches about 700 m/s (Kawase *et al.*, 1988) which is much higher than about 250 m/s in plasma spraying (Fauchais *et al.*, 1989), the bonding ratio of the D-gun coating is less than one-third plasma-sprayed Al_2O_3 coatings.

Based on the effect of spray conditions on the reported particle temperature and velocity (Vardelle *et al.*, 1980, 1983), Ohmori and co-workers (Ohmori *et al.*, 1990; Ohmori and Li, 1991) suggested that the bonding is mainly influenced by particle temperature rather than particle velocity. Because any attempt to increase the particle temperature leads to an increase of particle velocity and a reduction of dwell time of the particle in the spray flame, it is difficult to improve the bonding ratio through control of spray conditions. Recently, an approach through increasing the surface temperature on which spray droplets impact has been proposed to increase the bonding ratio by Xing *et al.* (2008a), and it was found that the lamellar interface bonding ratio can be increased to over 80% (Xing *et al.*, 2008a, 2008c). Through such an approach, the adjustable extent of the coating microstructure and properties can be significantly extended to fulfill the different requirements of diverse applications (Xing *et al.*, 2008c).

Effect of lamellar structure on the properties of ceramic coatings

Particular coating properties, such as Young's modulus, fracture toughness, hardness, thermal conductivity and so on, are essential for coating design and applications. Generally, the coating properties associated with unit area are lower than those of the identical bulk material. The porous features of thermal spray coating are usually correlated to the coating properties (Steffens and Fischer, 1989) because the various empirical relationships between porosity and properties for the porous materials processed by powder metallurgy processes have been well documented (Rice, 1977). However, owing to the two-dimensional feature of pores in the coating, which are remarkably different from the three-dimensional feature of pores in conventional porous materials, the above mentioned relationships between porosity and properties are not applicable to thermal spray coatings. Li and associates (Li *et al.*, 1992, 1997, 2002, 2004c, 2006; Ohmori and Li, 1993) have made efforts to establish the theoretical relationships between typical coating properties and

structure parameters. The results show that coating properties are dominated by the lamellar structure and lamellar bonding.

The critical kinetic strain energy release rate G_{Ic} is employed to characterize the fracture toughness of a deposit. G_{Ic} of 12–30 J/m² was observed for an Al₂O₃ deposit using the DCB (Double Cantilever Beam) method (Berndt and McPherson, 1980; Li *et al.*, 2004c). A G_{Ic} of around 90 J/m² was estimated for bulk Al₂O₃ with a fine grain structure of about 2 µm (Li *et al.*, 2004c). The ratio of alumina coating fracture toughness to bulk fracture toughness is 0.13 to 0.33. These values are consistent with the bonding ratio of 16% to 32% (Ohmori *et al.*, 1990a). Moreover, the measurement (Li *et al.*, 2004c) confirmed that the change of coating fracture toughness with spray distance follows the same dependence as that observed for the interface bonding as shown in Fig. 7.16. Those facts evidently indicate that the fracture toughness of a ceramic deposit is mainly governed by the interface bonding between flattened particles. The low fracture toughness resulting from limited bonding is associated with the failure of the thermal barrier coating through spalling along lamellar interfaces (Li *et al.*, 2009).

A study into erosion mechanisms revealed that the erosion of a brittle coating occurs through the de-bonding of ceramic particles exposed at the surface by the normal impact of abrasives. Therefore, the erosion of the deposit is inversely proportional to lamella interface bonding and is directly proportional to the lamellar thickness. This relationship has been confirmed experimentally (Li *et al.*, 2006). Therefore, the lamellar bonding and splat thickness will be significantly important in determining the erosion of the deposit.

Thermal conductivity is important for thermally conductive or thermal barrier coatings. At a perpendicular direction to the lamellae, thermal conduction is restricted to the bonded interface area. Moreover, additional contact resistance due to the limited conduction area (Bowden and Tabor, 1964) further reduces the conduction effect. Therefore, the thermal conductivity of the spray coating relative to the bulk material is generally less than the interface bonding ratio (McPherson, 1984; Ohmori and Li, 1993). Recent investigation into an electrically conductive La_{0.8}Sr_{0.2}MnO₃ coating and an ionic conductive YSZ coating indicated that the electrical conductivity of thermal spray coatings depends on interface lamellar bonding (Li *et al.*, 2005b,c; Xing *et al.*, 2008c).

Kuroda and Clyne (1991) measured the Young's modulus of various coatings in comparison with that of their corresponding bulk materials. They reported that the Young's modulus relative to bulk material is about one-third for metallic coatings and one-sixth for alumina. Li *et al.* (1997) established the relationship between Young's modulus perpendicular to the deposit plane and structural parameters based in the plate theory. The low relative Young's modulus of the deposits compared with bulk material is

qualitatively well explained. The anisotropy of Young's modulus of the thermal spray deposits is obvious with regard to the layered microstructure (McPherson and Cheang, 1991; Nakahira *et al.*, 1992). Young's modulus at a direction perpendicular to the lamellae, as mentioned above, is less than that along the lamellae direction.

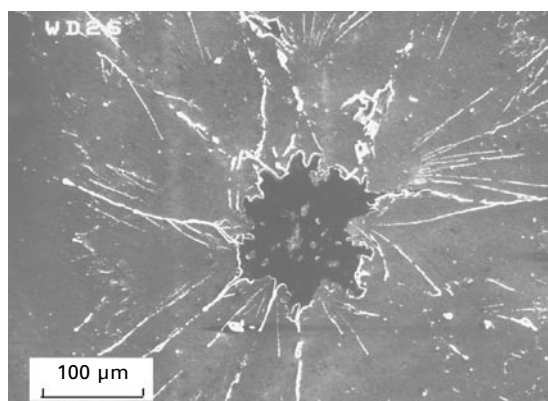
7.5 Bonding between coating and substrate

Sufficient adhesion between the substrate and the coating is key issue for a coating to perform. The factors influencing the adhesion include substrate preparation, coating processes and deposition conditions, temperature control, and coating design. The basic mechanisms of the adhesion include chemical bonding, physical bonding and mechanical interlocking (Pawlowski, 1995). With a substrate material of low melting points, such as Al alloy on magnesium alloy, the metallurgical bonding at the interface may form through the formation of intermetallics when the spray droplet materials are of a higher melting point. Mechanical interlocking is still the main mechanism for adhesion formation. Close contact between atoms of the coating lamella and of the substrate, achieved by the high velocity impact of the spray particles results in the effect of Van der Waals forces (Steffens and Müller, 1972) and thus adhesion can be enhanced through increasing particle kinetic energy on impact.

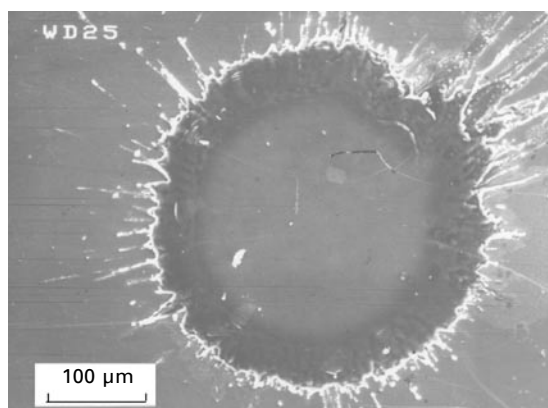
7.5.1 Effect of surface adsorbates on the splat formation and preheating on adhesion strength

The first layer of splats on the substrate determines the adhesion mechanisms of the coating. Thermal interaction between spray droplets and the substrate influences the establishment of adhesion. Heat transfer from the droplet melt to the substrate raises the substrate surface temperature. Rapid heating of the substrate surface may lead to explosive evaporation of surface adsorbates (possibly moisture, or oil), which causes splashing, or local melting of the substrate surface, depending on the heat content of the droplets.

When the substrate is covered by evaporative organics or moisture, heating of the substrate surface by the droplets will lead to rapid evaporation, which causes splashing of the droplets during spreading. Figures 7.18, 7.19 and 7.20 show the different irregular splats with significant splashing during splatting caused by surface adsorbates and near regular disk splats without severe splashing formed on a clean surface (Li and Li, 2004). As can be seen, when arms or sputters resulting from splashing are weakly adhered on the substrate surface, they hinder direct contact of a following splat with the substrate and result in weak adhesion (Fukumoto *et al.*, 1994). Therefore, it is necessary to remove surface adsorbates prior to coating deposition to



(a)

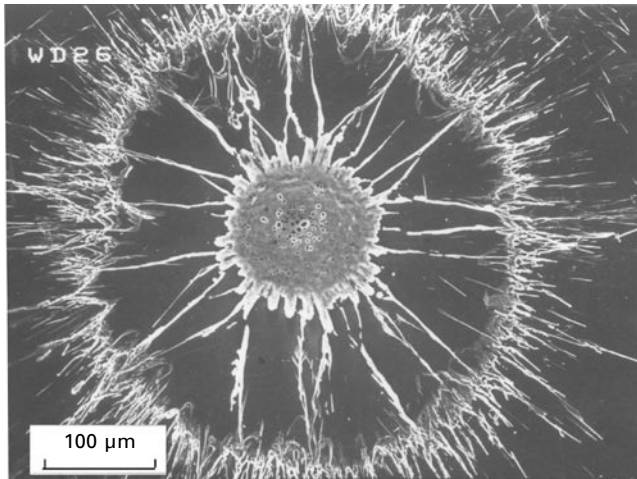


(b)

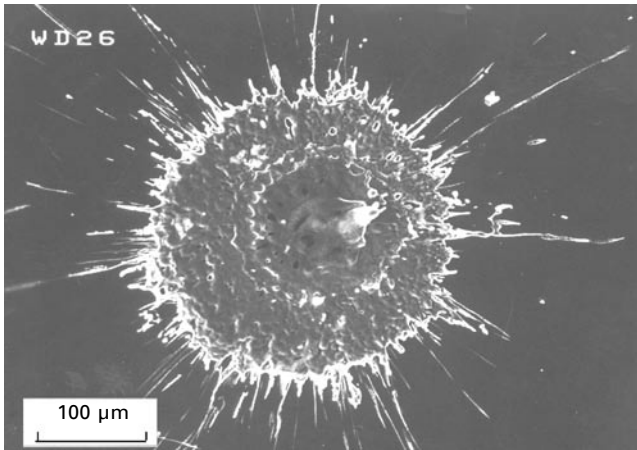
7.18 Typical morphology of Al splats obtained on a glycol adsorbed substrate surface at different preheating temperatures: (a) 150°C; (b) 250°C (After Li and Li, 2004).

bring about direct contact of metal splats with the substrate for enhancement of interfacial bonding.

Generally, organic contaminants can be removed chemically (Davis, 2004). Proper preheating of the substrate surface can remove moisture adsorbates (Li and Li, 2004) and increase the adhesive strength of a coating. Parco *et al.* (2007) reported that plasma spraying of NiAl5 results in the local melting of an Mg alloy surface, which leads to formation of metallurgical bonding. Preheating of the Mg substrate promotes the substrate melting and thus increases the adhesive strength of NiAl5. Even with spraying Al, melting of the Mg alloy substrate is observed, and can be enhanced by substrate preheating. However, with light metals such as Al, Mg and Ti alloys, preheating to a high temperature results in rapid formation of oxide scales on the substrate



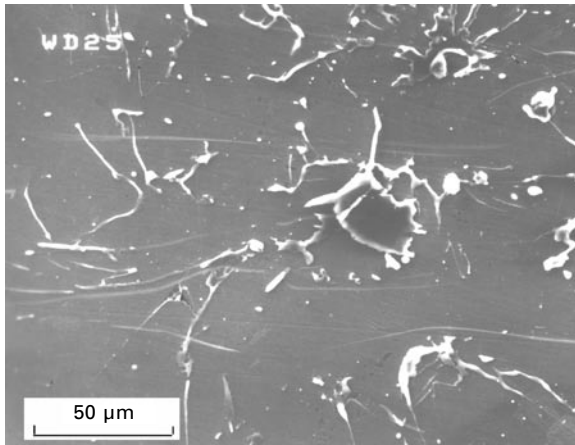
(a)



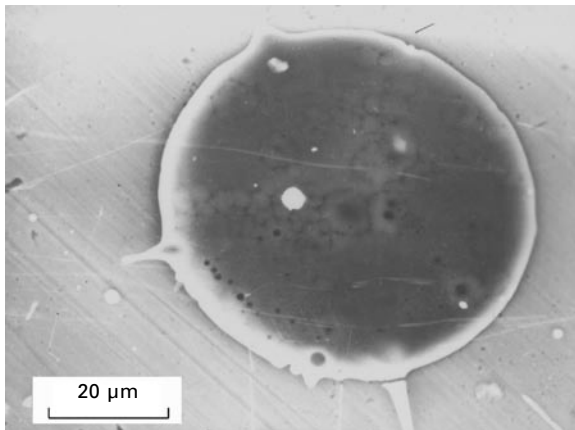
(b)

7.19 Typical morphology of Ni splats obtained on a glycerol adsorbed substrate surface at different preheating temperatures: (a) 250°C; (b) 350°C. (After Li and Li, 2004).

surface, which inhibit direct contact of the metal splats with the substrate and reduce adhesion. Therefore, caution should be paid to preheating these substrates when metal alloy coatings are sprayed onto them. However, with oxide ceramic coatings, preheating will benefit the increase of an adhesion. As reported by Fukunuma and Ohno (2003), the adhesive strength of an Al_2O_3 coating of about 500 μm plasma-sprayed on an Al substrate is increased with increase of substrate preheating temperature to about 200°C (see Fig. 7.21).



(a)

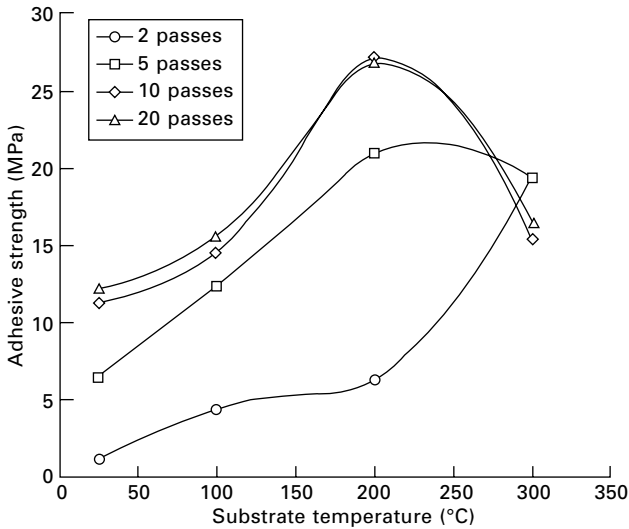


(b)

7.20 Typical morphology of Al_2O_3 splats obtained on a glycol adsorbed substrate surface at different preheating temperatures: (a) 150°C and (b) 250°C (After Li and Li, 2004).

7.5.2 Metallurgical interaction between spray particles and substrate

When droplet impact causes local melting of the substrate, a rapid reaction between droplet melt and substrate melt occurs to form a metallurgical bond. A contact temperature higher than the melting point of the substrate possibly leads to the metallurgical reaction between splat and substrate. Kitahara and Hasui (1974) observed experimentally the diffusion layer at the interfaces between molybdenum and tungsten coatings and aluminum substrate. This layer is due to the high melting points of Mo and W, which result in a local contact temperature higher than the melting point of the aluminum substrate.



7.21 Effect of substrate preheating temperature on the adhesive strength of Al_2O_3 coating plasma-sprayed on aluminum substrate. Marks indicate the passes of sand-blasting to adjust the surface roughness and higher numbers correspond to a higher surface roughness shown in Fig. 7.25 (After Fukunuma *et al.*, 2003).

Metallurgical bonding can be formed through the formation of intermetallic phases at the interface between sprayed metal coatings and aluminum substrate as reported by Kitahara and Hasui (1974). Intermetallic phases (Fe_2Mo , Fe_2W and Fe_7W_6) were also observed by these authors when Mo and W were sprayed onto a steel substrate (Houben and Liempd, 1983). Parco *et al.* (2007) reported that plasma spraying of NiAl5 results in the local melting of the Mg alloy substrate surface, which leads to metallurgical bonding. When Ni-Al composite powders are sprayed onto metals, including light metals and steel substrates, the exothermic reaction between the two elements in flight, through forming intermetallic phases, raises the particle temperature significantly, which possibly leads to formation of metallurgical bonding at local interface areas (Longo, 1966; Ingham, 1975). Oxidation of Al and Ni in flight can also contribute the increase of particle temperature (Sampath *et al.*, 1987). Thus, Ni-Al composite powders have been used as bond coat materials to enhance the adhesive strength of coatings such as ceramic coatings having poor adhesion when they are directly deposited.

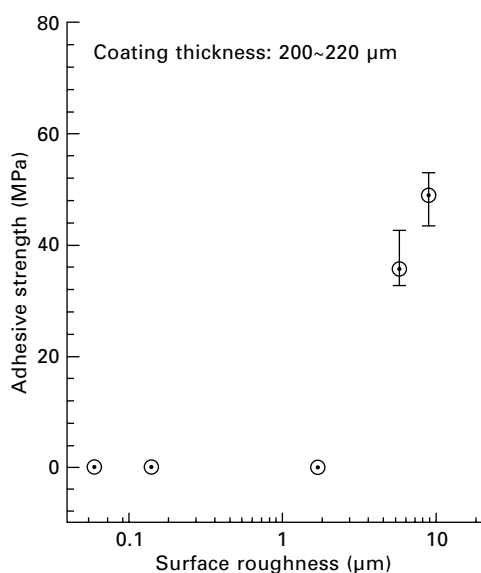
7.5.3 Effect of substrate surface roughening on the adhesion of coating

Proper substrate surface preparation prior to coating deposition is absolutely essential. Generally, the surface preparation includes cleaning, roughening

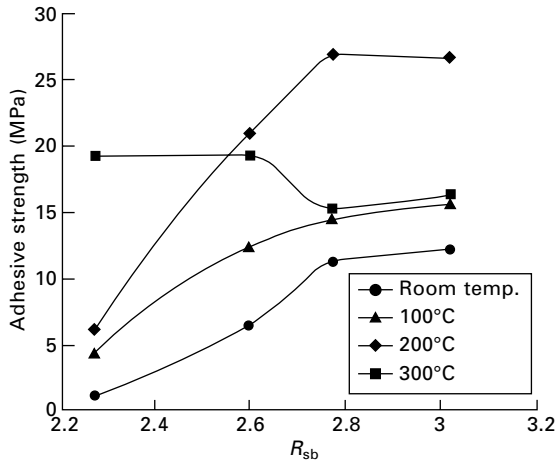
(sand blasting), machining, masking and preheating. Roughening is the most important step in preparing the surface to accept the sprayed coating. Fig. 7.22 shows the effect of surface roughness on the adhesive strength of a HVOF NiCrBSi coating deposited on stainless steel when the spray particles are in a fully melted state (Wang and Li, 2005). No effective adhesion is achieved when the surface roughness is less than 2 μm . With increase of substrate surface roughness, the adhesive strength is increased. An adhesive strength higher than 40 MPa was obtained when surface roughness became larger than 5 μm . Figure 7.23 shows the effect of surface roughness on the adhesive strength of a plasma-sprayed Al_2O_3 coating on an Al substrate. R_{sb} is the roughness index introduced by Fukanuma and Ohno (2003). Evidently, except for a coating deposited at a high (300°C) substrate preheating temperature, the adhesive strength is increased with increase of surface roughness. With an Al cylinder bore surface, Schlaefer *et al.* (2008) reported a mechanical roughening process to ensure the adhesive strength of an arc sprayed coating (see Fig. 7.24). Proper mechanical roughening will enhance the interface interlocking for effective adhesion.

7.5.4 Effect of spray materials and melting state on adhesion of thermal spray coatings

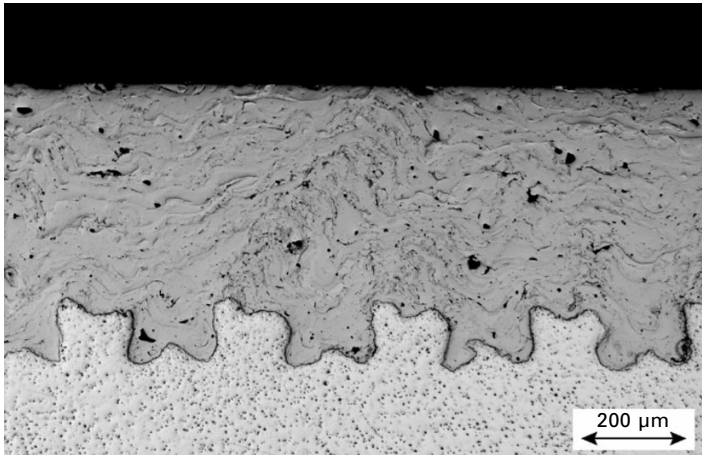
When molten droplet impact does not induce local substrate melting and subsequent formation of metallurgical bonding with the substrate, the adhesion



7.22 Effect of surface roughness on the adhesive strength of HVOF NiCrBSi alloy coatings on mild steel (After Wang and Li, 2005).



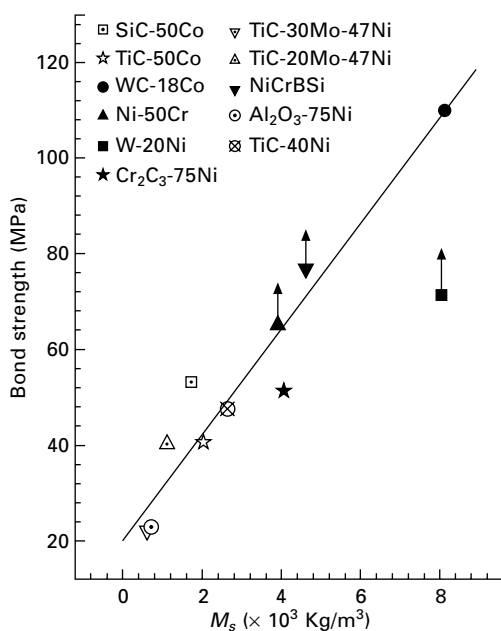
7.23 Effect of Al substrate surface roughness on the adhesive strength of plasma-sprayed Al_2O_3 coating (after Fukanuma *et al.*, 2003).



7.24 Microstructure of PTAW coating showing the well interlocked interface through mechanical cutting surface preparation (after Schlaefer *et al.*, 2008).

depends mainly on the mechanical locking effect of the roughened surface, as mentioned in the previous section. The effect of the spray materials on the adhesion is limited. However, when solid-liquid two-phase droplets impact on a substrate, as in HVOF process, the effect of the spray materials becomes significant. WC-Co coatings with excellent adhesive strength (over 70 MPa, corresponding to the strength of the adhesives in common use for tensile testing) can be easily deposited by the HVOF process. However,

an HVOF nickel-based coating deposited with well-melted particles has exhibited a limited adhesive strength (Li and Wang, 2002). Bolelli *et al.* (2009) showed that HVOF WC-CoCr particles at impact penetrated deeply into an Al alloy substrate which led to formation of a strong locking effect even when melting of the particles is limited. Trompetter *et al.* (2005) showed that even NiCr particles generated by a high-velocity air flame (HVAF) can substantially embed into an Al substrate, as observed in cold spraying. Li and associates (Li *et al.*, 2001; Li and Wang, 2002) suggested that a two-phase state contributes significantly to the good adhesion of HVOF WC cermet coatings and the two-phase state during HVOF spraying is a necessary condition for depositing coatings with high adhesion. Moreover, systematic experimental investigation showed that the adhesive strength of HVOF coatings deposited by solid-liquid state particles depends on the properties of the solid phase. Wang *et al.* (2006) introduced an 'effective mass fraction' of solid phase which is defined as the product of the density of the solid phase with the square of its volume fraction. Figure 7.25 shows the relationship between the coating adhesive strength and the effective mass of the solid phase for a mild steel substrate. With increase of the effective mass of the solid phase, adhesive strength is positively increased. Therefore, with high velocity spraying such as HVOF or HVAF, the high kinetic energy of



7.25 Effect of effective mass fraction of solid particles in the solid-liquid two-phase droplets on the adhesive strength of HVOF different coatings (after Wang *et al.*, 2006).

the solid particles in the two-phase droplets benefits intimate contact of the splat through high impact pressure (Wang *et al.*, 2006) and the penetrating effect into the soft metal alloy (Trompetter *et al.*, 2005; Bolelli, 2009) which leads to strong adhesion.

7.6 Case studies

7.6.1 Thermal spraying of Al cylinder bores

In the automotive industry, Al-based engine blocks are being developed to substitute the conventional iron-based materials for weight reduction, leading to a reduction of CO₂ emissions. However, wear resistance of Al alloy is lower than that of iron-based materials. Thermal spray processes have been widely employed for the development of wear-resistant coatings on the surface of Al cylinder bores. As summarized in Section 7.2.3 (see Table 7.3), various materials of coatings including cast iron, low carbon steel, nano-crystalline composites, cermet, and NiCrBSi, are under development through different spray processes such as atmospheric and plasma spraying, high velocity oxy-fuel, plasma transferred wire arc spraying. Iron-based coatings deposited by Rota-type plasma spraying and plasma transferred arc spraying have been field tested. Typical coating characteristics of concern are adhesive strength, hardness, porosity, compositions and phases. Sufficient adhesive strength is required to ensure the reliability of thermally-sprayed cylinder bores. Babezat and Harrison (2008) reported that, according to experience over ten years, the minimum required adhesive strength is 30 MPa for iron-based coatings on Al alloys. This adhesive strength is generally ensured through proper substrate surface roughening by grit-blasting. The adhesive strength of low-alloy carbon steel coatings deposited by plasma spraying reached 40–60 MPa on AlSi cast alloy (Barbezat, 2002). Schlaefer *et al.* (2008) reported a mechanical roughening process that obtained an adhesive strength of 60 MPa for a plasma transferred arc sprayed coating.

The hardness of the coating depends on materials. The hardness of a low alloyed carbon steel coating deposited by plasma spraying was 350–550 HV (Barbezat, 2002). The hardness of some high carbon steel coatings deposited by plasma transferred wire arc reached values of 650 to 750 HV (Bobzin *et al.*, 2007). It was found that the harder coatings were associated with better wear resistance (Bobzin *et al.*, 2007). However, high hardness may be limited by coating surface finishing (Barbezat and Harrison, 2008). A smooth honing with an Ra value between 0.1 and 0.3 μm is recommended, which is achieved by honing using diamond tools (Babezat and Harrison, 2008). Such finishing will reduce friction by 30% in comparison with cast iron. However, if the Ra value after machining becomes larger than 0.6 μm no improvement can be expected.

The coating porosity is also important for the cylinder bore operation. A residual porosity of the coating of about 2% gives, after honing, a suitable topography to keep residual lubricant oil in the microcavities. High porosity may lead to increase of wear. Therefore, spray conditions should be optimized to obtain suitable coating porosity. It was pointed out by Barbezat (2002) that honing with a cross line design must be avoided on sprayed coating because of its effect on oil consumption. With plasma spraying, it was confirmed by Barbezat (2002) that the coating hardness and porosity values were still within specification even when the main spray parameters varied by plus or minus 5%. Such characteristics indicate the robustness of the plasma spraying process for Al alloy cylinder bores.

During deposition of carbon steel coatings, oxidation, leading to the formation of iron oxides FeO and Fe₃O₄, benefits the wear resistance because these types of oxides act as solid lubricants. However, the formation of Fe₂O₃ should be avoided because of the abrasive effect of this type of oxide. Therefore, the design and selection of iron-based spraying materials should benefit the formation of desirable oxides.

Bobzin *et al.* (2007) also reported the repair of worn cylinder bores for remanufacturing. Deposition of high carbon steel coatings by plasma transferred wire arc spraying demonstrated the potential of the process for manufacturing or remanufacturing Al based cylinder bores.

Developments to date have demonstrated the feasibility of the thermal spray processes for surface coating of Al cylinder bores. However, economic issues usually arise with Al cylinder bores for automobiles. The application of spraying using a Rota-type plasma spraying system demonstrated the competitive cost versus galvanic processes, cast iron sleeves and composite solutions (Barbezat, 2007). The low-cost feature of wire arc spraying may easily fulfill the cost-effective requirements for iron-based coating deposition by plasma transferred wire arc spraying (Bobzin *et al.*, 2007). Therefore, thermal spraying is promising to promote the application for Al alloy cylinder bores and also remanufacture of cylinder bores.

7.6.2 Thermal spray of Ti body implants

Titanium and its alloys have been widely employed as biomaterial stems for hard tissue replacements and for cardiac cardiovascular applications, due to their low modulus, superior biocompatibility and good corrosion resistance (Liu *et al.*, 2004). Although titanium and its alloys exhibit good biocompatibility when they are implanted into the human body, they are generally separated by a thin non-mineral layer from bones (Thomsen *et al.*, 1998). The bond associated with osteointegration is attributed to mechanical interlocking of the titanium surface asperities and pores in the bones. Therefore, surface modification with various coatings is applied to make titanium biologically

bond to bones. Among the possible surface modification processes, thermal spraying, especially plasma spraying, has been widely employed to deposit biomaterial coatings onto titanium surfaces (Liu *et al.*, 2004; Heimann, 2006).

Among the various biomaterials, plasma spraying of hydroxyapatite (HA) has been intensively investigated and adopted by commercial producers of orthopedic implants (Liu *et al.*, 2004). This is because about 70% of the mineral fraction of bones has a HA-like structure and earlier fixation and stability, with more bone ingrowth or ongrowth, can be achieved through HA coatings. The most important issue involved in plasma-sprayed HA coatings is their low adhesive strength on the titanium substrate. Liu *et al.* (2004) have summarized the bond strength of plasma-sprayed HA coatings reported by different investigators (Table 7.6). Most plasma-sprayed HA coatings exhibit an adhesive strength less than 10 MPa owing to the low mechanical properties of HA itself. The poor adhesion may cause clinical application failure by chipping, spalling and delamination. To improve adhesion, the degree of melting of the HA particles injected into the plasma jet should be improved by an increase of the plasma enthalpy (McPherson *et al.*, 1995). However, high enthalpies lead to increasing thermal decomposition and thus to a decrease in the resorption resistance (Heimann, 2006). However, the addition of some other materials to HA to deposit a composite coating is likely to improve the adhesion of the coating (Chang *et al.*, 1997, Silva *et al.*, 1998).

Another important issue is the resorption of HA coatings in a biological environment. It is influenced by phase compositions and crystallinity of the coating. HA powders injected into the hot plasma jet suffer thermal decomposition in-flight. Depending on the degree of melting, plasma-sprayed HA coating may consist of HAp and metastable phases such as oxyhydroxyapatite (OHAp), oxyapatite (OAp), tricalcium phosphate (α -TCP), tetracalcium phosphate (TTCP), CaO, and amorphous calcium phosphate. HA phase is retained from the unmelted fraction of the particles. The amorphous

Table 7.6 Adhesive strength of plasma-sprayed HA coatings (tested following ASTM C633) (Liu *et al.*, 2004)

Authors	Compositions	Thickness (μm)	Adhesive strength (MPa)
Khor <i>et al.</i> (1997)	HA-Ti alloys composite	200	8.0
Chang <i>et al.</i> (1997)	ZrO ₂ -HA composite	210	32.49 $\pm$ 4.24
Khor <i>et al.</i> (1998)	HA	60–80	16.6
Silva <i>et al.</i> (1998)	HA-P ₂ O ₅ -CaO composite	100	35
Wang <i>et al.</i> (1998)	Calcium phosphate	220	6.67
Tsui <i>et al.</i> (1998)	HA	200	5.97 $\pm$ 0.78
Zheng <i>et al.</i> (2000)	HA-Ti composite	200	<20
Kweh <i>et al.</i> (2002)	HA	150	24.5 $\pm$ 2.4

TCP is formed through the quenching effect of the molten fraction of the HA particles on high velocity impact onto the substrate. The improved melting degree of HAp particles results in an increase in amorphous TCP (Heimann, 2006). It is reported that the amorphous and metastable phases are more soluble than the crystalline HA (Fazan and Marquis, 2000). Therefore, it is essential to control the phases and crystallinity of plasma-sprayed HA coatings. Increasing particle velocity (reducing dwelling time of particles in the hot plasma jet) with subsequent limited heating of HAp powder particles by high velocity plasma spraying, such as vacuum plasma spraying, leads to deposition of a well-crystallized hydroxyapatite layer with a minimum TCP content through partially melted particles (Liu *et al.*, 2004). However, a high content of crystallized HA will compromise coating adhesion.

One more property in need of control is the coating thickness, because the thickness of HA coatings influences their resorption and mechanical properties. A thin HAp coating (less than 50 μm) yields better adhesion compared with thicker coatings, owing to reduced residual coating stress (Heimann *et al.*, 2000). Plasma-sprayed HA coatings in a thickness of 50 to 75 μm are adopted by most commercial producers of orthopedic implants (Liu *et al.*, 2004). However, the thin HA coating will be rapidly resorbed in the course of bone integration. A thick coating (up to several hundred micrometers) may be required in some instances to ensure a more permanent bond to guarantee implant stability and avoid a replacement operation to exchange the implant.

To improve the mechanical properties of HA coatings and ensure long-term integrity of the interface between the HA coating and the titanium substrate, HA-based composites reinforced with bioinert ceramics, such as ZrO_2 (Gu *et al.*, 2004), have also been investigated. Also, bioactive glass coatings containing of CaO-SiO_2 have been investigated by thermal spraying. For more detailed information, refer to the review literature by Liu *et al.* (2004) and Heimann (2006).

7.7 Future trends

Over about 100 years, various thermal spray processes have been developed to enable the deposition of all kinds of material coatings, including metal alloys, oxide ceramics, cermets and composites and polymers. Various coating materials have been investigated to provide the surface of light metals and their alloys with different functions including wear protection, corrosion protection, thermal barrier, bioactivity and dielectrical properties.

Understanding the features of the different processes benefits the selection of most suitable thermal spray process for a particular material and application. Arc spraying is a cost-effective process in which only alloy wires or cored wires are applicable. Through controlling the velocity of the atomizing gas,

particle size and velocity can be adjusted to deposit coatings of different microstructures with control of oxide inclusions. HVOF has been widely employed to deposit WC-Co or Cr_3C_2 -NiCr cermet coatings with excellent abrasive wear performance. Suppression of decarburization of carbides during spraying is essential for optimization of coating performance, which may be compromised along with coating deposition efficiency and density. The use of proper cermet powders with reasonably small carbide particles densely bonded by the metallic binder phase benefits process optimization and wear performance.

Plasma spraying is a process by which all the materials of the coating can be deposited. An increase of the degree of melting of spray powder particles is directly associated with an improvement of deposition efficiency and coating cohesion. The large temperature gradient in the plasma jet and the wide size distribution of practical spray powder particles easily bring about different particle trajectories in the plasma jet, which results in different heating degrees of the powder particles using a common plasma spray torch into which powders are fed radially. The development of a plasma spray torch with axial powder feeding enables more effective heating and acceleration for all the powder particles and thus a consistent coating is easily deposited. Control of particle heating and acceleration is essential to control the thermal decomposition of spray materials such WC-Co and HA.

Oxidation of alloy powder particles occurs in two stages, viz, in-flight and post-flattening. The in-flight oxidation much depends on particle size. It was found that oxygen content is inversely increased with droplet size following an exponential relationship and reaches more than 10wt% for powders with a particle size less than 15 μm . When particle size is larger than 45 μm , post-flattening oxidation dominates the oxygen content of coatings, which is not then significantly influenced by particle size. The inclusion of oxides through *in-situ* oxidation of carbon steel benefits wear or tribological performance of steel coatings for Al engine cylinder bores. The oxide inclusion is controlled through the size of spray particles.

The splat size is determined by droplet particle parameters. With solid-liquid two-phase droplets, as is the case with WC-Co, high velocity impact tends to induce rebound of large size solid particles. Rebound also leads to decarburization of carbides during HVOF spraying of WC-Co and Cr_3C_2 -NiCr. Moreover, under high velocity impact in HVOF, solid-liquid two-phase particles are the necessary condition to achieve excellent adhesion. Solid particles in two-phase droplets can be embedded into soft, light-metal substrates to create strong physical bonding by an interlocking effect. A fraction of the metallurgical bonding between spray materials and Al or Mg alloy substrate is easily formed by local melting of the substrate surface. The rapid cooling feature involved in splat cooling results in the formation of metastable phases, even formation of amorphous phases.

Pores are present in thermal spray coating in a two-dimensional geometry which is different from those in bulk materials processed by conventional methods such as powder metallurgy. Therefore, one needs to be careful to correlate coating properties and performance with porosity. The pores in the as-sprayed coating are interconnected through a large fraction of the non-bonded lamellar interface areas between adjacent lamellae. Gaseous or liquid medium can penetrate through the coating to the interface between coating and substrate, causing galvanic corrosion. A post-spray treatment is necessary for complete protection of substrate materials such as Mg alloys from corrosion. On the other hand, suitable porosity in the coatings applied to Al cylinder bores enables the retention of lubricant oil for improving tribological wear performance.

It has been shown that coating properties are dominated by lamellar structure with limited interface bonding. The maximum interface bonding ratio is about 32% for a coating deposited under common spray procedures. This limited lamellar interface bonding ratio limits the mechanical properties index, thermal conductivity and electrical conductivity of thermal spray coatings. The applications of such coatings should therefore take the lamellar structure feature into consideration.

The features inherent in thermal spray processes and coating microstructures mentioned in the chapter can be considered as both advantages and disadvantages, according to the application. Therefore, optimization of spray conditions and coating microstructures must be made by taking specific applications into consideration.

7.8 Acknowledgements

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7.9 References

- Arata Y., Ohmori A., Li C.-J. (1988a), Study on the structure of plasma sprayed ceramic coating by using copper electroplating, *Proceedings of International Symposium on Advanced Thermal Spraying Technology and Allied Coatings (ATTAC'88)*, Japan High Temperature Society, Osaka, 1988, p. 205–210.
- Arata Y., Ohmori A., Li C.-J. (1988b), Electrochemical method to evaluate the connected porosity in ceramic coatings, *Thin Solid Films*, Vol. 156, pp. 315–325.
- Barbezat G., Muller E., Walser B. (1988), Applying tungsten carbide cobalt coatings by high velocity combustion spraying, *Sulzer Technical Review*, 4, 27–33.
- Barbezat G., Landes K. (2000), Plasma technology TRIPLEX for the deposition of ceramic coatings in industry, Thermal Spray: Surface Engineering via Applied Research, *Proceedings of the 1st International Thermal Spray Conference*, (ed.) C.C. Berndt, ASM International Ohio, 881–885.

- Barbezat G. (2002), Internal plasma spraying for new generation of automotive engine, *Proceedings of International Thermal Spray Conference, ITSC'2002*, Essen, DVS-German Welding Society, 158–160.
- Barbezat G. (2005), Advanced thermal spray technology and coating for lightweight engine blocks for the automotive industry, *Surf. Coat. Technol.*, 200, 1990–1993.
- Barbezat G. (2007), Importance of Surface Preparation Technology Prior to Coating Deposition on Cylinder Bores for High Performance Engines, *Thermal Spray 2007: Global Coating Solutions*; (Ed.) B.R. Marple, M.M. Hyland, Y.-C. Lau, C.-J. Li, R.S. Lima, and G. Montavon, Published by ASM International®, Materials Park, Ohio, USA, pp. 276–280.
- Barbezat G., Harrison K. (2008), Plasma spraying of lightweight engine blocks, *Proceedings of IOM3*.
- Berndt C.C., McPherson R. (1980), A fracture mechanics approach to the adhesion of flame and plasma sprayed coatings, *Proc. 9th Int. Thermal Spraying Conf.*, Hague, 1980, Nederland Inst. Voor Lastetechniek, 1980, p. 310–316.
- Bisson J., Moreau C., Dorfman M., Dambra C., Mallon J. (2005), Influence of hydrogen on the microstructure of plasma-sprayed yttria-stabilized zirconia coatings, *J. Therm. Spray Technol.*, 14, 85–90.
- Bobzin K., Lugscherder E., Ernst F., Zwick J., Schlaefel T., Verpoort C., Schwenk. A., Schreiber F., Wenz T., Cook D., Kowalsky K., Conti J. (2006), Coating bores of light metal crankcases, *Proceedings of the 2006 International Thermal Spray Conference*, Seattle, ASM International, Ohio, CD-ROM.
- Bobzin K., Ernst F., Schlaefel T., Cook D., Kowalsky K., Bird K., Gerke D.H., Sharp R.E., Raab K. R., Lindon S. (2007), Thermal spraying of cylinder bores with the PTWA internal coating system, *Proceedings of the ASME Internal Combustion Engine Division Fall 2007 Technical Conference*, ICEF07, October 14–17, 2007, Charleston, South Carolina, USA.
- Bollelli G., Lusvarghi, Barletta M., Karhail V. (2009), Wear and corrosion behaviour of HVOF-sprayed WC-CoCr coatings on Al alloys, *Thermal Spray 2009: Proceedings of the International Thermal Spray Conference*, Marple B.R., Hyland M.M., Lau Y.-C., Li C.-J., Montavon G. (eds), ASM International, Ohio, 1163–1168, doi:10.1361/cp2009itsc1163.
- Boulos M.I., Fuachais P., Vardelle A., Pfender E. (1993), Fundamentals of plasma particle momentum and heat transfer, In *Plasma Spraying: Theory and Applications*, Ed. Suryanarayanan R., World Scientific, 1993.
- Bourdin E., Fauchais P., Vardelle A. Pfender E. (1983), Transient heat conduction under plasma conditions, *Inter. J. Heat Mass Transfer*, 26, 567–582.
- Bowden F. P., Tabor D. (1964), *Friction and Lubrication of Solids*, Oxford University Press, p. 25.
- Chang E., Chang W.J., Wang B.C., Yang C.Y. (1997), Plasma spraying of zirconia-reinforced hydroxyapatite composite coatings on titanium, 1. Phase, microstructure and bonding strength, *J. Mater. Sci. Mater. Med.*, 8, 193–200.
- Chen W.R., Wu X., Marple B.R., Nagy D.R., Patnaik P.C. (2008), TGO growth behaviour in TBCs with APS and HVOF bond coats, *Surf. Coat. Technol.*, 202, 267–2683, doi:10.1016/j.surfcoat.2007.09.042
- Chivavibul P., Watanabe M., Kuroda S., Shinoda K. (2007), Effects of carbide size and Co content on the microstructure and mechanical properties of HVOF-sprayed WC-Co coatings, *Surf. Coat. Technol.*, 202, 509–521, DOI:10.1016/j.surfcoat.2007.06.026
- Cook D., Zaluzec M., Kowalsky K. (2003), Development of thermal spray for automotive

- cylinder bores, *Thermal Spray 2003, Advancing the Science & Applying the Technology*, (ed.) C. Moreau and B. Marple, ASM International, Materials Park, Ohio, 143–147.
- Davis J.R. (2004), *Handbook of Thermal Spray Technology*, ASM International, Materials Park, Ohio.
- Dresvin S.V. (1972), *Physics and Technique of Low Temperature Plasma*, Atomizdat, Moskva, Russia (In Russian).
- Espie G., Fauchais P., Labbe J.C., Vardelle A., Hannoyer B. (2001), Oxidation of iron particles during APS: Effect of the process on formed oxide. Wetting of droplets on ceramics substrates, (ed.) Berndt C C, Khor K A, Lugscheider E. *Thermal Spray 2001: New Surfaces For A New Millennium*, ASM International, Ohio, 821–827.
- Fauchais P., Vardelle M., Vardelle A., Coudert J.F. (1989), Plasma spraying of ceramic particles in argon–hydrogen D.C. plasma jets: Modeling and measurements of particles in flight correlation with thermophysical properties of sprayed layer, *Metall. Trans. B*, 20B, 263–276.
- Fazan F., Marquis P.M. (2000), Dissolution behavior of plasma-sprayed hydroxyapatite coatings, *J. Mater. Sci. Mater. Med.*, 11, 787–792.
- Fukanuma H., Ohno N. (2003), Influence of substrate roughness and temperature on adhesive strength in thermal spray coatings, *Thermal Spray 2003, Advancing the Science & Applying the Technology*, (ed.) C. Moreau and B. Marple, ASM International, Materials Park, Ohio, 1361–1368.
- Fukumoto M., Hayashi H., Yokoyama T. (1994), Effect of both substrate surface roughness and substrate temperature on adhesion strength of thermally sprayed coatings, *Thermal Spraying*, 32 (No. 3), pp. 29 (In Japanese).
- Gansert R.V. (2003), Influence of powder size in aluminum oxide coatings for use in the semiconductor industry, *Thermal Spray 2003, Advancing the Science & Applying the Technology*, (ed.) C. Moreau and B. Marple, ASM International, Materials Park, Ohio, 159–161.
- Gu Y.W., Khor K.A., Pan D., Cheng P. (2004), Activity of plasma sprayed yttria stabilized zirconia reinforced hydroxyapatite/Ti-6Al-4V composite coatings in simulated body fluid, *Biomaterials*, 25, 3177–3185.
- Hawthorne H.M., Erickson L.C., Ross D., Tai H., Troczynski T. (1997), The microstructural dependence of wear and indentation behavior of some plasma-sprayed alumina coatings, *Wear*, 20–204, 709–714.
- Heimann R.B., Grabmann O., Hempel M., Bucher R., Harting M. (2000), Applied Mineralogy in Research, Economy, Technology, Ecology, and Culture, *Proc. 6th Inter. Congress on Applied Mineralogy, ICMA 2000*, Gottingen, Germany, 2000, 155.
- Heimann R.B. (2006), Thermal spraying of biomaterials, *Surf. Coat. Technol.*, 210, 2012–2019.
- Houben J.M., Liempd G.G. (1983), Metallurgical interactions of Mo and steel during plasma spraying, *Proceedings of 10th International Thermal Spray Conference*, DVS-German Welding Research Institute, Dusseldorf, 66–71.
- Ingham H.S. Jr. (1975), Bonding of flame sprayed Ni-Al, *J. Vac. Sci. Technol.*, 12, 773–776.
- Ji G.-C., Li C.-J., Wang Y.-Y. (2006), Microstructural characterization and abrasive wear performance of HVOF sprayed Cr₃C₂-NiCr coating, *Surf. Coat. Technol.*, 200, 6749–6757.
- Jones H. (1971), Cooling, freezing and substrate impact of droplets formed by rotary atomization, *J. Phys. D: Appl. Phys.*, 4, 1657–1660.
- Jones H. (1973), Splat cooling and metastable phases, *Report on Progress in Physics*, 36, 425–1497, doi: 10.1088/0034-4885/36/11/002

- Karthikeyan J., Sinha A.K., Biswas A.R. (1996), Impregnation of thermally sprayed coatings for microstructural studies, *J. Thermal Spray Technol.*, Vol.5, p. 74–78.
- Kato N., Mizuno H., Ibe H., Kitamura J. (2006), Ceramic coatings prepared by plasma spraying for semiconductor production equipment, *Proceedings of 2006 International Thermal Spray Conference*, Seattle, ASM International, Ohio, in CD-ROM.
- Kawase R., Nakajima H., Maehira K., Koyama M., Abe H. (1988), Influence of spraying parameters on detonation coating properties, *Proceedings of International Symposium on Advanced Thermal Spraying Technology and Allied Coatings (ATTAC'88)*, Japan High Temperature Society, Osaka, 1988, p. 55–60.
- Kawase R. (1993), Evaluation methods for thermal spray coatings, *Proceedings of the 1993 National Thermal Spray Conference*, Anaheim, USA, ASM International Ohio, 575–579.
- Khor K.A., Yip C.S., Cheang P. (1997), Ti-6Al-4V/hydroxyapatite composite coatings prepared by thermal spray techniques, *J. Thermal Spray Technol.*, 6, 109–115.
- Khor K.A., Cheang P., Wang Y. (1998), Plasma spraying of combustion flame spheroidized hydroxyapatite (HA) powders, *J. Thermal Spray Technol.*, 7, 254–260.
- Kitahara S., Hasui A. (1974), A study of bonding mechanism of sprayed coatings, *J. Vac. Sic. Technol.*, 11, 747–753.
- Kitamura J., Ibe H., Mizuno H., Aoki I. (2008), Plasma sprayed coatings of high quality ceramics for semiconductor and flat-panel-display production equipments, *Proceedings of 2008 International Thermal Spray Conference*, DVS, Dusseldorf, CD-ROM.
- Kobayashi A., Arata Y. (1988), Formation of high quality ceramic coatings by gas tunnel type plasma spraying, *Proceedings of International Symposium on Advanced Thermal Spraying Technology and Allied Coatings (ATTAC'88)*, Japan High Temperature Society, Osaka, 1988, p. 107–112.
- Kowalsky K.A., Marantz D.R., Smith M.F., Oberkamp W.L. (1990), HVOF: Particle, flame diagnostics and coating characteristics, in Thermal Spray Research, *Proceedings of the National Thermal Spray Conference*, Long Beach, USA, ASM International, Ohio, 877–592.
- Kulkarni A., Gutleber J., Sampath S., Goland A., Lindquist W.B., Herman H., Allen A.J., Dowd B. (2004), Studies of the microstructure and properties of dense ceramic coatings produced by high-velocity oxygen-fuel combustion spraying, *Mater. Sci. Eng. A*, A369, 124–137.
- Kuroda S., Clyne T.W. (1991), The quenching stress in thermally sprayed coatings, *Thin Solid Films*, Vol. 200, p. 49–66.
- Kuroda S. (1995), Advanced Inorganic Films and Coatings, Evaluation of the pore structure in plasma-sprayed coatings, *Advances in Inorganic Films and Coatings*, ed. P. Vincenzini, Techna Srl., p. 373–380.
- Kweh S.W.K., Khor K.A., Cheang P. (2002), An *in vitro* investigation of plasma sprayed hydroxyapatite (HA) coatings produced with flame-spheroidized feedstock, *Biomaterials*, 23, 775–785.
- Lewis J.A., Gauvin W.H. (1973), Motion of particles entrained in a plasma jet, *AIChE J.*, 19, 982–990.
- Li C.-J., Ohmori A., McPherson R. (1992), A microstructural model for the elastic behavior of plasma sprayed ceramic coatings, *Proceedings of Austceram'92*, Melbourne, Aug., ed. M.J. Bannister, p. 816–821.
- Li C.-J., Ohmori A., Arata Y. (1995a), Effect of spray methods on the lamellar structure of Al₂O₃ coatings, *Thermal Spray, Current Status and Future Trends*, ed. A. Ohmori, Japan High Temperature Society, 1995, p. 501–506.

- Li C.-J., Ohmori A., Harada Y. (1995b), Effect of WC-particle size on the formation of HVOF sprayed WC-Co coatings, *Thermal Spray, Current Status and Future Trends*, ed. A. Ohmori, Japan High Temperature Society, pp. 869–875.
- Li C.-J., Ohmori A., Harada Y. (1996a), Effect of powder structure on the structure of thermally sprayed WC-Co coatings, *J. Mater. Sci.*, 31, 785–794.
- Li C.-J., Ohmori A., Harada Y. (1996b), Formation of an amorphous phase in thermally sprayed WC-Co, *J. Thermal Spray Technol.*, 5, 69–73.
- Li C.-J., Ohmori A. (1996), The lamellar structure of a detonation gun sprayed Al_2O_3 coating, *Surf. Coat. Technol.*, Vol. 82, 1996, p. 254–258.
- Li C.-J., Ohmori A., McPherson R. (1997), The relationship between microstructure and Young's modulus of thermally sprayed ceramic coatings, *J. Mater. Sci.*, Vol. 32, p. 997–1004.
- Li C.-J., Yang H., Li H. (1999a), Effect of gaseous conditions on HVOF flame and properties of WC-Co coatings, *Materials and Manufacturing Processes*, Vol. 14 (3), pp. 383–395.
- Li C.-J., Wang Y.-Y., Wu T., Ji G.-C. (2001), Effect of types of ceramic materials in aggregated powder on the adhesive strength of HVOF cermet coating, *Surf. Coat. Technol.*, 145, pp. 113–120.
- Li C.-J., Ohmori A. (2002), Relationship between the structure and properties of thermally sprayed deposits, *J. Thermal Spray Technol.*, 11, 365–374.
- Li C.-J., Wang Y.-Y. (2002), Effect of particle state on the adhesive strength of HVOF sprayed metallic coating, *J. Thermal Spray Technol.*, 11, 523–529.
- Li C.-J., Ji G.-C., Wang Y.-Y., Sonoya K. (2002), The dominant mechanism of carbon loss during HVOF spraying of $\text{Cr}_3\text{C}_2\text{-NiCr}$, *Thin Solid Films*, 419, 137–143.
- Li C.-J., Li W.-Y. (2003), Effect of sprayed powder particle size on the oxidation behaviour of MCrAlY materials during HVOF deposition, *Surf. Coat. Technol.*, 162(1), 31–41.
- Li C.-J., Yang G.-J., Ohmori A. (2003a), Potential strengthening of erosion performance of plasma-sprayed Al_2O_3 coating by adhesives impregnation, *J. Mater. Sci. Lett.*, Vol. 22, 1499–1501.
- Li C.-J., Yang G.-J., Ohmori A. (2003b), Improvement of the properties of thermally sprayed ceramic coating by the infiltration of the adhesives, *Thermal Spray: Advancing the Science and Applying the Technology*, (Ed.) C. Moreau and B. Marple, Published by ASM International, Materials Park, OH-USA, pp. 1311–1316.
- Li C.-J., Li J.-L. (2004), Evaporated-gas-induced splashing model for splat formation during plasma spraying, *Surf. Coat. Technol.*, 184, 13–23.
- Li C.-J., Sun B. (2004a), Effects of spray parameters on the microstructure and property of Al_2O_3 coatings sprayed by a low power plasma torch with a novel hollow cathode, *Thin Solid Films*, 450, 282–289.
- Li C.-J., Sun B. (2004b), Microstructure and properties of molybdenum coatings deposited by microplasma spraying torch with a novel hollow cathode, *Tagungsband Conference Proceedings (2004 Int. Thermal Spray Conf.)*, Ed. E. Lugscheider, German Welding Research Institute, Dusseldorf, 625–631.
- Li C.-J., Wang W.-Z. (2004), Quantitative characterization of lamellar microstructure of plasma-sprayed alumina coating by visualization of voids distribution, *Materials Science and Engineering A*, 386, 10–19.
- Li C.-J., Wang Y.-Y., Li H. (2004a), Effect of nano-crystallization of HVOF-sprayed NiCrBSi alloy on properties of coatings, *J. Vacuum Sci. & Technol. A*, 22, 2000–2004.
- Li C.-J., Wang Y.-Y., Yang G.-J., Ohmori A., Khor K.A. (2004b), Effect of solid carbide

- particle size on deposition behavior, microstructure and wear performance of HVOF cermet coatings, *Materials Science and Technology*, 20, 1087–1096.
- Li C.-J., Wang W.-Z., He Y. (2004c) Dependency of fracture toughness of plasma-spray Al_2O_3 coatings on the microstructure, *J. Thermal Spray Technol.*, 13, 425–431.
- Li C.-J., Liao H.-L., Gougen P., Montovon G., Coddet C. (2005a), Experimental determination of relationship between flattening degree and Reynolds numbers for molten spray droplet, *Surf. Coat. Technol.*, 191, 375–383.
- Li C.-J., Li C.-X., Wang M. (2005b), Effect of Spray Parameters on the Electrical Conductivity of Plasma-sprayed $\text{LA}_{1-x}\text{SR}_x\text{MnO}_3$ coating for the cathode of SOFCs, *Surf. Coat. Technol.*, 198, 278–282.
- Li C.-J., Ning X.-J., Li C.-X. (2005c), Effect of Densification Process on the Properties of Plasma-sprayed YSZ Electrolyte Coatings for Solid Oxide Fuel Cell, *Surf. Coat. Technol.*, 190, 60–64.
- Li C.-J., Yang G.-J., Ohmori A. (2006), Relationship between particle erosion and lamellar microstructure for plasma sprayed alumina coatings, *Wear*, 260, 1166–1172.
- Li Y., Li C.-J., Zhang Q., Yang G.-J., Li C.-X. (2009), Influence of TGO composition on the thermal shock lifetime of thermal barrier coatings with cold-sprayed MCrAlTaY bond coat, *J. Thermal Spray*, 19, doi: 10.1007/s11666-009-9372-8
- Liao H.-L., Zhu Y.-L., Bolot R., Coddet C., Ma S.-N. (2005), Size distribution of particles from individual wires and the effects of nozzle geometry in twin arc spraying, *Surf. Coat. Technol.*, 200, 2123–2130; doi:10.1016/j.surfcoat.2004.12.025
- Lima R.S., Marple B.R. (2007), Thermal spray coatings engineered from nanostructured ceramic agglomerated powders for structural, thermal barrier and biomedical applications: A review, *J. Thermal Spray Technol.*, 16, 40–63.
- Lima R.S., Kucuk A., Berndt C.C. (2002), Bimodal distribution of mechanical properties on plasma sprayed nanostructured partially stabilized zirconia, *Mater. Sci. Eng. A*, A327, 224–232.
- Liu X.Y., Paul K.C., Ding C.X. (2004), Surface modification of titanium, titanium alloys, and related materials for biomedical applications, *Mater. Sci. Eng.*, R 47, 49–121.
- Longo F.N. (1966), Metallurgy of flame sprayed nickel aluminide coatings, *Welding Research Supplement*, 66s–69s.
- Lovelock H.L. (1998), *J. Thermal Spray Technol.*, 1998, 7, 357–373.
- Madjeski J. (1976), Solidification of droplets on a cold surface, *Int. J. Heat Mass Transfer*, 19, 1009–1013.
- Magnani M., Suegama P.H., Benedetti A.V., Espallarga N., Dosta S., Guilemany J.M. (2008), The application of Cr_3C_2 -NiCr coatings to improve the corrosion and wear properties of an AA7050 alloy, *Proceedings of ITSC'2008*, DVS, Dusseldorf, Germany.
- Marple B.R., Voyer J., Simard S. (1999), Tungsten carbide-based coatings as alternatives to electrodeposited hard chromium, *Proceedings of United Thermal Spray Conference 1999*, DVS-German Welding Research, Dusseldorf, 122–127.
- Maruo H., Hirata Y., Kato J., Matsumoto Y. (1988), Development of new plasma spraying torch with three electrodes, *Proceedings of International Symposium on Advanced Thermal Spraying Technology and Allied Coatings (ATTAC'88)*, Japan High Temperature Society, Osaka, 1988, p. 153–160.
- Matejicek J., Kolman B., Dubsky J., Neufuss K., Hopkins N., Zwick J. (2006), Alternative methods for determination of composition and porosity in abrasible materials, *Mater. Characterization*, 57, 17–29.
- McPherson R., Shafer B.V. (1982), Interlamellar contact within plasma-sprayed coatings, *Thin Solid Films*, Vol. 97, p. 201–204.

- McPherson R. (1984), A model for the thermal conductivity of plasma-sprayed ceramic coatings, *Thin Solid Films*, Vol. 112, p. 89–95.
- McPherson R. (1988), The microstructure of thermally sprayed coatings, *Proceedings of International Symposium on Advanced Thermal Spraying Technology and Allied Coatings (ATTAC'88)*, Japan High Temperature Society, Osaka, 1988, p. 25–30.
- McPherson R., Cheang P. (1991), Elastic anisotropy of APS alumina coatings and its relationship to microstructure, *High Performance of Ceramic Films and Coatings*, ed. P. Vincenzini, Elsevier, p. 277–290.
- McPherson R., Gane N., Bastow T.J. (1995), Structural characterization of plasma-sprayed hydroxyapatite coatings, *J. Mater. Sci., Mater. Med.*, 6, 327–334.
- Moreau C., Cielo P., Lamontagne M. (1992), Flattening and solidification of thermally sprayed particles, *J. Therm. Spray Technol.*, 1, 317–324.
- Nakahira H., Tani K., Miyajima K., Harada Y. (1992), Anisotropy of thermally sprayed coatings, *Proceedings of 13th ITSC*, ed. C.C. Berndt, ASM International, Materials Park, OH USA, p. 1011–1018.
- Ohmori A., Li C.-J., Arata Y. (1990a), Influence of plasma spray conditions on the structure of Al_2O_3 coatings, *Trans. Jpn. Weld. Res. Inst.*, Vol. 19, p. 259–270.
- Ohmori A., Li C.-J., Arata Y., Inoue K., Iwamoto N. (1990b), The dependency of the connected porosity in plasma-sprayed Al_2O_3 coatings on microstructure, *J. Jpn. High Temp. Soc.*, 16 (Supplement), 332–340, (In Japanese).
- Ohmori A., Li C.-J. (1991), Quantitative characterization of the structure of plasma sprayed Al_2O_3 coating by using copper electroplating, *Thin Solid Films*, Vol. 201, p. 241–252.
- Ohmori A., Park K.C., Inuzuka M., Arata Y., Inoue K., Iwamoto N. (1991), Electrical-conductivity of plasma-sprayed titanium-oxide (rutile) coatings, *Thin Solid Films*, 201, 1–8.
- Ohmori A., Li C.-J. (1993), The structure of thermally sprayed ceramic coatings and its dominant effect on the coating properties, *Plasma Spraying, Theory and Applications*, ed. S. Surayanarayanan, World Scientific Publishing Co., 1993, p. 179–200.
- Parco M., Zhao L., Zwick J., Bobzin K., Lugscheider E. (2006), Investigation of HVOF spraying on magnesium alloy, *Surf. Coat. Technol.*, 201, 3269–3274, doi:10.106/j.surfcoat.2006.06.047
- Parco M., Zhao L., Zwick J., Bobzin K., Lugscheider E. (2007), Investigation of particle flattening behaviour and bonding mechanisms of APS sprayed coatings on magnesium alloys, *Surf. Coat. Technol.*, 201, 6290–6296, doi:10.1016/j.surfcoat.2006.11.034.
- Pardo A., Casajus P., Mohedano M., Coy A.E., Viejo F., Torres B., Matykina E. (2009a), Corrosion protection of Mg/Al alloys by thermal sprayed aluminum coatings, *Appl. Surf. Sci.*, 255, 6968–6977, doi:10.1016/j.apsusc.2009.03.022
- Pardo A., Merino M.C., Mohedano M., Casajus P., Coy A.E., Arrabal R. (2009b), Corrosion behaviour of Mg/Al alloys with composite coatings, *Surf. Coat. Technol.*, 203, 1252–1263, doi:10.1016/j.surfcoat.2008.10.030
- Pawlowski L. (1995), *The Science and Engineering of Thermal Spray Coatings*, John Wiley & Sons Ltd., Chichester, England.
- Pokhmurska H., Wielage B., Lampke T., Grund T., Student M., Chervinska N. (2008), Post-treatment of thermal spray coatings on magnesium, *Surf. Coat. Technol.*, 202, 4515–4524, doi:10.1016/j.surfcoat.2008.04.036
- Rangaswamy S., Herman H. (1986), Metallurgical characterization of plasma sprayed WC-Co, in: *Advances in Thermal Spray*, Welding Institute of Canada, Pergamon Press, pp. 101–110.

- Rauch J., Manzat A., Killinger A., Gadow R. (2009), HVOF and HVAFS coatings for reduction of wear and friction in cylinder liners, *Thermal Spray 2009: Proceedings of the International Thermal Spray Conference*, Marple B.R., Hyland M.M., Lau Y.-C., Li C.-J., Montavon G. (eds), ASM International, Ohio, 1100–1105, doi:10.1361/cp2009itsc1100.
- Rice R.W. (1977), Microstructure dependence of mechanical behavior of ceramics; properties and Microstructure (*Treatise on Materials Science and Technology, Vol.11*), ed. R.K. MacCrone, Academic Press, p. 199.
- Ruhl R.C. (1967), Cooling rates in splat cooling, *Mater. Sci. Eng.*, 1, 313–320.
- Sampath S., Herman H., Rangaswamy S. (1987), Ni-Al re-evaluated, *Proceedings of 1st National Thermal Spray Conference*, Orlando, Florida, ASM International, Ohio, 47–53.
- Schlaefter T., Bobzin K., Ernst F., Richardt K., Verpoort C., Schreiber F., Schwenk A., Flores G. (2008), Plasma transferred arc spraying of novel wire feedstock onto cylinder bore walls of AlSi engineering blocks, *Proceedings of ITSC2008*. CD-ROM, DVS, Dusseldorf.
- Silva P.L., Santos J.D., Montero F.J., Knowles J.C. (1998), Adhesion and microstructural characterization of plasma-sprayed hydroxyapatite/glass ceramic coatings onto Ti-6Al-4V substrates, *Surf. Coat. Technol.*, 102, 191–196.
- Smith M.F., McGuffi D.T., Henfling J.A., Lenling W.B. (1992), A comparison of techniques for the metallographic preparation of thermal sprayed samples, *Thermal Spray Coating, Properties, Processes and Applications*, ed. T.F. Bernecki, ASM International, Materials Park, OH, USA, p. 97–104.
- Steffens H.-D., Müller K.-N. (1972), Grundlagen der Haftung thermisch gespritzter Schichten, *Adhäsion*, 2, 34–38.
- Steffens H.D., Fischer U. (1989), Correlation between microstructure and physical properties of plasma sprayed zirconia coatings, *Proceedings of 2nd National Thermal Spray Conference*, ASM International, p. 167–173.
- Stewart D.A., Shipway P.H., McCartney D.G. (1999), Abrasive wear behaviour of conventional and nanocomposite HVOF-sprayed WC–Co coatings, *Wear*, 225, 789–798, doi:10.1016/S0043-1648(99)00032-0
- Sturgeon A.J., Reignier C., Laing I., Perrin C. (2003), Development of HVOF sprayed aluminium alloy engine bearing, *Thermal Spray 2003, Advancing the Science & Applying the Technology*, (ed.) C. Moreau and B. Marple, ASM International, Materials Park, Ohio, 825–828.
- Subrahmanyam J., Srivastava M.P., Sivakumar R. (1986), Characterization of plasma-sprayed WC-Co coating, *Mater. Sci. Eng.*, 84, 209–214.
- Sun J., Han Y., Cui K. (2008), Innovative fabrication of porous titanium coating on titanium by cold spraying and vacuum sintering, *Mater. Lett.*, 62, 3623–3625.
- Suryanarayanan R. (1993), *Plasma Spraying: Theory and Applications*, World Scientific, 1993.
- Thomsen P., Larsson B., Ericson L.E., Sennerby L., Lausmaa J., Kasmo B. (1998), Structure of the interface between rabbit cortical bone and implants of gold, zirconium and titanium, *J. Mater. Sci., Mater. Med.*, 8, 653–665.
- Trompetter W.J., Hyland M., Munroe P., Markwitz A. (2005), Evidence of mechanical interlocking of NiCr particles thermally sprayed onto Al substrate, *J. Therm. Spray Technol.*, 14, 524–529.
- Tsui Y.C., Doyle C., Clyne T.W. (1998), Plasma sprayed hydroxyapatite coatings on titanium substrates. Part 1: Mechanical properties and residual stress levels, *Biomaterials*, 19, 2015–2029.

- Tsunekawa Y., Kozaki T., Iwata K., Okumiya M. (2008), Increase in graphite carbon in plasma-sprayed cast iron coatings based on flying droplet diagnostic, *Proceedings of International Thermal Spraying Conference 2008*, DVS, Dusseldorf.
- Tucker Jr. R.C. (1974), Structure property relationships in deposits produced by plasma spray and detonation gun techniques *J. Vac. Sci. Technol.*, 11, 725–734.
- Turunen E., Varis T., Hannula S.-P., Vaidya A., Kulkarni A., Gutleber J., Sampath S., Herman H. (2006), On the role of particle state and deposition procedure on mechanical, tribological and dielectric response of high velocity oxy-fuel sprayed alumina coatings, *Mater. Sci. Eng. A*, A415, 1–11.
- Vardelle M., Besson J.L. (1981), γ -alumina obtained by arc plasma spraying: A study of the optimization of spraying conditions, *Ceram. Inter.*, Vol. 7, p. 48–54.
- Vardelle A., Vardelle M., McPherson R., Fauchais P. (1980), Study of the influence of particle temperature and velocity distribution within a plasma jet coating formation, *Proc. 9th Int. Thermal Spraying Conf*, Hague, 1980, Nederland Inst. Voor Lastetechniek, p 155–161.
- Vardelle M., Vardelle A., Fauchais P. (1983), Study of trajectories and temperatures of powders in a DC plasma jet – Correlation with alumina sprayed coatings, *Proc. 10th Int. Thermal Spraying Conf.*, Essen, May 1983, German Welding Society, p 88–92.
- Vardelle M., Vardelle A., Leger A.C., Fauchais P., Gobin D. (1995), Influence of particle parameters at impact on splat formation and solidification in plasma spraying processes, *J. Therm Spray Technol.*, 4, 50–58.
- Vinayo M.E., Kassabji F., Guyonnet J., Fauchais P. (1985), Plasma sprayed WC-Co coatings – Influence of spray conditions (atmospheric and low-pressure plasma spraying) on the crystal-structure, porosity, and hardness, *J. Vac. Sci., Technol. A*, 3, 2483–2489.
- Wagner N., Gnädig K., Kreye H., Kronewetter H. (1984), Particle velocity in hypersonic flame spraying of WC-Co, *Surf. Technol.*, 22, 61–71.
- Wang W.-Z., Li C.-J., Sonoya K. (1995), Study of lamellar microstructure of plasma-sprayed ZrO_2 -8wt.% Y_2O_3 coatings, *Tagungsband Conference Proceedings (2005 Int. Thermal Spray Conf.)*, Ed. E. Lugscheider, May 2–5, Bussel, Switzerland, German Welding Research Institute, Germany, pp. 1506–1510.
- Wang Y., Khor K.A., Cheang P. (1998), Thermal spraying of functionally graded calcium phosphate coatings for biomedical implants, *J. Thermal Spray Technol.*, 7, 50–57.
- Wang Y.-Y., Li C.-J. (2005), Effect of substrate surface conditions on the bonding mechanism of HVOF coatings, *Thin Solid Films*, 485, 141–147.
- Wang Y.-Y., Li C.-J., Ohmori A. (2006), Examination of factors controlling bonding strength of HVOF sprayed coatings, *Surf. Coat. Technol.*, Vol. 200, 2923–2928.
- Whitmore O.J. (1981), Mercury porosimetry of ceramics, *Powder Technol.*, Vol. 29, p. 167–175.
- Wilden J., Frank H. (2003), Formation of intermetallic phases by laser alloying of thermally sprayed Ti and Al coatings for enhanced wear resistance of light metals, *Thermal Spray 2003, Advancing the Science & Applying the Technology*, (ed.) C. Moreau and B. Marple, ASM International, Materials Park, Ohio, 475–483.
- Xing Y.-Z., Li C.-J., Li C.-X., Yang G.-J. (2008a), Influence of through-lamella grain growth on ionic conductivity of plasma-sprayed yttria stabilized zirconia as an electrolyte in solid oxide fuel cells, *J. Power Sources*, 176, 31–38.
- Xing Y.-Z., Li C.-J., Li C.-X., Yang G.-J. (2008b), Influence of substrate temperature on microcrack formation in plasma-sprayed yttria-stabilized zirconia splats, *Key Engineering Materials*, Volume: 373–374, 69–72.

- Xing Y.-Z., Li C.-J., Zhang Q., Li C.-X., Yang G.-J. (2008c), Influence of Microstructure on the Ionic Conductivity of Plasma-sprayed Ytria-stabilized Zirconia Deposits, *J. Amer. Ceram. Soc.*, 91, 3931–3936, doi:10.1111/j.1551-2916.2008.02775.x
- Xu B., Zhu Z., Ma S., Zhang W., Liu W. (2004), Sliding wear behavior of Fe-Al and Fe-Al/WC coatings prepared by high velocity arc spraying, *Wear*, 257, 1089–1095.
- Yue T.M., Wang A.H., Man H.C. (1999), Corrosion resistance enhancement of magnesium ZK60/SiC composite by Nd:YAG laser cladding, *Scripta Mater.*, 40, 303–311.
- Zheng Z., Huang M., Ding C. (2000), Bond strength of plasma-sprayed hydroxyapatite/Ti composite coatings, *Biomaterials*, 21, 841–849.
- Zimmermann S., Kreye H. (1996), Chromium carbide coatings produced with various HVOF spray systems, *Thermal Spray: Practical Solutions For Engineering Problems, 9th National Thermal Spray Conference & Exposition, 1996 CINCINNATI*, ASM International, Ohio, 147–152.

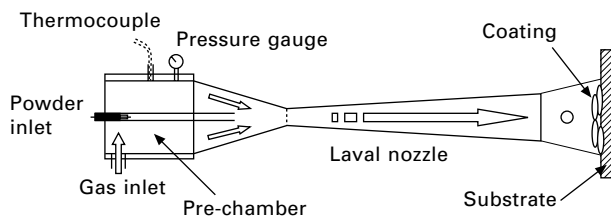
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Abstract: Cold spraying (CS) is a very promising technology for the manufacture of coatings and composites, the spray-forming of near-net components, and the surface protection of materials. This chapter overviews the applications of cold spraying technology for such light alloys as Ti, Al and Mg alloys. The microstructure and properties of cold-sprayed coatings of these alloys depend on the nature of the coating materials in terms of density, strength and activity. The processing parameters must be carefully adjusted to produce the expected coating for the required application. Finally, surface protection of light alloys by the cold spraying technology is also discussed.

Key words: cold spraying; aluminium alloy; titanium alloy; magnesium alloy; microstructure.

8.1 Introduction: General features of cold spraying (CS)

Cold spraying (CS), also termed cold gas-dynamic spraying (CGDS) or kinetic spraying (KS), is a new, emerging coating technology. The general principle of CS is illustrated in Fig. 8.1. In this process a high-pressure gas is preheated and led into a specially designed nozzle (Laval type mostly) at a very high velocity. The fluidized CS powder is fed axially and centrally into the nozzle. In the divergent section, gas and powder particles are accelerated to high velocities (typically 300 to 1200 m/s) and subsequently deposited on an appropriate substrate to form a uniform coating with very little porosity, through an impacting process. Since the coating is formed through plastic deformation or pseudo-deformation of sprayed particles upon



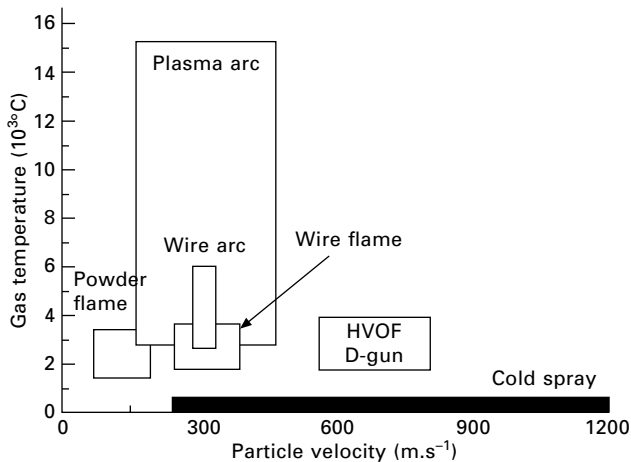
8.1 Schematic diagram of CS process.

impact at a high velocity and in a completely solid state (at a temperature much lower than the melting point of the sprayed materials), the sprayed materials experience little microstructural change, oxidation or decomposition. Consequently, oxidation-free metallic coatings of Al, Ti, Mg, Cu and their alloys can be easily obtained.

The distinguishing feature of CS compared with conventional thermal spray (TS) processes, as shown in Fig. 8.2, is their ability to produce coatings with preheated gas temperatures in the range of room temperature to 700°C, a range that is generally lower than the melting temperatures of the sprayed materials. Consequently, the deleterious effects of high-temperature oxidation, evaporation, residual stresses and other concerns associated with TS methods employing a liquefaction step are minimized or eliminated (Papyrin, 2001). For this reason, CS seems very attractive for depositing oxygen-sensitive light alloy materials such as aluminium alloys, magnesium alloys and titanium alloys to fabricate high purity, thick coatings. In addition, adhesive and cohesive strengths of CS coatings are comparable to those of conventional TS coatings. This makes CS a promising process not only to deposit coatings but also to form near-net shape materials. To summarize, CS is endowed with the following advantages and disadvantages.

Advantages:

- Low temperature process, no bulk particle melting and very little oxidation; retains composition/phases of initial particles
- High hardness, cold worked microstructure and low defect coatings
- Eliminates solidification stresses, enables thicker coatings with compressive stress



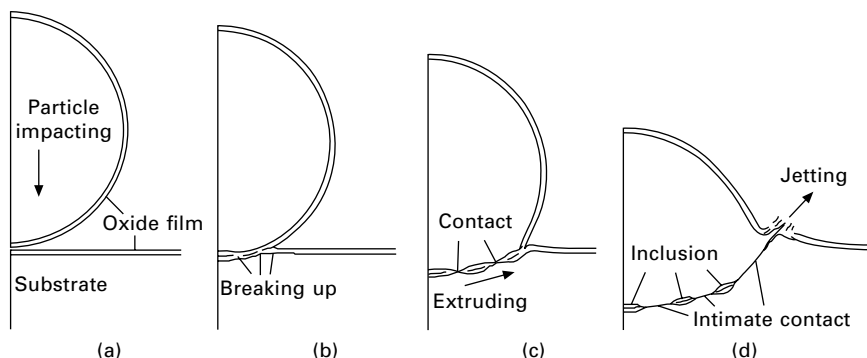
8.2 Comparison of CS with different TS processes in terms of employed gas temperature and particle velocity.

- Lower heat input to work pieces reduces cooling requirement; possible elimination of grit blast substrate preparation; no fuel gases or extreme electrical heating required and probably reduce need for masking; lower cost with the use of air as accelerating gas
- High deposition efficiency and rate by powder particle recycling

Disadvantages

- Hard materials such as ceramics cannot be sprayed without using ductile binders; not all substrate materials will accept coating
- High gas flows, high gas consumption; Helium, believed as the best propulsive gas, is very expensive unless recycled
- Still in research and development (R&D) stage, little coating performance data

Although many coatings have been obtained by CS, the mechanisms by which the solid-state particles deform and bond, both to a substrate and to each other, are not yet well understood. The most prevailing theory of the particle bonding process is that, as is shown in Figure 8.3, the high-velocity impact disrupts the oxide films on the particle and substrate surfaces. As the impact progresses, plastic flow of the interfacial materials extrudes the crashed oxide films to the periphery of the contact interface. The interface fresh metals are pressed into intimate contact with one another under momentarily high interfacial pressures and temperatures. This hypothesis is supported by a number of experimental findings such as: (i) a wide range of ductile (metallic) materials can be successfully cold sprayed while non-ductile materials such as ceramics can be deposited only if they are co-cold-sprayed with a ductile (matrix) material; (ii) the mean deposition particle velocity should exceed a minimum (material-dependent) critical velocity to achieve a deposition which suggests that sufficient kinetic energy must be available to plastically deform the solid material and/or disrupt the surface film; and (iii) the particle kinetic



8.3 Schematic diagram of particle impacting and bonding processes in CS.

energy at impact is typically significantly lower than the energy required to melt the particle, suggesting that the deposition mechanism is primarily, or perhaps entirely, a solid-state process (Grujicic *et al.*, 2003). This theory would also explain the observed minimum critical velocity necessary to achieve deposition, since sufficient kinetic energy must be available to plastically deform the solid material and break up surface oxides.

8.2 Potential applications of CS technique

The CS process was originally developed in the mid-1980s at the Institute of Theoretical and Applied Mechanics of the Russian Academy of Science in Novosibirsk by Papyrin and his colleagues. They deposited a wide range of pure metals, metal alloys, and composites onto substrate materials, and demonstrated the feasibility of CS for a number of applications. A US patent was issued in 1994, and a European patent in 1995 (Papyrin, 2001). Currently, a variety of CS research work is being conducted at various laboratories, academic institutions, and companies in Germany, United States, China, France, Canada, Russia, South Korea, Japan, United Kingdom, and other countries (Gartner *et al.*, 2006; Karthikeyan, 2006; Kroemmer and Heinrich, 2006; Marx *et al.*, 2006). In Europe, Germany is leading the technology development and applications. In the USA, CS technology has been more private industry-driven than government funded. A consortium of companies including Alcoa, ASB Industries, Ford, K-Tech, Pratt & Whitney, and Siemens Westinghouse had funded Sandia National Lab (SNL) to execute a Cooperative Research and Development Agreement (CRADA) on CS technology. SNL and Penn State University have taken up small developmental activities with funds available from private companies such as Alcoa, Ford and P&W. ASB Industries have teamed up with NASA GRC, Pratt & Whitney and many aerospace industries to develop application coatings for the aerospace and gas turbine industries (Karthikeyan, 2004). More recently, The Army team at the Army Research Laboratory have led an international effort to develop the CS manufacturing process and the accompanying Manufacturing Process Standard, MIL-STD-3021, entitled 'Materials Deposition, Cold Spray' (DOD, 2008). Studies conducted by the Army and its partners show that, with a small investment, the Army will achieve millions of dollars of cost-avoidance savings in not having to purchase new parts.

8.2.1 Protective coatings

Corrosion resistant coatings

CS has potential application in depositing corrosion protective coatings for steels in industrial and natural corrosive environments. In contrast to the relatively porous and oxidized conventional TS protective coatings, such

as Zn, Al and their alloys, cold sprayed protective coatings have higher resistance to corrosive media and longer service life. Moreover, the production costs for CS protective coatings are comparable to those of traditional arc sprayed coatings. It is also easy to deposit some cathodic coatings, such as Ti (Wang *et al.*, 2007), Ni and stainless steel, to protect steels in some severe environment. The key problem for these CS protective coatings is to develop industrial equipment and techniques to economically and easily deposit coatings on large and complex surfaces.

High-temperature resistant coatings

Typical high-temperature protective coatings include MCrAlY, (M = Co, Ni or Co/Ni) coatings for high temperature protection and bond coats for thermal barrier coatings (TBCs) (Marrocco *et al.*, 2006a), Cu-Cr layers for oxidation protection of alloy structures, and Cu-Cr-Nb deposits (Li *et al.*, 2006) for high thermal and electrical conductivities at elevated temperatures in rocket engines.

Wear-resistant coatings

These applications involve CS coatings of wear-resistant materials such as cermets (Kim *et al.*, 2005; Li *et al.*, 2007e; Wolfe *et al.*, 2006), metal matrix composites (Weinert *et al.*, 2006; Maev and Leshchynsky, 2006) and anti-attrition alloys (such as Al alloys, Zn alloys, bronzes). The use of these coatings significantly improves the wear performance of industrial components. In addition, abradable coatings are designed to preferentially abrade when contact is made with a mating part. TS abradable coatings have been used for gas path clearance control in gas turbine engines, while for CS, it is promising to fabricate these coatings (such as Al-12Si alloy (Wu *et al.*, 2006), Al-bronze, Ni-Cr-Al alloys and their composites) with polymer or graphite additions.

8.2.2 Functional coatings

As CS technology developed, large amounts of functional coatings were evolved including amorphous coatings (Ajdesztajn *et al.*, 2006a; Yoon *et al.*, 2006), biomaterials and composites (Wang *et al.*, 2007), intermetallic layers (Lee *et al.*, 2006; Spencer and Zhang, 2009), nanostructured coatings (Ajdesztajn *et al.*, 2006b, 2006c), photocatalytic TiO₂ coatings (Han *et al.*, 2006) and thermoplastic deposits (Xu and Hutchings, 2006). However, this kind of coating is not just limited to these materials. Many other coatings may also be developed in various industries in the near future.

8.2.3 Spray forming

Apart from technological advances, other goals of process improvement are cost and lead-time reductions. To achieve these reductions, all aspects of the manufacturing process involved in the fabrication of specific components must be examined. It has been found that CS has a great potential to directly fabricate Ti components (Marrocco *et al.*, 2006b). Not only Ti, but also its alloys and other engineering materials, such as Al and its alloys (Weinert *et al.*, 2006), Cu and its alloys, Ni and its alloys, can be spray-formed to economically produce near-net parts for most industrial applications.

8.2.4 Repair and restoration

An important recent development in the area of rapid tooling repair involves the use of massive TS deposits of steel over ceramic moulds to form tooling used in sheet metal forming. Typically, the spray deposits used in this process are made from twin-wire arc deposition of carbon steels and contain a relatively high fraction of oxide, as well as carbon, rendering the material difficult to repair or adjust by tungsten inert gas (TIG) or metal inert gas (MIG) welding, which is the usual industry practice. CS of high-purity iron as an intermediate layer was found to permit the use of more conventional welding processes for repair and material build-up on dies formed by the TS process. In addition, Al and its alloy coatings are being investigated for repair/refurbishment of space shuttle solid rocket boosters and others, repair and retrieval of parts and plate stocks used in aircraft structures, and repair/refurbishment of gas turbine casings. Similarly to Al, studies are being pursued with copper, titanium and tantalum, etc. in rapid tooling repair (Kroemmer and Heinrich, 2006).

8.3 CS of aluminium (Al) and its alloys

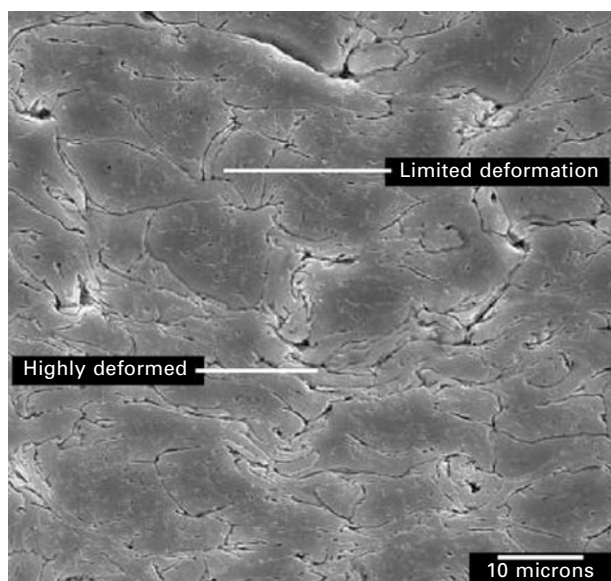
Aluminium and its alloys are widely used as materials for engineering components in the automotive and aeronautical industries because of their light weight and high corrosion resistance. However, sometimes cracks may develop in aluminium components which have to be repaired by welding and conventional thermal spray techniques. CS can be used as an alternative technique to repair such cracks in aluminium components (Ogawa *et al.*, 2008). Due to their low-density, aluminium and its alloys are good candidates for CS, easily achieving the spray velocities required for coating deposition. In addition, aluminium is ductile and therefore can easily undergo plastic deformation when impacting onto the substrate, achieving good bonding with the substrate. Cold-sprayed Al coatings can be applied to protect metal surfaces from atmospheric degradation, because a very thin and impervious

oxide layer is formed on the aluminium surface. Instead of replacing the whole structure, repair and reclamation of the coating are possible, with the required protection coming from the sprayed aluminium structure. Hence, the cold-spray process is highly attractive, enabling tremendous savings by becoming an inherent part of an integral manufacturing process for Al and its alloys.

8.3.1 Microstructure of cold-sprayed Al and its alloy coatings

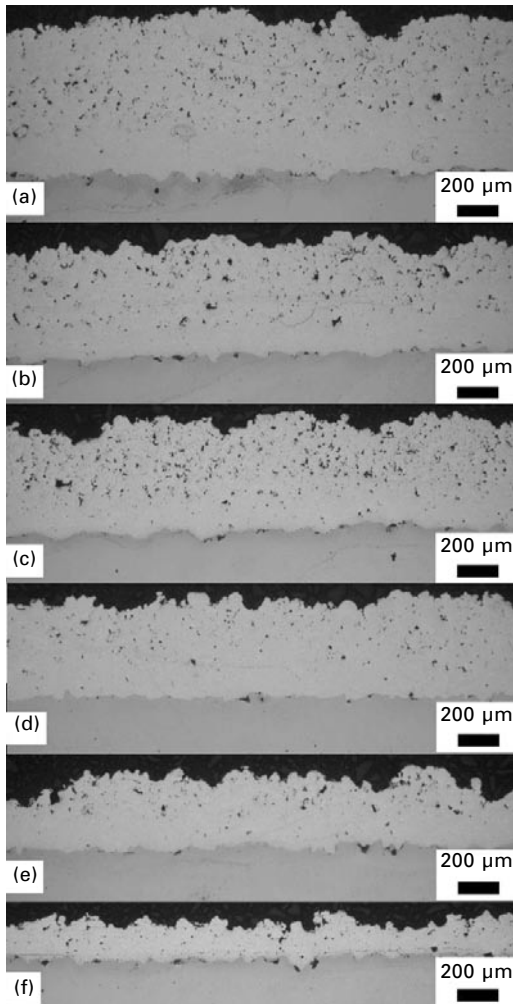
Figure 8.4 shows an etched cross-sectional microstructure of the cold-sprayed Al coating (Morgan *et al.*, 2004). It can be seen that the coating is made up of individual, highly deformed powder splats and some porosity can be observed within the coating although this is limited. Most particles are deformed into long thin splats. However, in some regions, the particles do not appear significantly deformed, with only a slight change to the aspect ratio (width/height) of the particle.

According to the results obtained both by experiment and numerical simulation, many factors influence the particle velocity in CS, including nozzle geometry, accelerating gas conditions and properties of the particles. When the nozzle dimensions are fixed, the standoff distance from nozzle exit to substrate influences the particle velocity and thus the deposition efficiency



8.4 The cross-sectional microstructure of cold-sprayed Al coating (Morgan *et al.*, 2004).

and coating microstructure. Figure 8.5 shows some cross-sectional optical microscopy (OM) micrographs of the as-cold-sprayed Al coatings at different standoff distances (Li *et al.*, 2008a). It was found that the coating thickness decreased with increase of the standoff distance. On the other hand, it was found that the standoff distance has little effect on coating microstructure, but did affect the coating thickness for Al coatings. However, Al coatings present a porous structure, and the porosities are 1–3%. This porous structure for Al coatings has been reported in the literature (Steenkiste *et al.*, 1999;



8.5 OM micrographs of Al coatings deposited at the different standoff distances (a) 10 mm, (b) 30 mm, (c) 50 mm, (d) 70 mm, (e) 90 mm and (f) 110 mm.

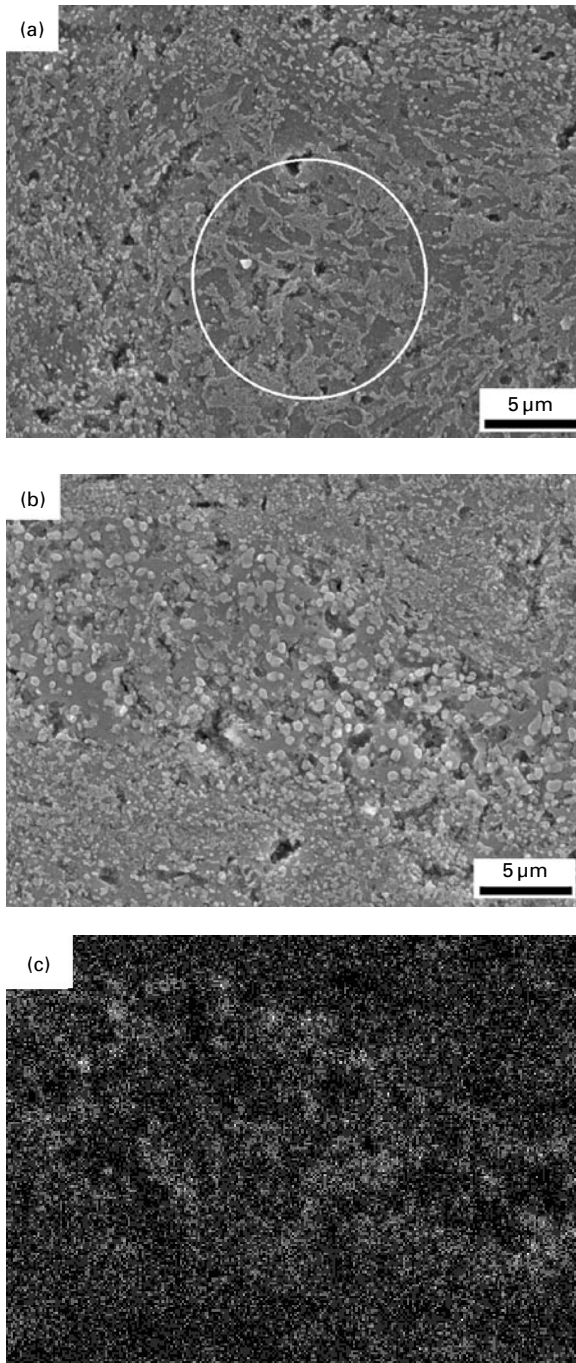
Li *et al.*, 2007a). Generally, the extent of deformation of deposited particles accounts mainly for the porosity of cold sprayed coatings. The deformation extent of a particle is determined by its strength as well as its density, which will influence the kinetic energy of particle at the same velocity (Li *et al.*, 2007a). Therefore, it is difficult to form a low porosity Al coating due to its low density (Van Steenkiste *et al.*, 1999; Li *et al.*, 2007a).

Aluminium alloys with high silicon contents exhibit high strength, low thermal expansion coefficients and high wear resistance. Due to these qualities, together with their excellent castability and reduced density, these alloys are very interesting for the automotive industry where they can successfully replace cast iron parts in heavy wear application. Figure 8.6 shows the microstructure of a cold-sprayed Al-12Si coating (Li *et al.*, 2007b). It was found that, besides α -Al phase in dark grey, many fine silicon cuboids (<1 μm in diameter) and pre-existing silicon particulates in light grey contrast were formed in the coating. There are also some zones with an almost unchanged structure compared to the feedstock, as marked by the white circle in Fig. 8.6a, which indicates the little-deformed part of the particle. These results may indicate that the dissolution and ageing processes have occurred during the coating deposition under the thermal effect of high-temperature gas on the substrate or previously deposited coating surfaces.

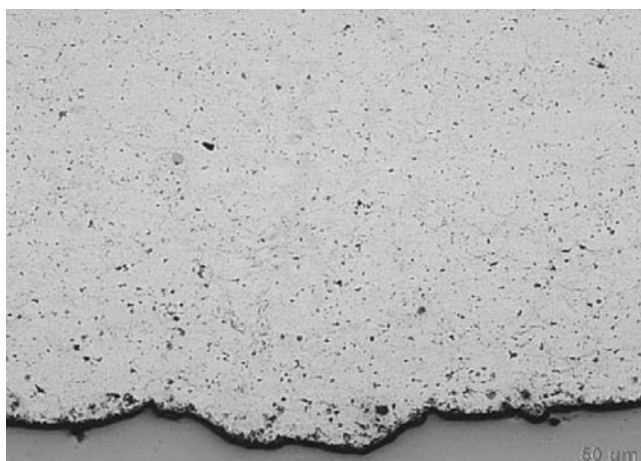
Al-Sn binary alloys are commonly used as sliding bearing materials in the automotive industry. In this binary alloy system, tin is a necessary soft phase in the aluminium matrix. Due to its excellent anti-adhesion characteristics with iron, its low modulus and its low strength, tin can provide a suitable shear surface during sliding. Figure 8.7 shows some optical cross-sectional micrographs of Al-10Sn coatings (Ning *et al.*, 2008). The coatings present a relatively dense structure with some pin holes (indicated as dark spot in Fig. 8.7a). It can be observed that the coatings showed lamellar structures due to deformation during particle impacting. It is quite difficult to distinguish the single particles since the intensive deformation of the particle make a thicker deformation layer, as shown in Fig. 8.7b.

Al-Cu alloys have been extensively used in aerospace, aeronautical and automotive applications due to their high strength. The addition of alloying elements to Al-Cu alloys (such as Mg, Fe, Ag, or Ni) may result in the formation of novel metastable intermetallic phases (such as Al_2Cu , Al_2CuMg , or Al_9FeNi) and consequently improve their mechanical properties. Figure 8.8 shows a cold-sprayed 2618 Al alloy coating (Al-Cu-Mg-Fe-Ni) modified with 0.16 wt.% Sc (Ajdelsztajn *et al.*, 2006b). It can be seen that the coating was very dense and very little porosity is present in the coating. Additionally, the intermetallic Al_2CuMg at the grain boundaries and Al_9FeNi precipitates distributed throughout the matrix can be seen clearly, as shown in Fig. 8.8b.

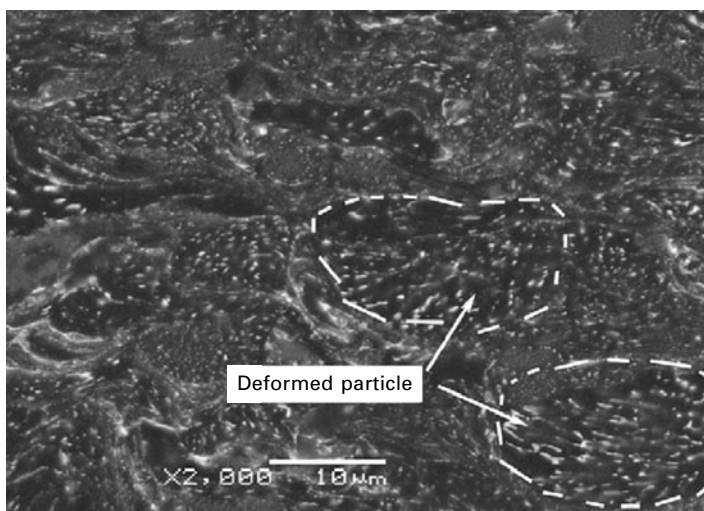
In CS, metals can be deposited ‘in air’ without significant oxidation.



8.6 SEM micrographs of the etched cross-section of CS Al-12Si coating (a, b) and Si element map (c) by EDS analysis of (b).



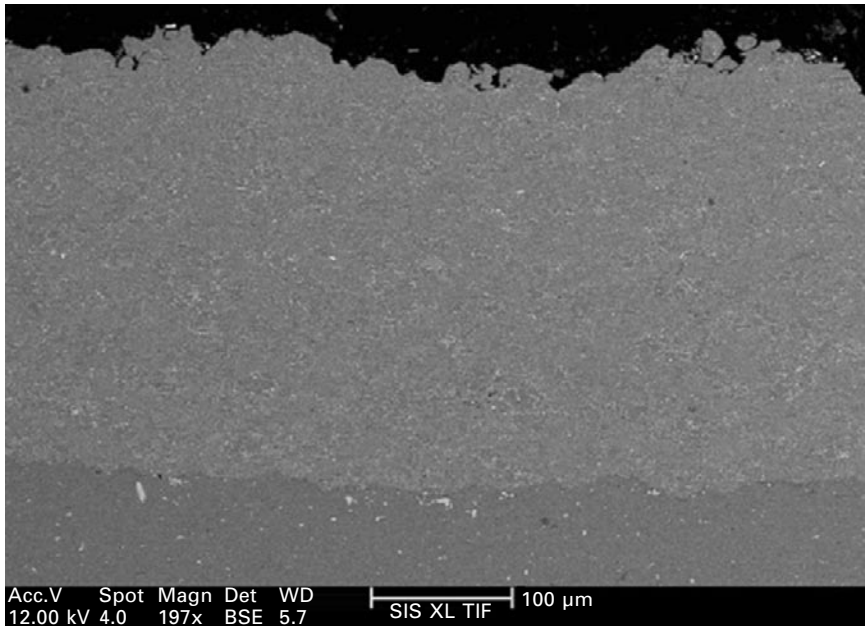
(a)



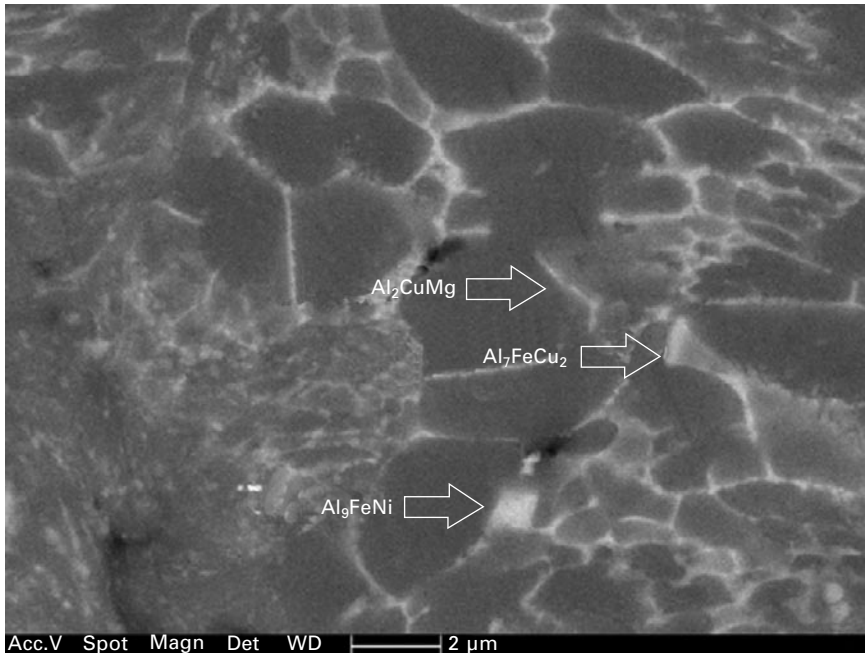
(b)

8.7 Cross-sectional microstructure of Al-10Sn (a) and high magnification (b) (Ning *et al.*, 2008).

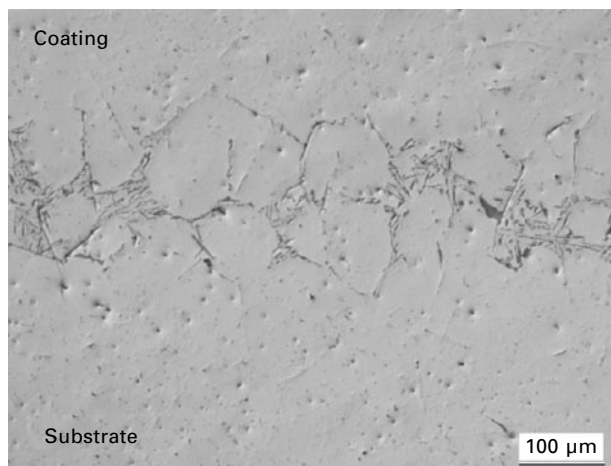
Therefore, the CS process is also very interesting for brazing technology. A braze alloy, Al12Si, was deposited onto an aluminium alloy 6063 by the CS process and the deposited samples were heat-treated at 500 and 615°C under an argon atmosphere (Zhao *et al.*, 2006). Figure 8.9 shows a cross-section of a sample brazed under an argon atmosphere with a very small amount of flux (Zhao *et al.*, 2006). It can be seen that the deposited part and uncoated part were brazed together. The original boundary between the coating and substrate totally disappeared. The substrate shows a very good



(a)



8.8 Microstructure of cold-sprayed 2618+Sc coating (a) low magnification and (b) high magnification micrograph showing the presence of Al_3FeNi and Al_7FeCu_2 precipitates (Ajdelsztajn *et al.*, 2006b).

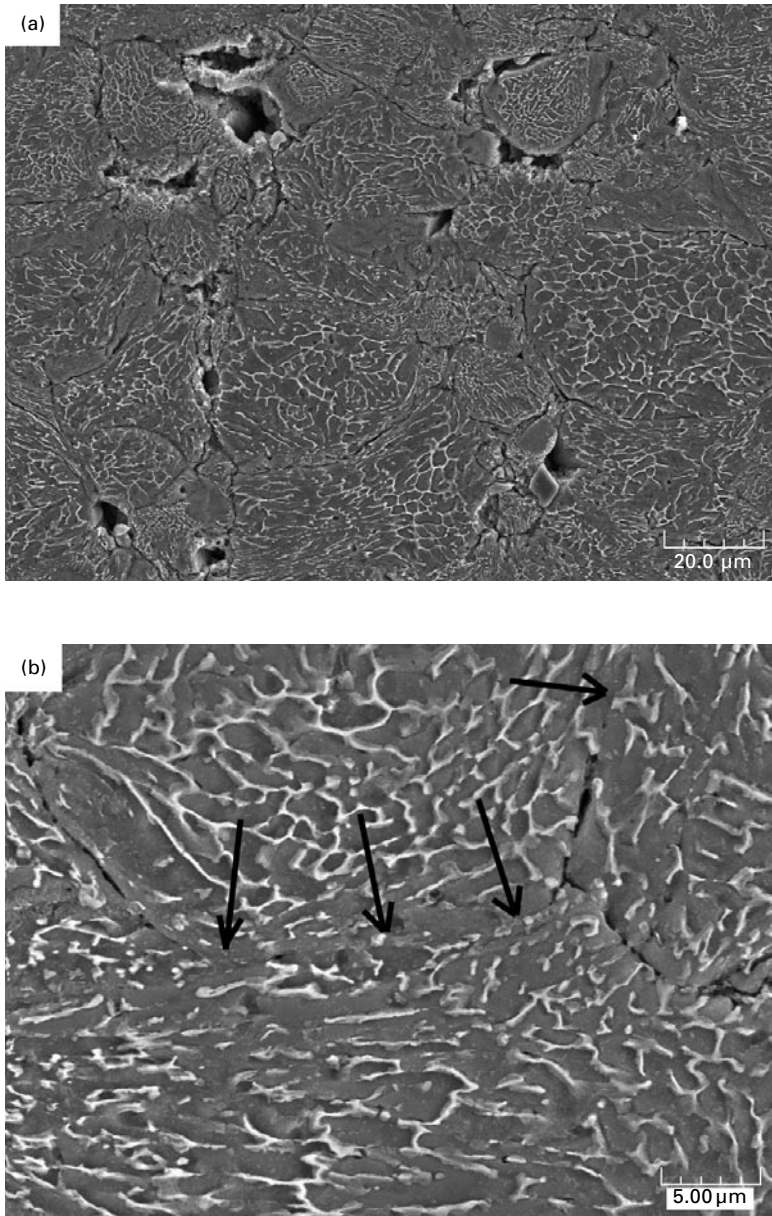


8.9 Microstructure of a sample brazed under argon atmosphere (Zhao *et al.*, 2006).

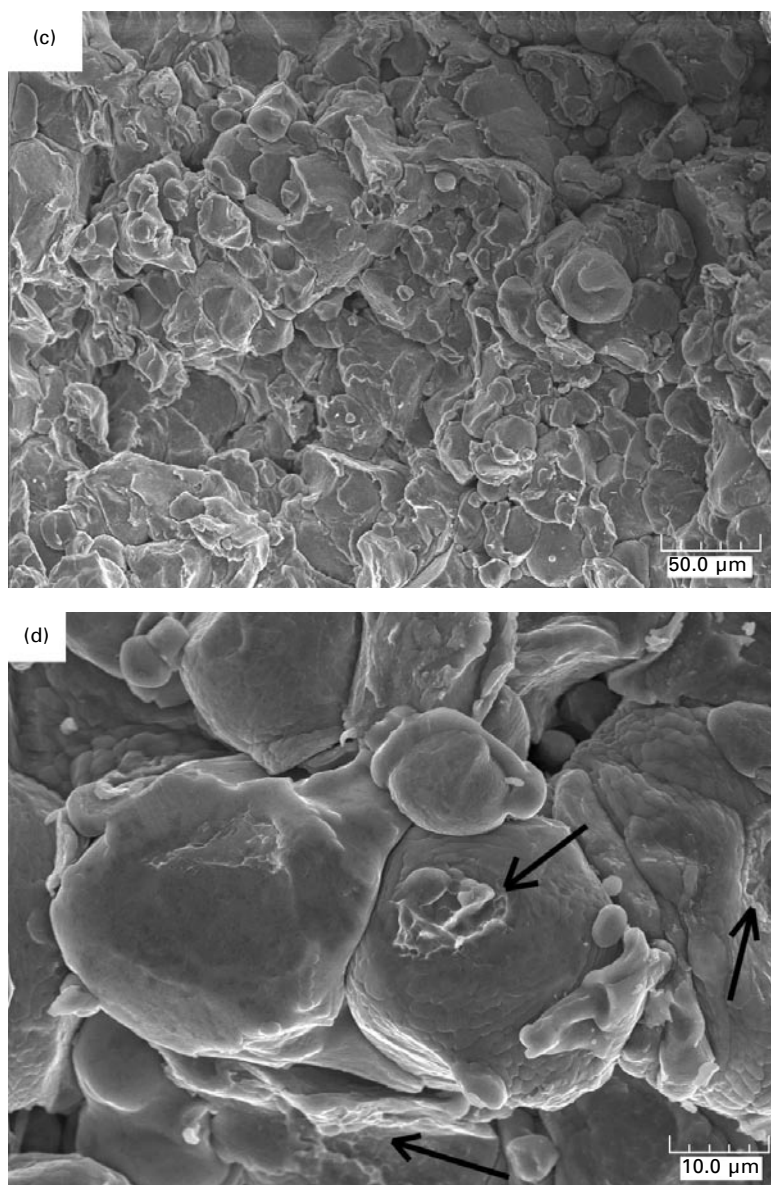
metallurgical bonding with the braze alloy. The results show that the pre-deposition of brazing alloys by the CS process can be a very useful tool for brazing aluminium alloys.

In the past few years, some evidence has come to light of interfacial melting in cold spraying, particularly with low-melting-point metals and alloys. Li *et al.* (2005) proposed that the fine, amorphous particles observed in cold-sprayed zinc were in fact trapped, molten material that had been produced by interfacial jetting. Figure 8.10 shows SEM micrographs of the etched cross-section and of the fractured surface of an Al2319 (Al: 91.4-93.8%, Cu: 5.8-6.8%, Mn: 0.2-0.4%, Fe: ~0.3%, Si: ~0.2%) coating (Li *et al.*, 2007a). It is observed that the Al2319 particles in this coating have experienced intensive plastic deformation, but there are still some pores between the particles. From the fractured surface, by bending, the local melting could be observed with a ductile fracture, marked by an arrow in Fig. 8.10d. It was found that a metallurgical bonding could be formed at some local interfaces in Al2319 coating, as marked by arrows in Fig. 8.10b. From the pull-off test, the adhesive strength of the Al2319 coating was about 34 MPa, which is relatively high taking into account its bulk strength. It was considered that the metallurgical bonding could be associated with the impact fusion during deposition.

Figure 8.11 shows the as-sprayed and fractured surface morphologies of Al-12Si coatings deposited at a high gas temperature of 560°C (Li *et al.*, 2007b). The evidence of melting on a crater caused by the rebounded particle could be observed as marked by arrows in Fig. 8.11b. This is similar to the results observed for cold-sprayed Zn coatings. From the fractured surface, by bending, it is seen that the failure mainly occurred across the flattened

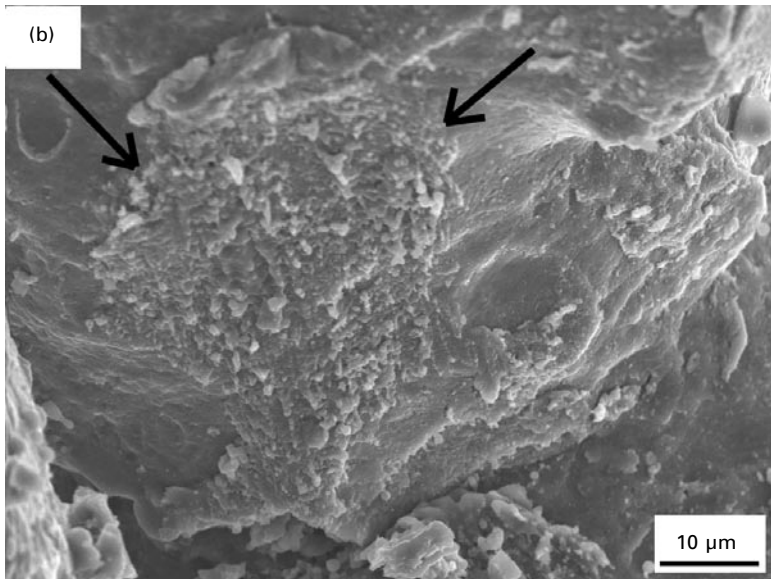
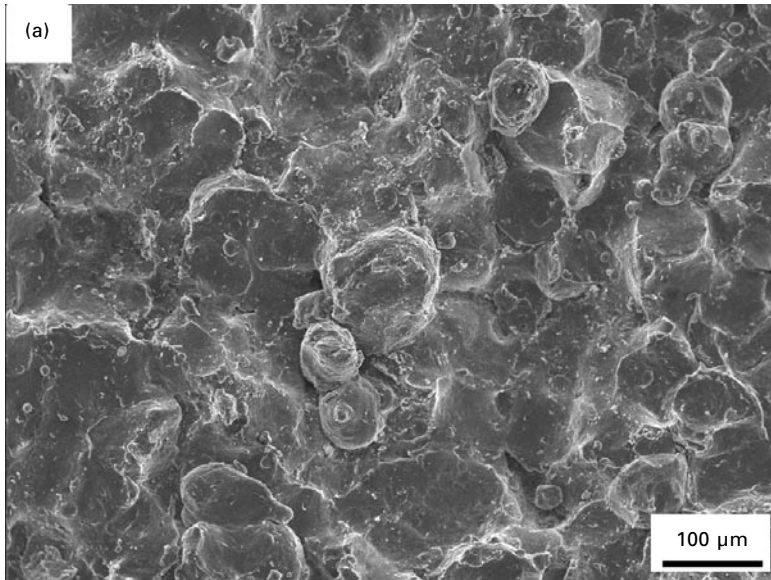


8.10 SEM micrographs of cross-section of Al2319 coating in the etched state (a,b) and fractured surface morphologies (c,d). (b) and (d) are high magnifications of (a) and (c), respectively. The arrows in (b) indicate the local bonding between the deposited particles. The arrows in (d) indicate the ductile fracture appearing as small dimples.

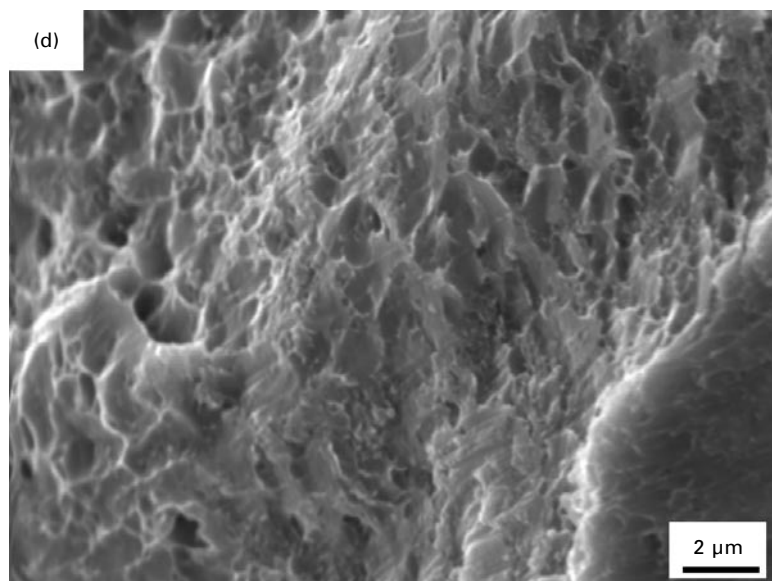
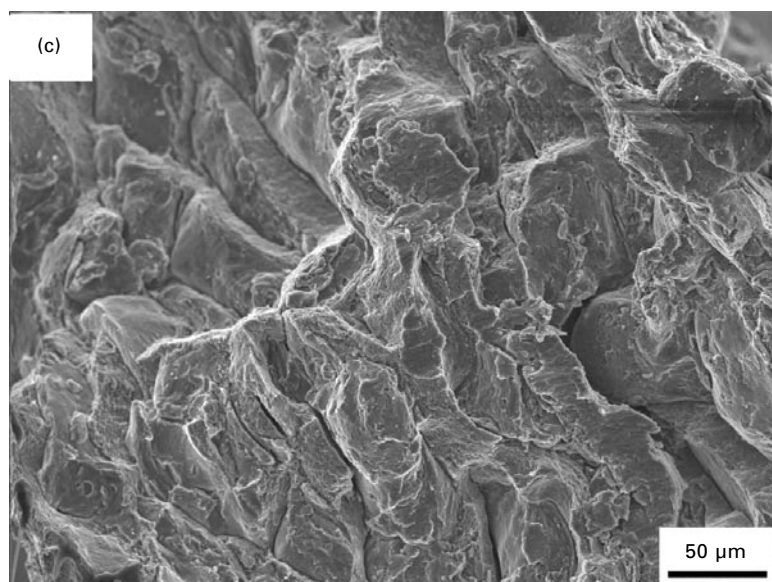


8.10 Continued

particles with a typical ductile fracture. Many dimples were present at the fractured zones, as shown in Figure 8.11d. This fact may suggest a good bonding between the deposited particles. The adhesive strength of the Al-12Si coating was not less than 50 MPa (fracture in the used adhesive), which is relatively high taking into account its bulk strength. A strong metallurgical bonding could be formed in this condition.



8.11 SEM surface morphologies of as-sprayed Al-12Si coating (a,b) and fractured surface morphologies (c,d). (b) and (d) are high magnifications of (a) and (c), respectively. The arrows in (b) indicate the local melting. (d) indicates the ductile fracture appearing as small dimples.



8.11 Continued

8.3.2 Microstructure of cold-sprayed nanostructured Al and its alloy coatings

Nanostructured materials are of widespread interest to the scientific community because of the unique and unusual properties offered by these

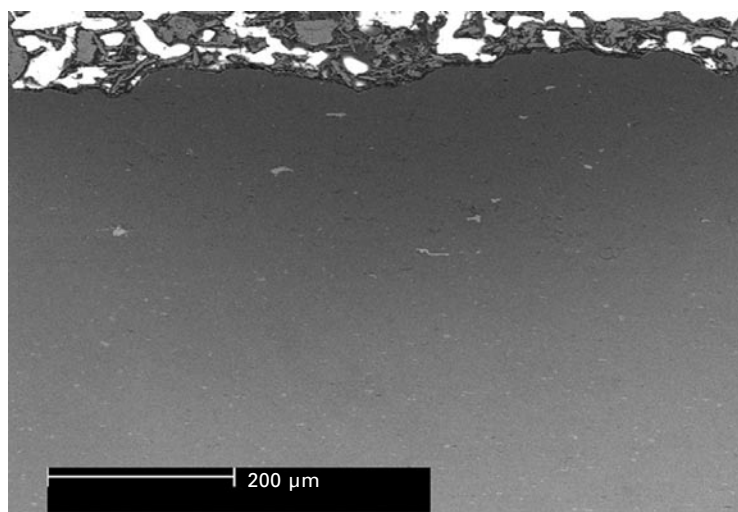
materials. The high grain boundary content of nanocrystalline materials results in grain boundary properties contributing significantly to the bulk material properties. One of the most challenging problems associated with nanocrystalline materials is the consolidation of these small powders into larger shapes that can be used for practical applications. Because in the CS process the particle adheres to the substrate following a solid-state plastic deformation process (with no or very little melting at the local interface), the process is likely a controllable method for preparing metal coatings and bulk metal shapes with homogeneous nanocrystalline microstructures (Ajdelsztajn, 2005). Figure 8.12 shows the microstructure of a cold-sprayed nanocrystalline Al 5083 coating using a cryomilled powder (Ajdelsztajn, 2005). It can be seen that the interface between the coating and the pure Al substrate is almost undetectable in the SEM image, suggesting a good bonding between the coating and the substrate. A TEM analysis performed on the coating indicates the presence of nanocrystalline grains with a grain size distribution from 10 to 30 nm, as shown in Fig. 8.12b.

The CS technique is under development as a method for rapid prototyping and manufacturing, due to its high deposition efficiency. Therefore, cold spraying of cryomilled (or other types of milled) powder could offer a new and alternative approach to existing consolidation techniques for the fabrication of large bulk nanocrystalline metallic samples with reasonable cost. Figure 8.13 shows an example of a cone-shaped nanocrystalline Al 5083 deposit produced using the CS process (Ajdelsztajn, 2005). The production of large nanocrystalline samples will not only benefit engineering applications but will also provide the scientific community with the opportunity to investigate the mechanical behaviour of large bulk nanocrystalline items.

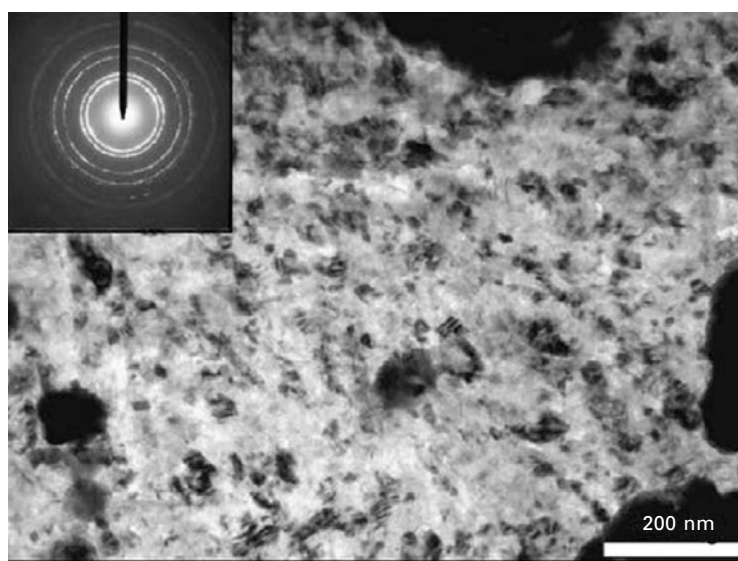
8.3.3 Microstructure of cold-sprayed Al metal matrix composite (MMC) coatings

In some applications, such as heat sinks in electronic packages, only composite materials meet the requirements. Various metallic composites such as Al-Fe (Wang *et al.*, 2008), Al-Cu (Price *et al.*, 2007), Al-Ni (Lee *et al.*, 2007) and Al-Ti (Novoselova *et al.*, 2006) coatings have been successfully deposited. Composite coatings are usually sprayed from preliminarily prepared powder mixtures. Then, the obtained composite coatings can be post-treated to modify their physical and chemical properties (Klinkov *et al.*, 2008).

Figure 8.14 shows the cross-sectional microstructure of the as-sprayed Al-Fe composite deposit examined in the SEM backscattering mode (Wang *et al.*, 2008). It is clear that the coating presents a dense microstructure. Both Fe (light) and Al (dark) can be readily distinguished according to their respective contrast, and were uniformly distributed in the coating. Being softer than iron, aluminium deforms more easily and formed a uniform,



(a)

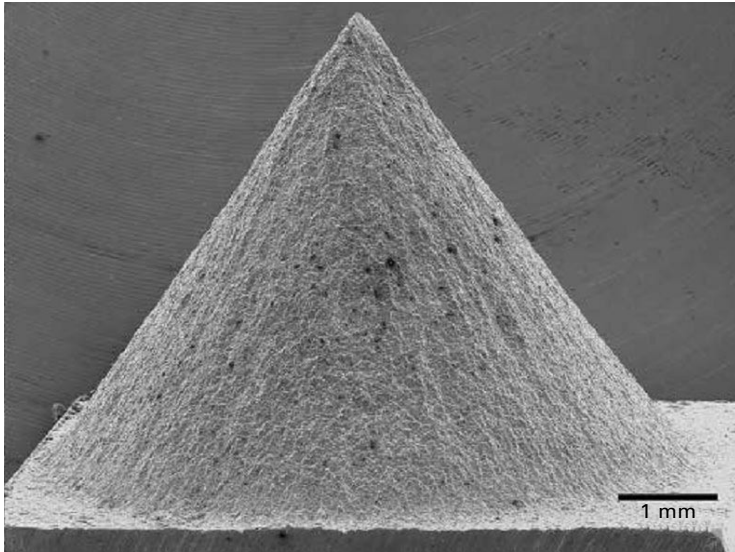


(b)

8.12 SEM images of (a) the cross-section of the nanocrystalline cold-sprayed Al 5083 coating and (b) bright-field TEM image with a SAD pattern (Ajdelstajn *et al.*, 2005).

pore-free matrix, in which Fe appears as isolated particles with relatively less deformation, as shown in Fig. 8.14b.

Figure 8.15 shows the microstructure of a cold-sprayed Al-Cu composite deposit examined in backscattering mode (Price *et al.*, 2007). The copper particles exhibit brighter contrast in the image, due to their higher atomic



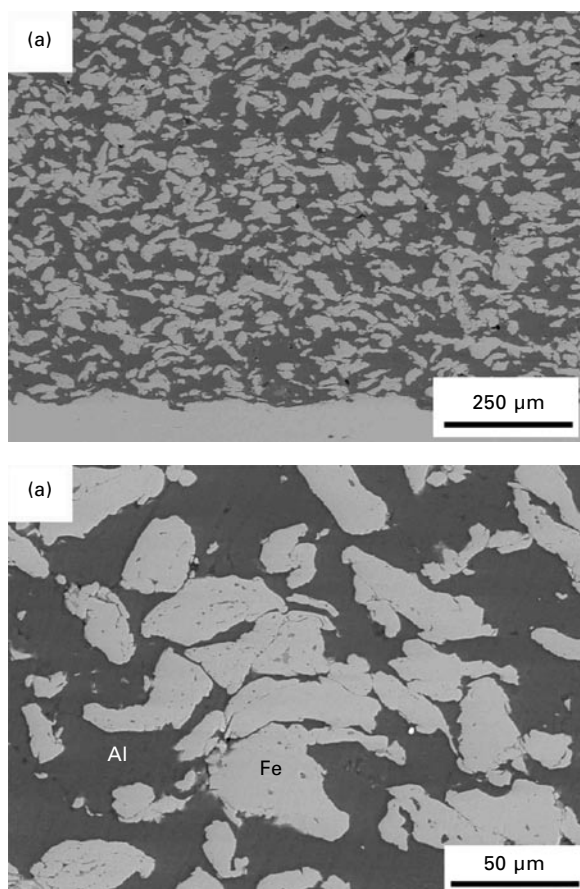
8.13 Nanocrystalline Al 5083 cold-sprayed deposit (Ajdelsztajn *et al.*, 2005).

number. There appears to be little porosity, with good interparticle contact, as shown in Fig. 8.15a. Following heat treatment of the deposits, it was found that one or more intermetallic phases formed at interparticle boundaries, but the coverage of the Al-Cu interfaces was incomplete, as shown in Fig. 8.15b.

Figure 8.16 shows optical microscope images of as-coated Al-Ni coatings (Lee *et al.*, 2007). Ni particles embedded in the continuous Al matrix maintain their overall original size and it is believed that during the process, most of dynamic energy dissipations for the Ni particles were consumed by splatting of the soft Al component. The Ni particles became larger with annealing because of the reaction between Al and Ni particles in the coatings, as shown in Fig. 8.16b.

Besides metal-metal composites, the fabrication of metal-ceramics composites, such as Al-Al₂O₃ (Irissou *et al.*, 2007), Al-SiC (Eesley *et al.*, 2003), Al-TiN (Li *et al.*, 2007d, 2008b) and Al₁₂Si-SiC (Sansoucy *et al.*, 2008) is of great significance in applications, owing to their excellent combination of higher specific strength and improved wear resistance over their base alloys.

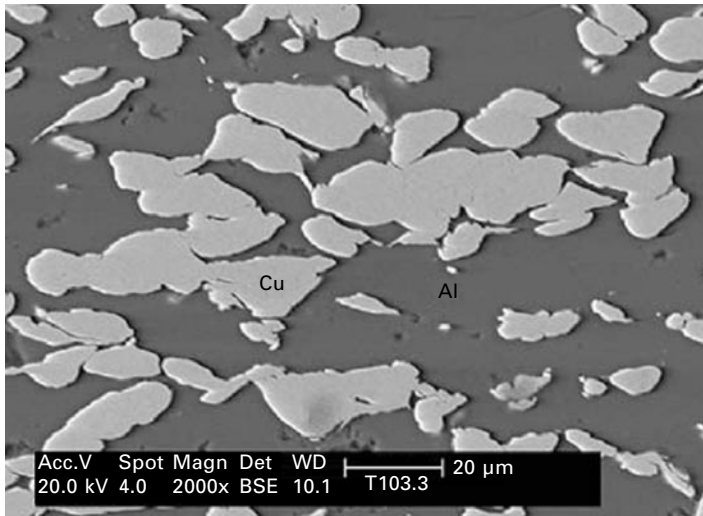
Figure 8.17 shows cross-sectional SEM micrographs of a Al5356/TiN (50 wt.%) composite deposited with a ball-milled blend (BM composite) (Li *et al.*, 2008b). The BM composite presents a dense structure and TiN particles are uniformly dispersed in it. In addition, there are many fine TiN particulates in the BM composite (Fig. 8.17b). Therefore, it is difficult to



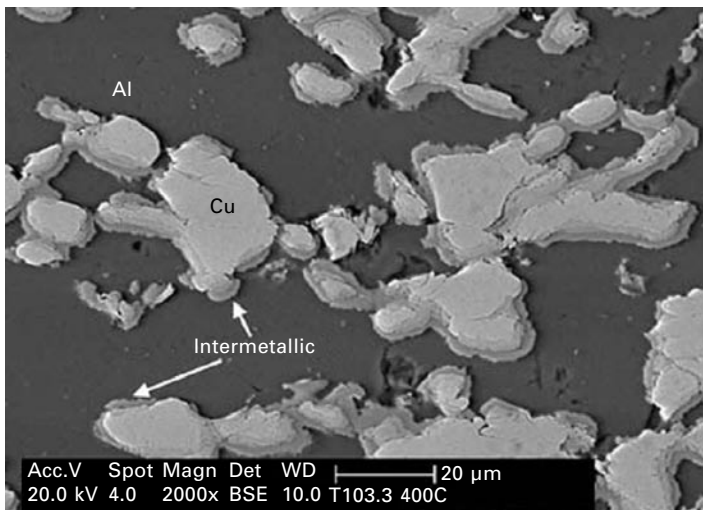
8.14 Cross-sectional images of the as-sprayed aluminium/iron composite deposit (a) overview; (b) high magnification (Wang *et al.*, 2008).

estimate the TiN volume fraction, because of the dispersed superfine TiN particulates. Figure 8.18 shows cross-sectional fracture morphologies of the BM composite obtained by bending the substrate to peel the coating (Li *et al.*, 2008b). The BM composite presents a distinguishing fracture pattern from the pure Al5356 deposit, where the fracture mostly occurred at the weak interfaces between the deposited particles. It seems that the fracture occurred from both the interfaces between TiN particles with the matrix and those between the deposited Al5356 particles. Apparently, the deposited Al5356 particles in the composite presented higher plastic deformation before the fracture occurred. This fact is closely related to the pinning effect of the ceramic particles on the deposited Al5356 particles.

A comparison of the friction behaviour between the ball-milled blend



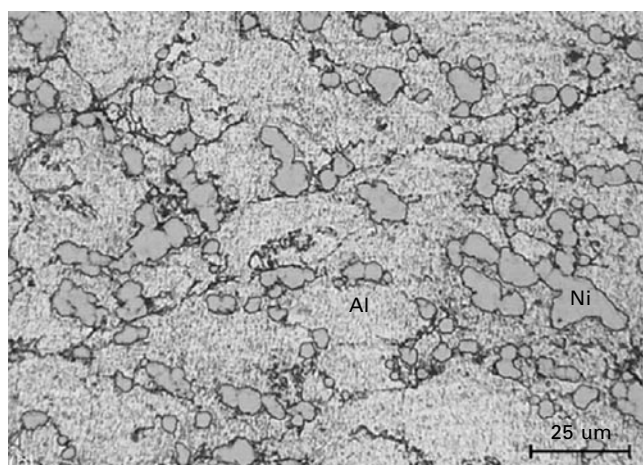
(a)



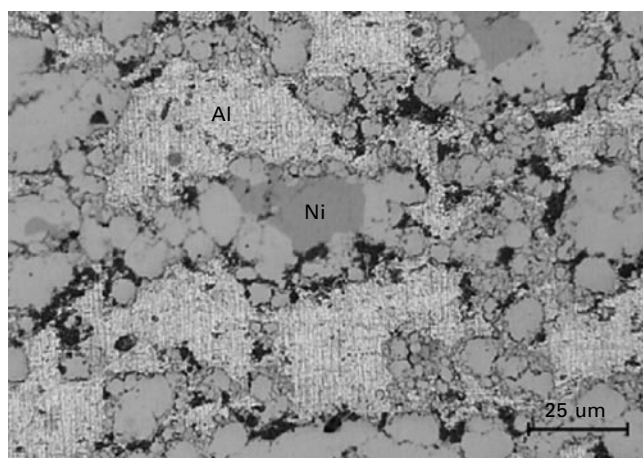
(b)

8.15 SEM images of (a) the as-sprayed Al-Cu deposits and (b) the heat-treated Al-Cu deposits, showing Cu (bright), Al (dark) and an intermetallic layer of intermediate contrast at the interface (Price *et al.*, 2007).

(BM) and the mechanically mixed (MM) composite was carried out. Figure 8.19 shows the morphologies of the worn track of the BM Al5356/TiN (50 wt.%) composite coating after a friction test with a ball-on-disc configuration. It was found that the width of worn track was less than that of the mechanically mixed (MM) composite (Li *et al.*, 2007d). The BM



(a)

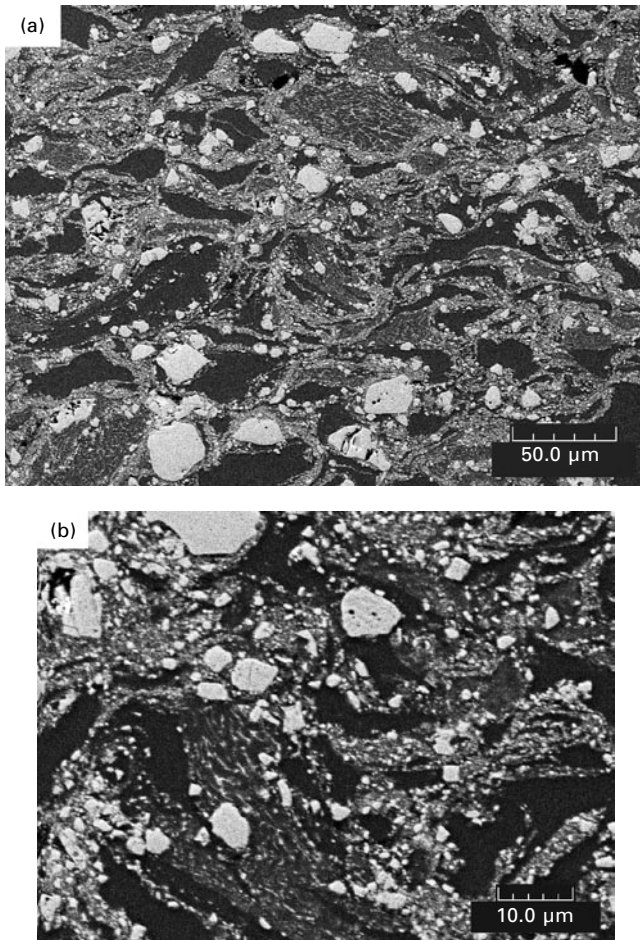


(b)

8.16 Cross-section images (OM) of (a) as-sprayed Al-Ni composite coatings and (b) the heat-treated Al-Ni coatings (Lee *et al.*, 2007).

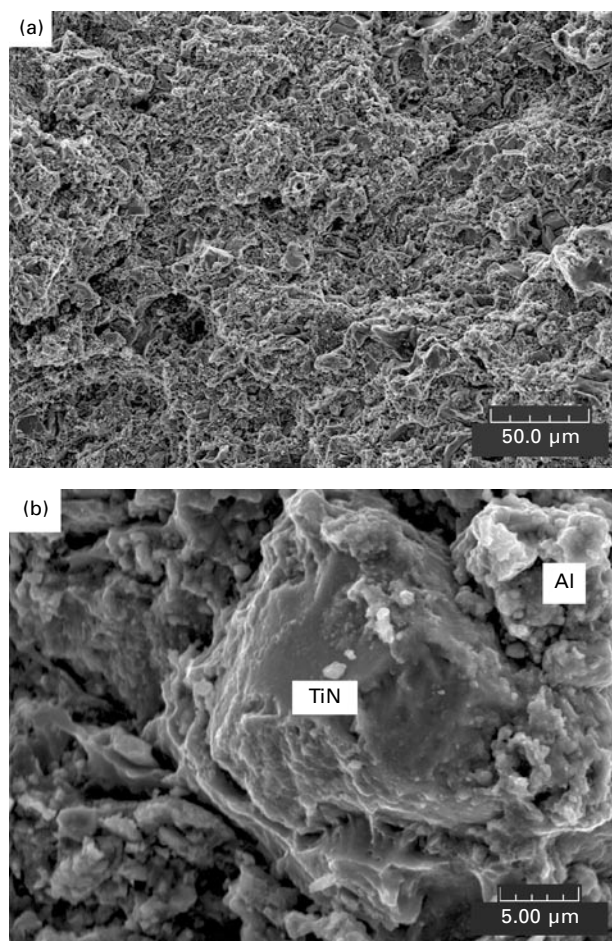
composite coating exhibited a better wear resistance; the wear rate was only half that of the MM composite coating. For the BM composite, more and finer TiN particles were found in the worn track than in the MM composite deposit. Therefore, taking into account the third-body rolling action, it could be considered that the superfine TiN particulates contributed to the further decrease in of wear-rate of the BM composite.

SiC-reinforced Al-12Si alloy coatings were produced using a cold gas dynamic spraying process, as shown in Fig. 8.20 (Sansoucy *et al.*, 2008). It can be seen that the coatings show a dense and clean microstructure and consist of deformed Al-12Si particles that surround the SiC particles. Porosity levels



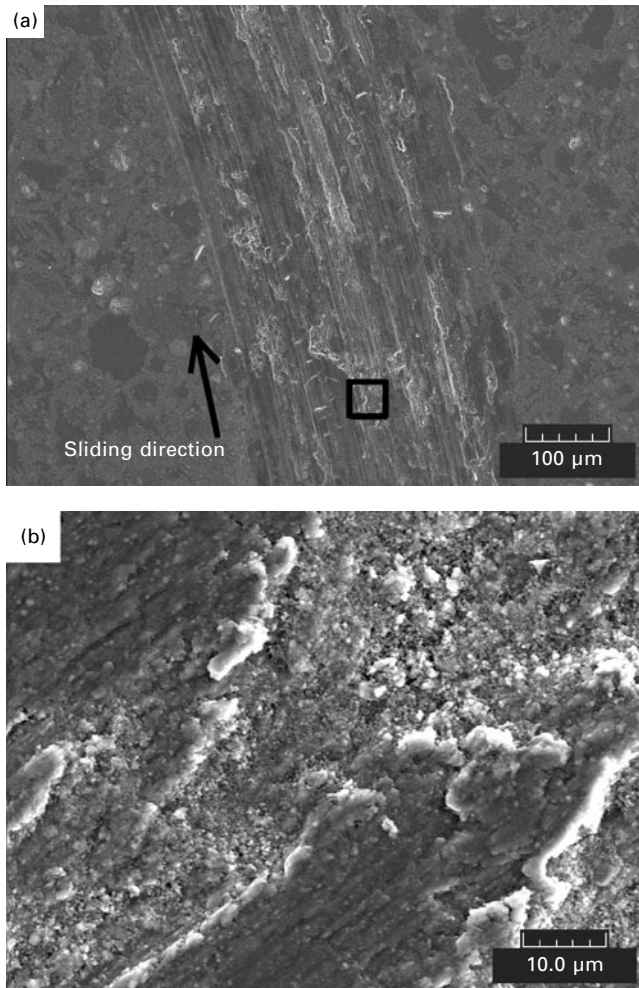
8.17 Typical SEM (backscattered electrons) micrographs of cross-section of BM composite (a) and (b) high magnification of (a). Bright phase is TiN and dark phase is Al5356.

below 1% were found in the composite coatings. The interface between the particles of the matrix is difficult to detect as a result of significant plastic deformation upon impact. The individual SiC particles, corresponding to the darker spots, are randomly distributed and homogeneously dispersed within the aluminium alloy matrix. Agglomerations of SiC particles, often experienced in the casting and powder metallurgy of Al-SiC composites, were not observed in the coatings. Examination at a higher magnification reveals the presence of fractured SiC particles, as shown in Fig. 8.20b. Break-up of the SiC particles most likely occurred during the spray process when SiC particles collided with the SiC particles on the surface of the coating previously deposited.



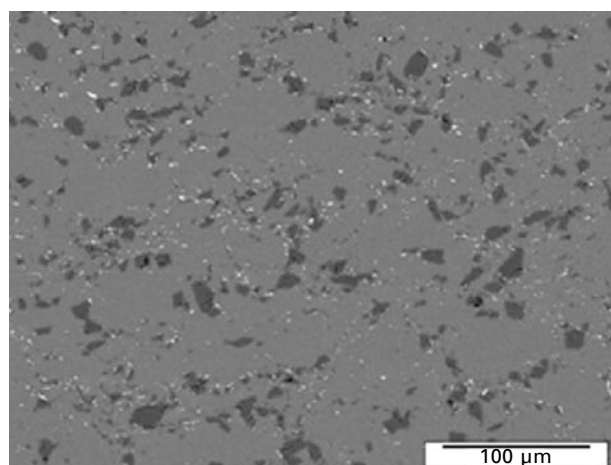
8.18 Fractograph of BM composite obtained by bending the substrate to peel the coating (a) and (b) high magnification of (a).

Figure 8.21 shows the microstructure of an aluminium–alumina (Al–Al₂O₃) composite coating that was processed using a powder blend (Gartner *et al.*, 2006). The hard phases (Al₂O₃) are homogeneously dispersed within the aluminium matrix. Such composites combine high electrical and thermal conductivity with enhanced wear resistance. Since the adhesion between ceramics and metals requires activation of the interfaces to ensure bonding, a substantial amount (50 vol.%) of the hard phase that is present in the powder blend is not incorporated into the coating. Nevertheless, it is worth noting that the embedded amount (of about 15 vol.%) of the hard phase already reduces two-body abrasive wear to half of that obtained for pure aluminium. In comparison to high-performance aluminium alloys, two-body wear is reduced by one third.

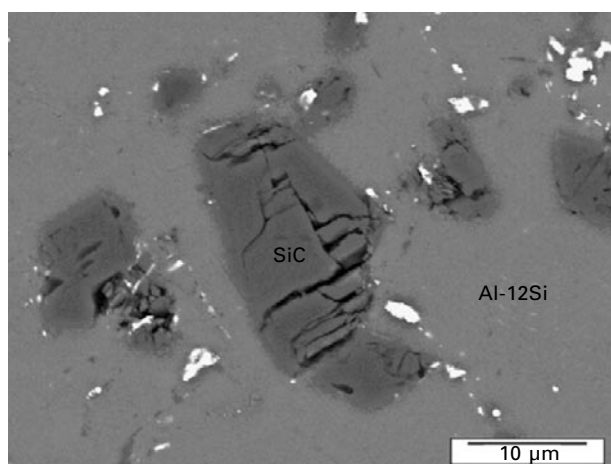


8.19 Worn surface of the BM composite.

High-energy rare earth permanent magnets, such as samarium–cobalt and neodymium–iron–boron alloys, have been the subject of considerable attention in recent years. These materials can be plasma-sprayed, but the resulting coating exhibits porosity, oxidation, and degradation of magnetic properties (Overfelt *et al.*, 1986). Rare earth permanent magnets are hard and brittle, so CS requires the magnetic powder to be mixed with a ductile metallic powder and the two to be sprayed together to form a metal matrix composite. Figure 8.22 shows microstructures of the Al–Nd₂Fe₁₄B composite deposits. It can be seen that many Nd₂Fe₁₄B particles had fractured due to Nd₂Fe₁₄B-on-Nd₂Fe₁₄B impacts (King *et al.*, 2007). Small fragments and



(a)

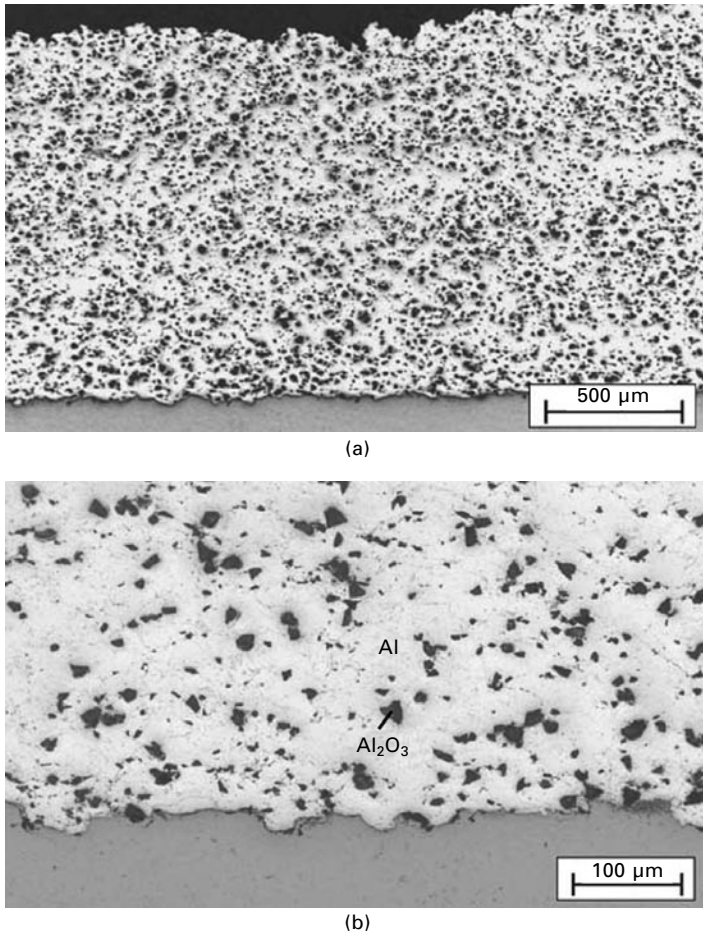


(b)

8.20 SEM images of the cross-sections of Al-12Si/SiC composite coatings (a) and (b) high magnification of (a) (Sansoucy *et al.*, 2008).

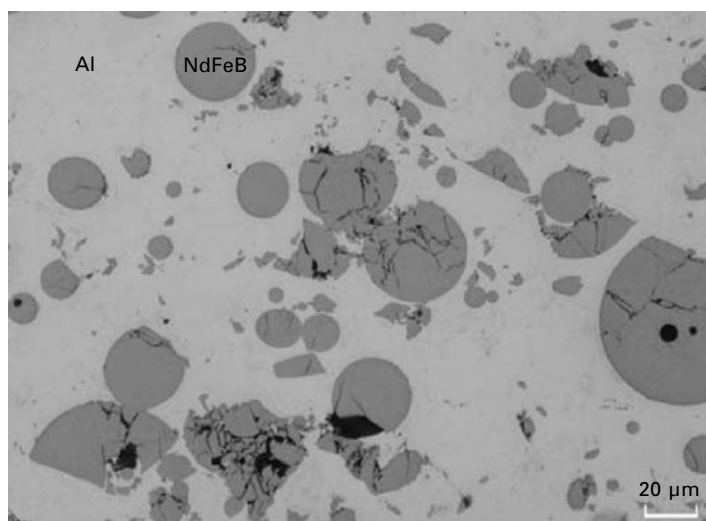
large unbroken particles alike were trapped and completely surrounded by the aluminium matrix. The result shows that the magnetic properties of the Nd₂Fe₁₄B remained unaffected by the CS process (King *et al.*, 2007).

Carbon nanotubes (CNTs) have been used as reinforcement for polymer ceramic and metal matrix composites (MMC) due to their excellent mechanical properties, such as strength and stiffness, up to 63 GPa and ~1 TPa respectively (Yu *et al.*, 2000) and thermal conductivity of up to 3000 W/mK (Kim *et al.*, 2001). Some of the processing techniques used in the fabrication of CNT-reinforced MMCs are conventional powder metallurgy techniques (Feng *et al.*, 2005), electroplating (Arai *et al.*, 2004) from CNT-containing electrolytic



8.21 Cold-sprayed Al-Al₂O₃ composite coating on a steel substrate; (a) overview; (b) close-up (Gartner *et al.*, 2006).

baths, spark plasma sintering (Kim *et al.*, 2006) and thermal spraying (Laha *et al.*, 2004). The manufacture of a uniform dispersion and alignment of nanotubes within the metal matrix composites is still a challenge. The CS process provides a new method for the fabrication of composites reinforced with CNTs. Figure 8.23 shows optical micrographs of the Al-CNT composited coatings (Bakshi *et al.*, 2008). It can be seen that thick and dense coatings in the order of 500 μm were formed by CS. Three distinct features seen in the optical micrographs are: deformed Al particles; Al-Si particles from the collapse of the spray dried particles; and porosity. As seen in Figs 8.4c and d, the Al-Si particles were between the deformed Al particles. The Al particles had undergone a large amount of plastic flow to form elongated disc-like particles which are often referred to as splats (Bakshi *et al.*, 2008).

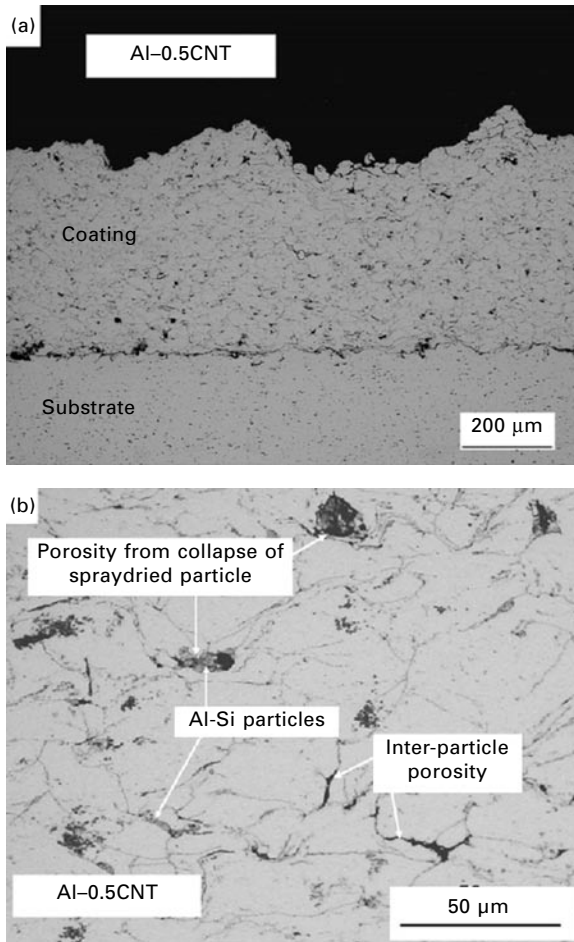


8.22 Microstructure of cold-sprayed Al-Nd₂Fe₁₄B composite deposit (King *et al.*, 2007).

8.3.4 Properties of cold-sprayed Al and its alloy coatings

Cold-sprayed Al coatings can be applied to protect metal surfaces from atmospheric degradation, because a very thin and impervious oxide layer is formed on the aluminium surface. Potentiodynamic polarization studies can detail the corrosion behaviour of the Al alloy. Figure 8.24 shows the corrosion behaviour of cold-sprayed 1100 Al coatings using 100 vol.% He and a mixture of He-20 vol.% N₂ as carrier gases, and the substrate, at pH of 0.9 using H₂SO₄ as an electrolyte (Balani *et al.*, 2005). Both the coatings, as well as the substrate, exhibit continuous passivity after a potential of ~0.11 V. This is a consequence of the continuous dissolution of aluminium and simultaneous surface healing by rapid oxide formation on the surface of the coatings and the substrate. The passivation current density was found to be similar for the two coatings. The higher current values of the coatings than the substrate signify the faster protective layer formation in the case of coatings at 0.9 pH. This is attributed to the presence of porosity and the residual stress in the coating. Additionally, addition of nitrogen in the carrier gas improved the corrosion resistance of the aluminium-sprayed deposition on 1100 Al substrate (Balani *et al.*, 2005).

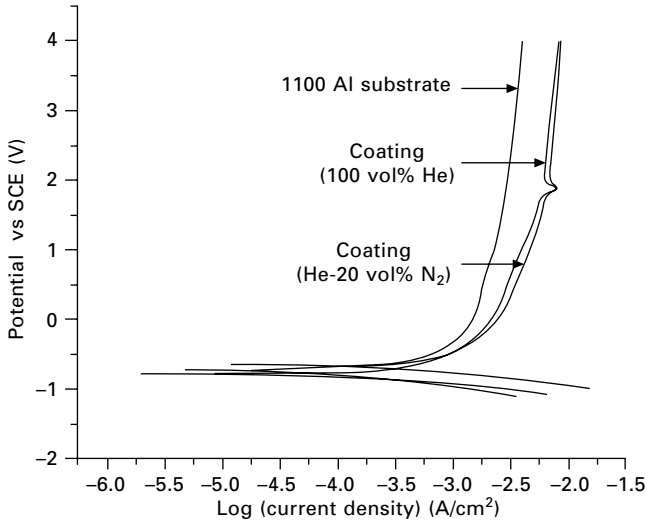
Van Steenkiste *et al.* (2002) studied the microstructure, mechanical behaviour and dynamics of cold-sprayed Al coatings. They found that the cold-sprayed Al coating demonstrates classic metallic behaviour, consisting of a linear region followed by a yielding by a strain-hardening region and



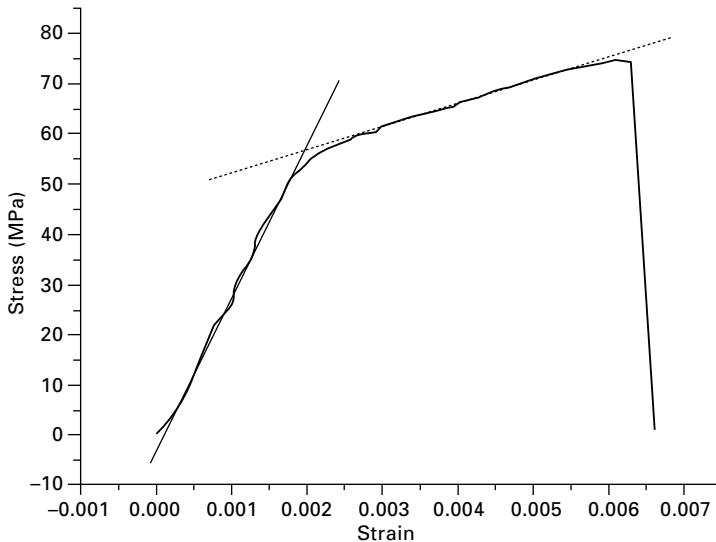
8.23 Optical micrograph of Al-0.5CNT coating (a) and (b) high magnification of (a) (Bakshi *et al.*, 2008).

finally a failure as the strain increases, as shown in Fig. 8.25. In addition, the measured results showed that the elastic modulus, yield point, and ultimate tensile strength of cold-sprayed Al coating were 30.8GPa, 56MPa and 75MPa, respectively, compared with those of 69GPa, 12MPa and 47MPa, respectively, for the annealed Al (Van Steenkiste *et al.*, 2002).

For thermally-sprayed coatings, post-spray heat treatment can be applied to release the residual stress, to decrease porosity, or to improve the properties of coatings (Pawlowski, 1995). Many investigators have examined the effect of post-spray annealing treatment on the microstructure of cold-sprayed coatings, aiming at the modification of coating service performance (Calla *et al.*, 2006; Li *et al.*, 2006; Ogawa *et al.*, 2008; Li and Li, 2004, 2006;



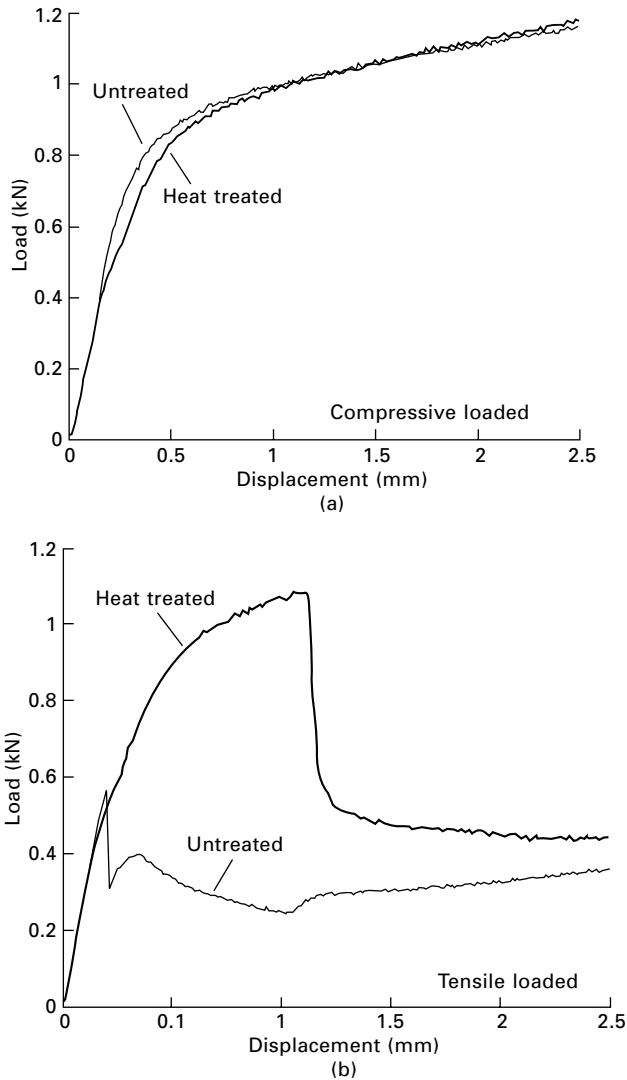
8.24 Comparison of potentiodynamic polarization behaviour for 1100 Al and the two different 1100 Al coatings, cold sprayed with 100 vol.% He and He with 20 vol.% N₂ as carrier gas at 0.9 pH (Balani *et al.*, 2005).



8.25 Tensile testing of a cold-sprayed Al coating (Van Steenkiste *et al.*, 2002).

McCune *et al.*, 2000; Hall *et al.*, 2006). It is expected that the incompleteness of interface bonding can be healed and modification of the inner particle structures in a cold-sprayed coating can be achieved through post-spray

heat treatment, and consequently the coating properties improved. Figure 8.26 shows the results of four-point bending tests on the heat-treated (HT) cold-sprayed Al specimens (Ogawa *et al.*, 2008). It can be seen that, in the case of compressive loading, the un-heat-treated specimens showed a higher strength as compared to the HT specimens because of the decrease in the hardness value after heating. On the other hand, in the case of tensile loading, the HT specimens showed a significantly higher strength and displacement



8.26 Results of four-point bending tests of heat-treated Al specimens. (a) Compressive loaded and (b) Tensile loaded (Ogawa *et al.*, 2008).

as compared to the untreated specimens; the strength of the former is two times higher than that of the latter. Moreover, the displacement of the HT specimens is five times higher than that of the untreated specimens.

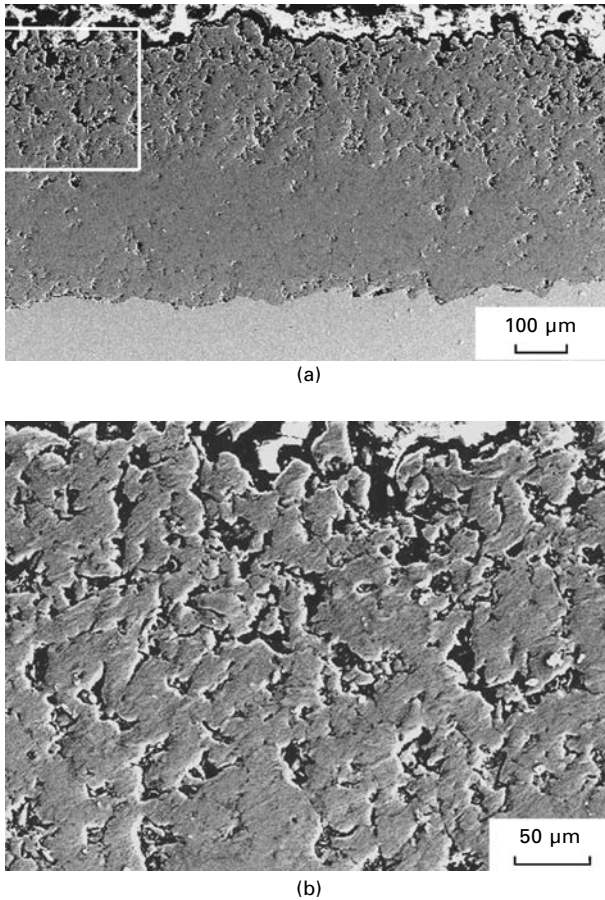
8.4 CS of titanium (Ti) and its alloys

Titanium and its alloys have wide applications in aerospace, implant, and corrosive environments due to their unique properties, such as high strength-to-weight ratio, excellent corrosion resistance, specific corrosion/oxidation resistance and biocompatibility (Zhou and Ning, 1993). However, the high-oxygen affinity of titanium limits the affordability of this material due to expensive production processes that require a controlled atmosphere, such as vacuum melting (Lutjering and Williams, 2003). Because cold-spraying is a 100% solid-state process, the deposition ‘in air’ of titanium coatings without significant oxidation represents an important technical achievement and provides a cost-effective alternative in direct fabrication of titanium products (Zahiri *et al.*, 2009).

8.4.1 Microstructure of cold-spray Ti and its alloy coatings

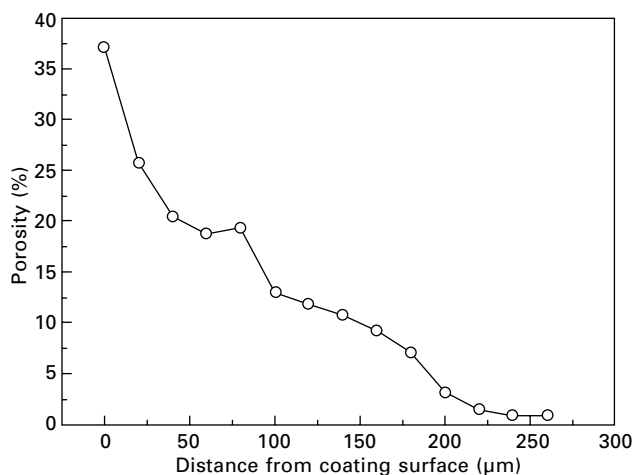
Figure 8.27 shows the typical microstructure of a cold-sprayed Ti coating deposited with angular Ti feedstock and using N₂ as the driving gas (Li and Li, 2003). It was observed that the coating consisted of two distinguishable regions: a porous top layer, as shown in Fig. 8.27b and a dense inner one. The porous layer was about 150–200 µm deep from the coating surface under the used spray conditions (Li and Li, 2003). It was confirmed that the thickness of this porous layer was almost independent of the whole coating thickness (Li, 2005). Figure 8.28 shows the porosity distribution along the thickness from this coating surface, which was measured from the coating surface at intervals of 20 µm (Li and Li, 2004). It can be noticed that the porosity decreased with the distance from the coating surface. These facts indicate that Ti spray particles were deposited on the substrate surface to form a porous coating owing to limited deformation. Those particles were deformed successively during the deposition of following spray particles. Accordingly, the deposited layer was gradually densified by succeeding particles, which tamped the deposited porous layer. The cumulative tamping effect of successive impacts led to a gradual densification of the porous layer. The most recently deposited particles experienced less tamping effect than the previously deposited particles. Therefore, with increase of coating thickness, the surface coating always kept a porous structure and the deeper coating became denser.

Using a porous sponge Ti feedstock, the formation of a very porous Ti



8.27 (a) Typical microstructure of cold-sprayed Ti coating deposited using N₂ and (b) high magnification of the top layer.

coating was reported by Kathikeyan *et al.* (2000), even deposited using He gas. According to our findings and those reported in the literature, it is proposed that the tamping effect that results in densification of the deposited coating in cold spraying depends on the momentum of the impacting particles and particle morphology. For particles of low density, such as Al and Ti, less tamping occurs than with Cu powder. Therefore, the top porous layer with Cu is far less obvious than with Ti coatings. Because of the tamping effect, it can be considered that if the particle velocity is increased, the tamping effect will be enhanced. As a result, the thickness of the porous layer will be decreased. Figure 8.29 shows the typical microstructure of a Ti coating deposited with the same angular Ti feedstock and using He as the driving gas (Li and Li, 2003). This coating also presents two typical regions. As



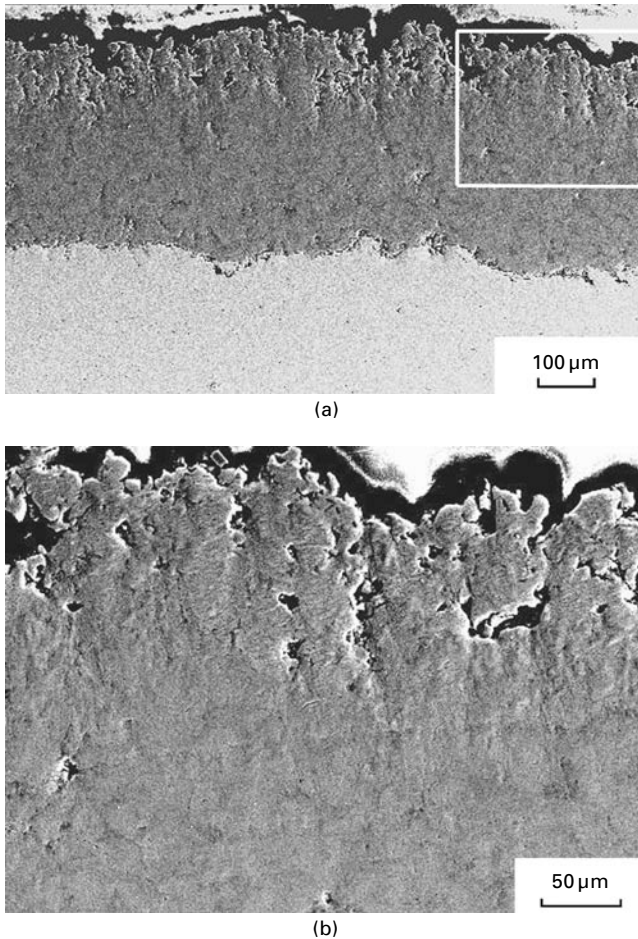
8.28 Change of the porosity in Ti coating (Fig. 8.27) with the distance from coating surface.

seen from Fig. 8.29b, the thickness of the porous layer was about 100 μm which is less than that in the coating deposited using N₂ gas. Investigations have shown that spray particles can reach a much higher velocity using He as the driving gas than using N₂. Therefore, the tamping effect is enhanced by using He gas.

In addition, the investigation also showed that the porous feature of the coating was little affected by the powder morphology (Li, 2005). Figure 8.30 shows the typical microstructure of a cold-sprayed Ti coating deposited using spherical Ti powder and N₂ gas (Li, 2005). It could be seen that this coating also had a porous top layer. The shapes of the micropores were slightly different from those in the coating deposited with the angular Ti powder, as shown in Figs 8.27 and 8.29, but with the porous sponge Ti powder, the as-sprayed Ti coating presented a much more porous structure, no matter which gas was used (Karthikeyan *et al.*, 2000).

Finally, the tamping effect also depends on the hardening effect occurring during deformation (Li, 2005). The less hardening materials are more easily deformed and consequently a less porous layer is formed under the same spray conditions.

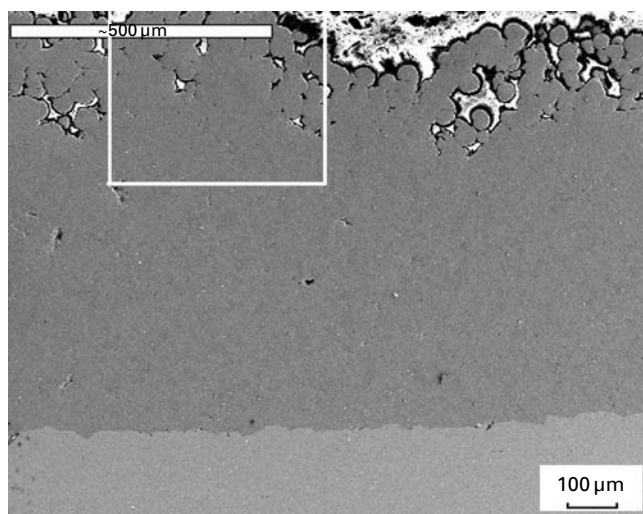
As mentioned, the tamping effect will take place under all spray conditions, but its influencing extent will depend on the particle conditions. A recent study (Li *et al.*, 2007a) indicated that the formation mechanism of a porous coating structure in cold spraying depends mainly on the particle conditions, e.g. particle velocity, strength, particle surface activity and oxide films. These effects will be discussed in the following section.



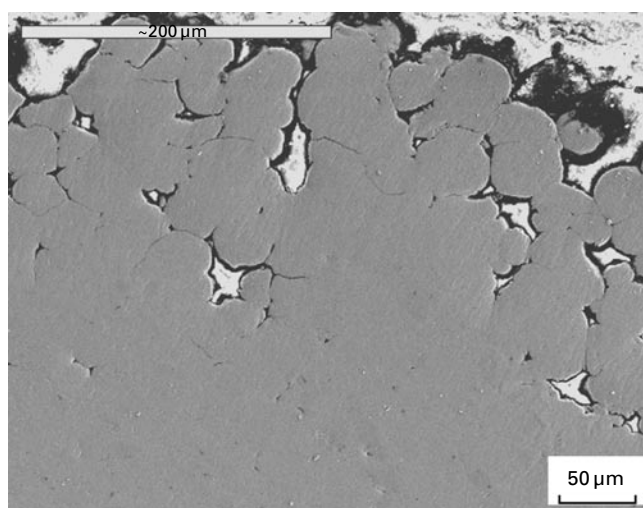
8.29 (a) Typical microstructure of cold-sprayed Ti coating using He and (b) high magnification of the top layer.

8.4.2 Formation mechanisms of the porous microstructure of cold-sprayed Ti and its alloy coatings

Generally, the deformability of the sprayed metallic particles accounts mainly for the micropores in the as-cold-sprayed coatings. As reported in the literature, it is easy to produce dense coatings of pure Cu, Zn, Fe, etc. (Stoltenhoff *et al.*, 2002; Li and Li, 2004; Van Steenkiste *et al.*, 1999) owing to their good deformability, whereas it is difficult to form dense coatings for some high strength alloys, such as stainless steel and MCrAlY (Schmidt *et al.*, 2006; Stoltenhoff *et al.*, 2002). Moreover, it is difficult to produce a



(a)



(b)

8.30 Typical microstructure of cold-sprayed Ti coating with spherical Ti feedstock and using N₂.

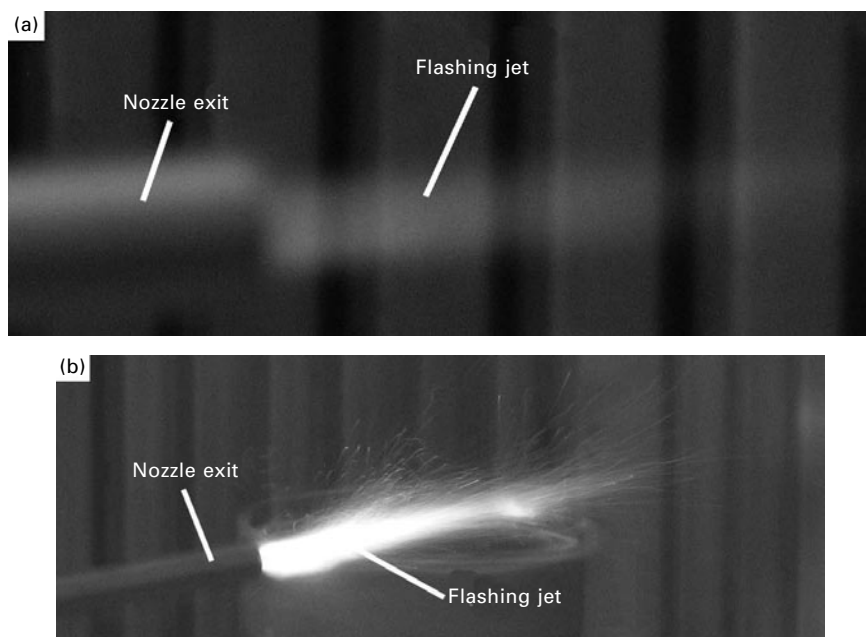
dense coating using larger particles, due to their relatively lower velocities and wider gaps to be filled between the deposited particles during spraying (Schmidt *et al.*, 2006; Van Steenkiste *et al.*, 2002). However, for Al and Ti powders, although they have relatively low strength, it is still difficult to form a dense coating, especially for Ti (similar to tantalum coating (Van Steenkiste and Gorkiewicz, 2004)). Although the accumulative tamping effect plays a role in the formation of a porous structure, a large number of experimental

results have recently demonstrated that there are still other important factors influencing the porous coating microstructure. Essentially, the pores are associated with insufficient deformation of the deposited particles for some reason – maybe because of the lower deformability of the particles, or the larger particle sizes and lower velocities, or for other reasons.

For a better understanding of the deposition behavior of different materials, many types of powders were used in the study (Li *et al.*, 2007a), such as Cu, Zn, Fe, Ni, Al, Ti, Ni-Cu alloy, Cu-Sn alloy, Al-12Si alloy, Ti-6Al-4V, FeAl, NiAl, 316L stainless steel, and MCrAlY. It was found that particle surface reactivity plays an important part in the formation of porous Ti and Ti-6Al-4V alloy coatings (Li *et al.*, 2007a).

It was reported by Schmidt *et al.* (2006) that the critical velocity for Ti particles of 25 μm was about 750 m/s. According to this critical value and the simulation result of particle velocity under the spray conditions used in the work of Li *et al.* (2007a), only Ti particles less than 6 μm can be deposited. This suggests a deposition efficiency of less than 5%. However, the actual deposition efficiency of the Ti powder was estimated to be higher than 75%. Therefore, there must be other important factors influencing the deposition.

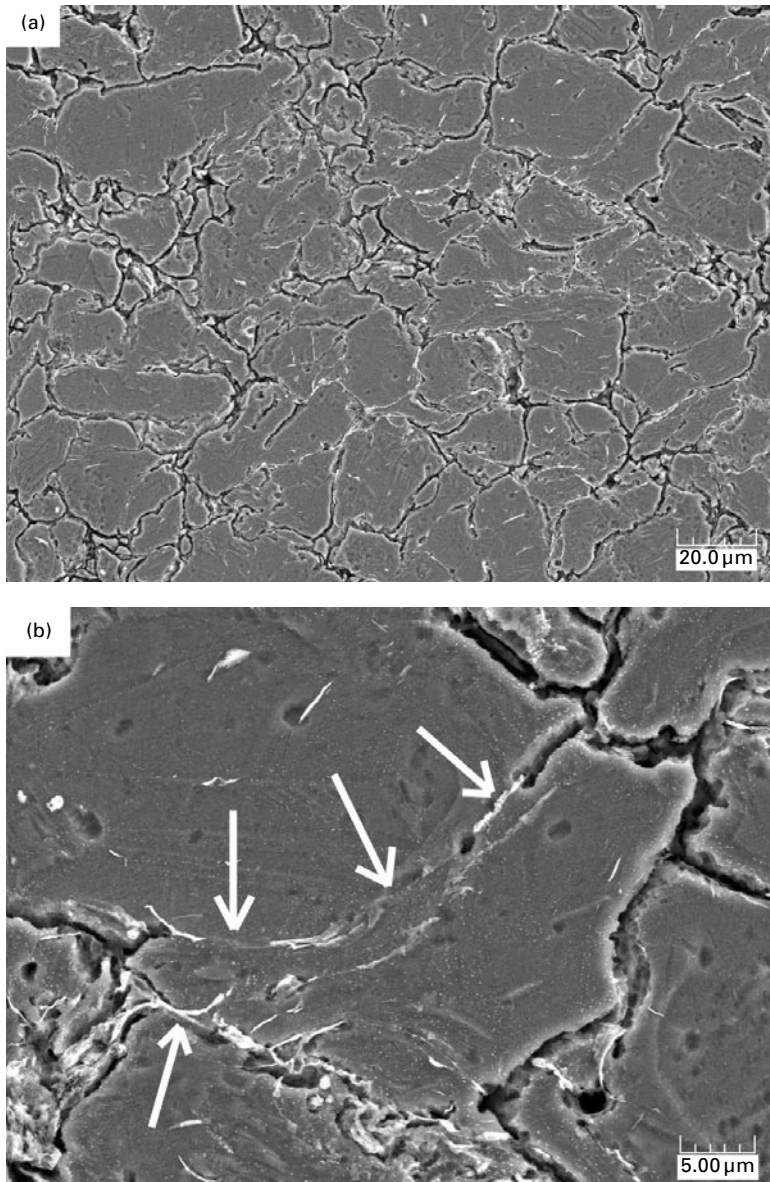
During all the experiments with Ti powder, it was of much interest to observe that the powder triggers a flashing jet at the nozzle exit. Figure 8.31 shows this interesting phenomenon. It was found that a flashing jet of about 10 cm outside the nozzle exit could be clearly observed, even without preheating of the driving gas, as shown in Fig. 8.31a. When the driving gas was preheated to 520°C, the flashing jet became brighter and longer than 40 cm, as shown in Fig. 8.31b. The flashing jet could also be obviously observed with nitrogen and helium as the driving gases for the Ti powder. It seems that the ignition of the Ti particle surfaces had occurred. The higher oxygen content in the Ti coating (0.60wt.%) than that in the Ti powder (0.31wt.%) could explain this point (Li *et al.*, 2007a). According to the literature (Zhou and Ning, 1993; Li, 2003), titanium is one of the more reactive metals and easily reacts with oxygen in the air at a relatively high temperature of about 550°C. But it needs a higher temperature to react with nitrogen. The nitrogen content in the as-sprayed Ti coating (0.10wt.%) is comparable to that in the Ti powder (0.07wt.%). This fact suggests that the powder particles react with oxygen rather than nitrogen during deposition. Therefore, it could be considered that during cold spraying of Ti powder, the particles' friction with the driving gas and/or the nozzle inner wall breaks up the oxide film and generates a relatively high surface temperature. When the particles fly out of the nozzle exit, their fresh surfaces are oxidized by oxygen in the entrained or employed air, and thus a flashing jet is generated. In the local contact interfaces of the deposited particles, a metallurgical bonding may be formed because of the relatively high interfacial temperature resulting from



8.31 Photos of the flashing jet with Ti powder particles outside nozzle exit. (a) Air, 2.8 MPa, without preheating, jet length from nozzle exit: ~10 cm; (b) Air, 2.8 MPa, with preheating of gas at 520°C, jet length from nozzle exit: ~40 cm.

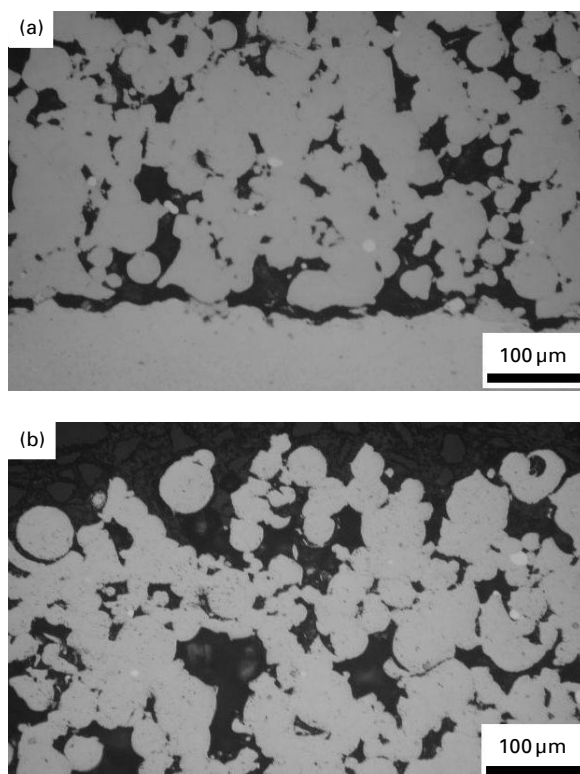
both the friction and the adiabatic impacting process. Figure 8.32a shows a typical SEM microstructure of the Ti coating in an etched state. It was seen that the deposited Ti particles are deformed a little and thus a relatively high porosity in the coating appears. Also, at some interfaces between the deposited particles, a metallurgical bonding has been formed, as marked by arrows in Fig. 8.32b. This metallurgical bonding will enhance the coating adhesion. Consequently, Ti particles can be deposited with high deposition efficiency, even without using a high velocity and thus an extensive plastic deformation. Therefore, it is considered that the reactivity of Ti particle surfaces can be attributed to the porous structure of the Ti coating.

When Ti-6Al-4V powder was used as feedstock, a flashing jet could also be observed clearly during spraying using air as the driving gas, regardless of the preheating of the gas. A similar flashing jet appeared when using helium as the driving gas. Figure 8.33 shows the typical microstructure of a Ti-6Al-4V coating deposited at an air pressure of 2.8 MPa and a temperature of about 520°C in the pre-chamber. It is clearly observed from Fig. 8.33 that the as-cold-sprayed Ti-6Al-4V coating presents much porous structure. The porosity of this Ti-6Al-4V coating was about 22.4% (Li *et al.*, 2007a). Many deposited Ti-6Al-4V particles experienced almost no plastic deformation,



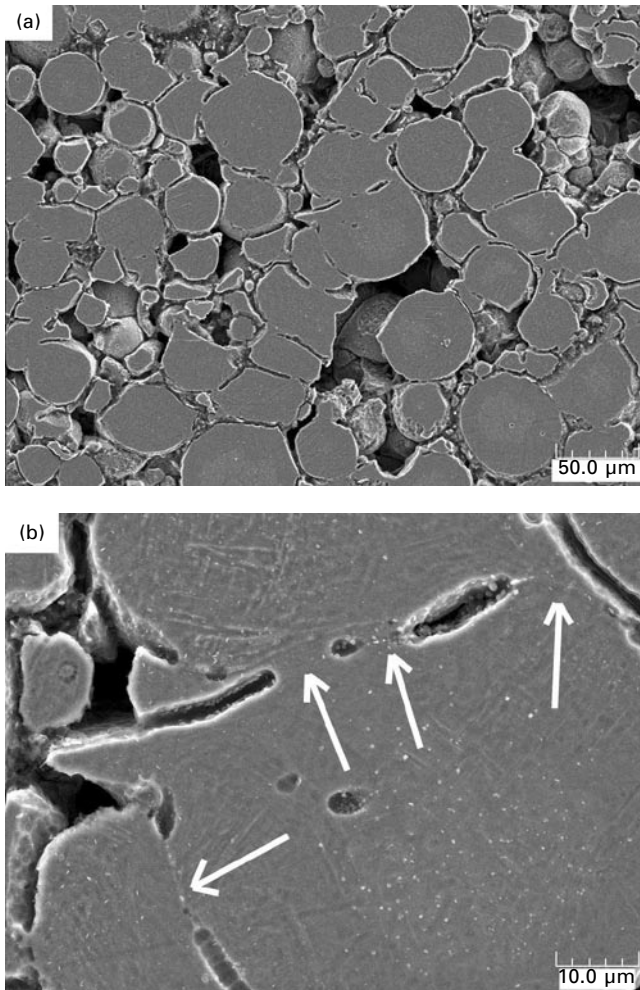
8.32 SEM microstructure of the as-deposited Ti coating in the etched state.

owing to their high strength, as shown in Fig. 8.33. This can be clearly seen from the SEM micrographs in the etched state, as shown in Fig. 8.34. According to numerical simulation results, the particle velocities under these spray conditions were much lower. Based on the previous understanding of the bonding mechanism of cold sprayed particles, the critical velocity of Ti-



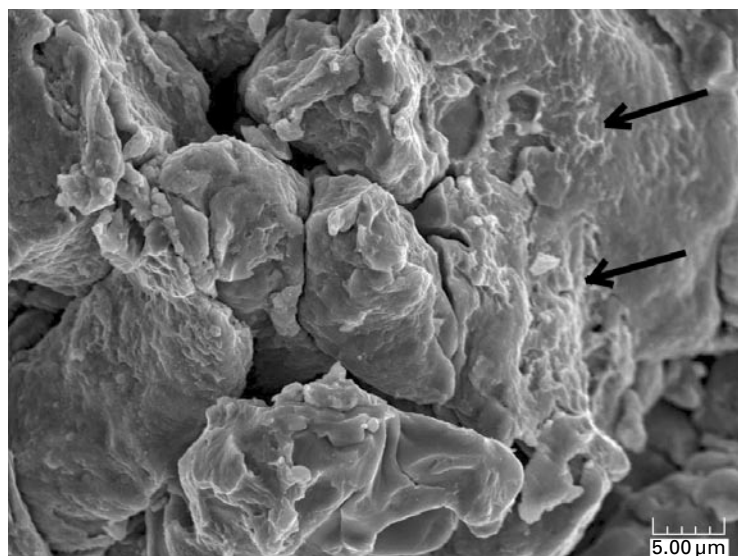
8.33 Typical OM micrograph of Ti-6Al-4V coating (>2mm) (a) coating substrate interface, and (b) coating surface.

6Al-4V will be much higher than that of Ti owing to its high strength and thus it is more difficult to deform. Therefore, it seems impossible for Ti-6Al-4V particles to be deposited under these spray conditions. However, in fact, the Ti-6Al-4V particles were deposited and the deposition efficiency was estimated to be higher than 60%. Bloise (2005) also reported the deposition of a porous Ti-6Al-4V coating using helium as the driving gas at a temperature of 530°C. The coating porosity was 18%, but the deposition efficiency was as high as 86% (Bloise, 2005). Therefore, it could be considered that the surface reactivity of Ti-6Al-4V particles also plays an important role in the formation of the porous Ti alloy coating. The oxygen content of the Ti-6Al-4V coating (0.57wt.%) was higher than that of the Ti-6Al-4V powder (0.42wt.%), while the nitrogen content is the same (0.003wt.%) (Li *et al.*, 2007a). These facts signify that reaction between the Ti-6Al-4V powder and oxygen also occurred. It is also observed from Fig. 8.34b that at the local interfaces, metallurgical bonding was formed, as marked by the arrows. Therefore, the particles can adhere together with a small contact area without obvious plastic deformation



8.34 SEM microstructure of the as-deposited Ti-6Al-4V coating in the etched state.

(low particle velocity) because of the active surfaces. Further study showed that the limited metallurgical bonding provides the main strength of these Ti alloy coatings. Observation of the fractured surface morphologies of Ti and Ti-6Al-4V coatings further proved this, as shown in Figures 8.35 and 8.36, respectively (Li *et al.*, 2007a). It was observed that at some interfaces between the deposited Ti particles, metallurgical bonding was formed, as indicated by the ductile fracture appearing as small dimples, marked by arrows in Fig. 8.35. However, due to the relatively high porosity of the Ti coating, the adhesive strength of the coating was about 15 MPa, despite the fact that the metallurgical bonding may have enhanced the coating cohesion.

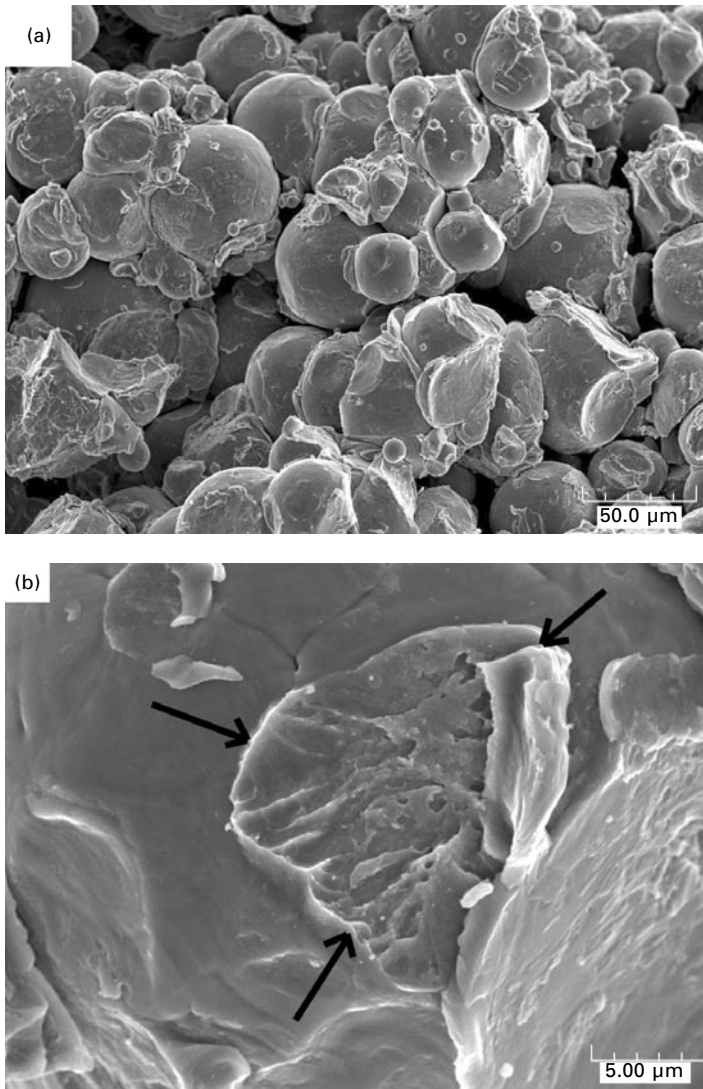


8.35 SEM micrograph of fractured surface morphology of Ti coating. The arrows indicate the ductile fracture appearing as small dimples.

For the Ti-6Al-4V coating, the melting zones can be clearly observed from the fractured surface, as indicated by the arrows in Fig. 8.36b. It is also clear that the deposited Ti-6Al-4V particles experienced little deformation. Therefore, the particles could adhere together with a small contact area. However, the strength of this porous Ti-6Al-4V coating was about 10 MPa, which is relatively low and similar to that (<15MPa) reported by Blose using helium as an accelerating gas (Blose, 2005).

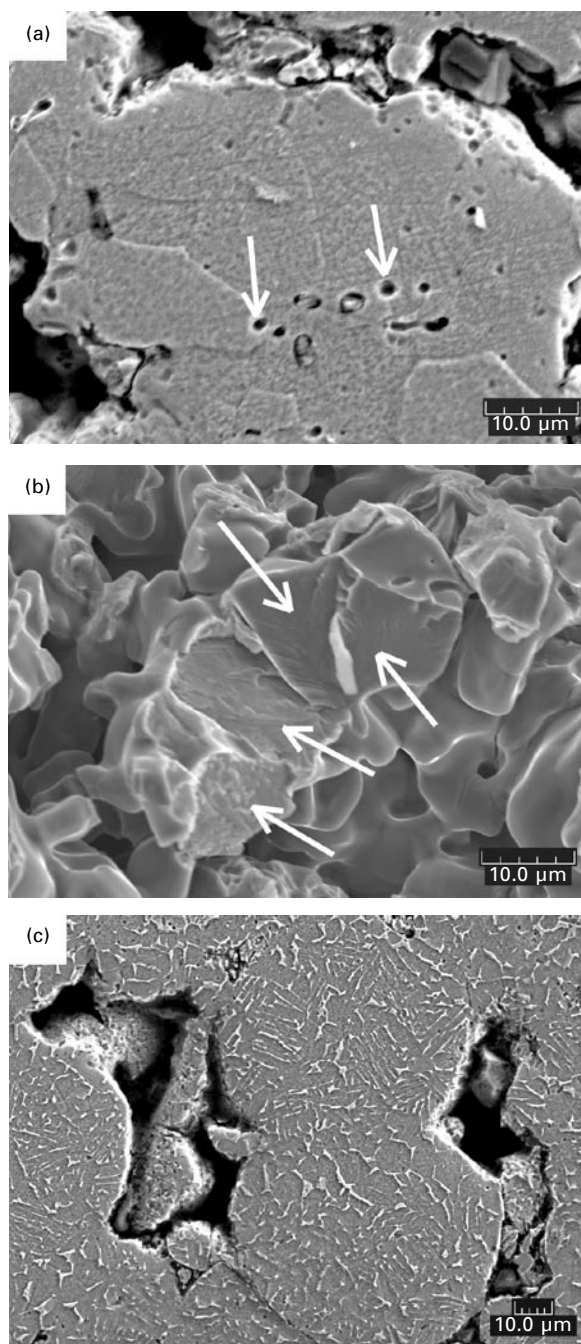
It has been mentioned that post-spray annealing treatment has a significant effect on the microstructure and properties of cold-sprayed coatings. This is expected to heal up the incomplete interfacial bonding and modify the inner particle structures in cold-sprayed Ti and its alloy coatings through post-spray heat treatment, and consequently improve the coating properties. Figure 8.37 shows the microstructures of the annealed Ti and Ti-6Al-4V coatings (Li *et al.*, 2007c). Through the examination of the cross-sections and fractured surface morphologies, it was found that a strong metallurgical bonding was formed for both coatings, with great improvement of tensile strength (Li *et al.*, 2007c). These coating are promising for bio-medical applications.

Titanium and its alloys have excellent corrosion resistance in the severe seawater environment and so have been widely used for the protection of steel structures. Figure 8.38 shows the corrosion potential of the as-sprayed Ti coating and pure Ti metal (TA2) in seawater (Wang *et al.*, 2007). It can be seen that the steady open-circuit potential (OCP) of the as-sprayed Ti coating was near -400 mV. However, the OCP of TA2 was more positive

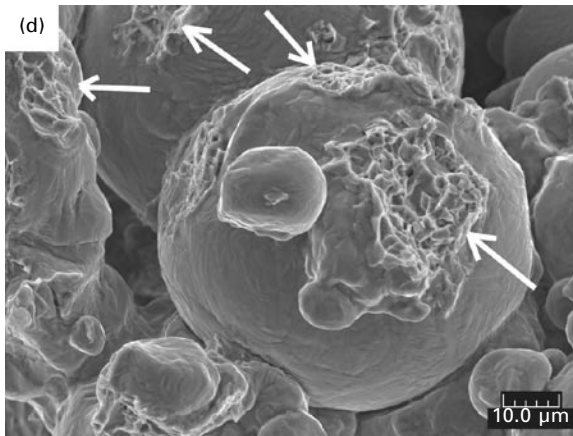


8.36 SEM micrographs of the fractured surface morphologies of Ti-6Al-4V coating. (b) is high magnification of (a). The arrows in (b) indicate the ductile fracture appearing as small dimples.

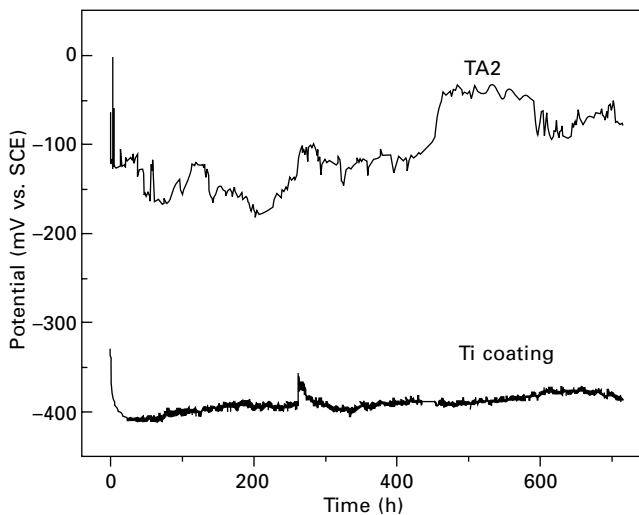
and shifted in a wide range from 0 mV to -200 mV. There is a tendency for the OCP of TA2 to shift later to positive, indicating that surface passivation occurs. The OCP of the coating was more negative than the metal from 200 mV to 300 mV. This could be attributed to the porous surface structure of the cold sprayed Ti coating, which leads to a more active surface than that of TA2 (Wang *et al.*, 2007).



8.37 Microstructures of the annealed Ti (a,b) and Ti-6Al-4V (c,d) coatings. (a,c) SEM micrographs in the etched state; (b,d) Fractured surface morphologies.



8.37 Continued

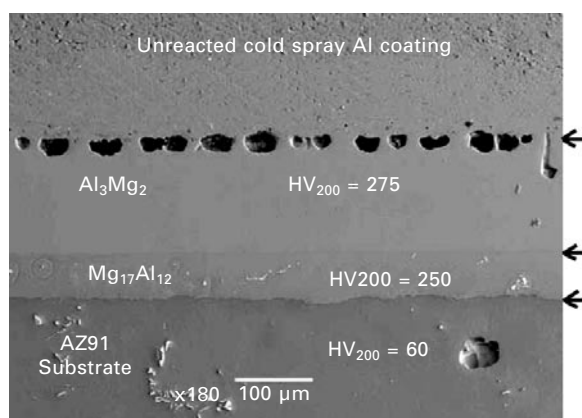
8.38 Change of corrosion potential versus time for the as-sprayed Ti coating and TA2 in seawater (Wang *et al.*, 2007).

8.5 Surface modification of magnesium alloys by CS

Magnesium is the lightest of all structural metals, 35% lighter than aluminium, 78% lighter than steel, and it has exceptional stiffness and damping capacity (Yamauchi *et al.*, 1991). As a constituent of many minerals, it represents about 2% of the mass of rocks, and 0.13% of seawater. Their lightweight characteristics and wide availability make magnesium alloys ideal for aircraft, car and light truck components. However, magnesium is a very active metal

electrochemically and is anodic to all other structural metals (see Chapter 1). Therefore, it must be protected against galvanic corrosion in mixed-metal systems because it will corrode preferentially when coupled with virtually any other metal in the presence of an electrolyte or corrosive medium (Gonzalez-Nunez *et al.*, 1995). For example, many corrosion problems associated with magnesium helicopter components occur at the contact points between inserts or mating parts, where ferrous metals are located, creating galvanic couples. In addition, magnesium alloys are also very sensitive to surface damage due to impact, which occurs frequently during manufacture and/or overhaul and repair. Scratches from improper handling or tool marks can result in preferential corrosion sites, if the scratches penetrate the protective coating system down to the base metal.

Surface alloying of Mg alloys with Al and Al-Si has been considered an effective approach to improve both corrosion and wear resistance through the formation of Mg/Al intermetallic compounds. Diffusion coating techniques are more used than conventional methods to produce alloyed surface layers containing a higher fraction of the $\text{Mg}_{17}\text{Al}_{12}$ phase, which shows improved wear and corrosion resistance. However, in order to promote diffusion of Al into the Mg substrate, the diffusion coating has to be carried out at temperatures over 450°C (Liu *et al.*, 2008). Such temperatures are too high to be of practical use because they result in surface melting and cracking. Spencer and Zhang (2009) have found that CS deposition of Al on AZ91 Mg substrates and subsequent heat treatment at 400°C can produce a layer of Mg/Al intermetallic compound at the coating/substrate interface. This is considered a useful starting point because CS coatings can be produced quickly and are inexpensive. Figure 8.39 shows the cold-sprayed Al diffusion coating on an AZ91E substrate heat treated at 400°C for 20 h (Spencer and



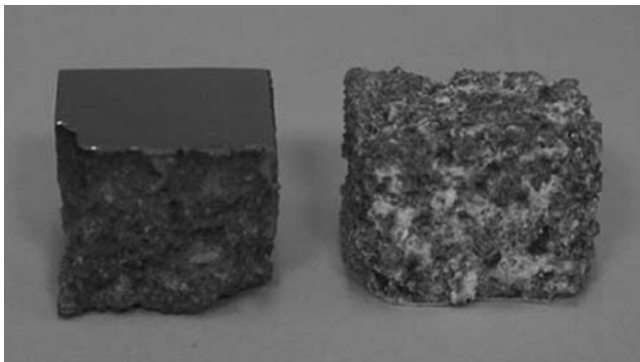
8.39 Backscatter SEM image of a cold sprayed Al diffusion coating on an AZ91E substrate heat treated at 400°C (Spencer and Zhang, 2009).

Zhang, 2009). It can be seen that the intermetallic layers are continuous and have a uniform thickness. Two diffusion layers, Al_3Mg_2 and $\text{Mg}_{17}\text{Al}_{12}$, with a small amount of solid solution Zn, were observed. The thickness of the Al_3Mg_2 layer is about 150 μm and the $\text{Mg}_{17}\text{Al}_{12}$ layer is 50 μm . Figure 8.40 shows an example of an AZ91 sample with an Al_3Mg_2 coating compared with an AZ91E sample after 48 h immersion in a neutral 5% NaCl solution (Spencer and Zhang, 2009). The AZ91 sample shows extensive and deep pitting while the Al_3Mg_2 surface shows only minor discolouration from the salt. The good performance of the intermetallic layer suggests that it would perform well under real-use conditions. It has been suggested that continuous immersion or salt spray tests are overall conservative when compared with real conditions when predicting corrosion resistance of exposed parts in service in automobiles.

Although few references could be found in the open literature dealing with cold spraying of Mg or its alloys, the CS process also has potentials in their fabrication and protection. But much work needs to be done in the future.

8.6 Future trends

As an emerging new coating process, cold spraying has proved to be able to deposit a great variety of materials including metal alloys, cermets and even ceramics. The low temperature features of the process make it suitable for depositing light alloys with high purity. Adhesive strength of CS coatings is comparable to that of conventional thermal spray coatings. This makes CS a promising practical process not only to deposit coatings but also to form near-net shapes of materials.



8.40 AZ91E sample with Al_3Mg_2 coating on top (left) and AZ91E (right) after 48 h immersion test in 5% NaCl (Spencer and Zhang, 2009).

With the progress of fundamental research, the CS process is expected to be applied to many industrial fields, such as aerospace and aeronautics, automotive, metallurgy, power plant, nuclear, electronics, biotechnology, defence, and chemical. There are also many other new application fields to be explored where the CS process may find new uses, such as brazing/joining bond layers, and conductive polymers.

8.7 References

- Ajdelsztajn L, Jodoin B, Kim G E, *et al.* (2005), 'Cold Spray Deposition of Nanocrystalline Aluminum Alloys', *Metall Mater Trans A*, 36A, 657–666.
- Ajdelsztajn L, Jodoin B, Richer P, *et al.* (2006a), 'Cold gas dynamic spraying of iron-base amorphous alloy', *J Therm Spray Technol*, 15(4), 495–500.
- Ajdelsztajn L, Zuniga A, Jodoin B, *et al.* (2006b), 'Cold spray processing of a nanocrystalline Al-Cu-Mg-Fe-Ni alloy with Sc', *J Therm Spray Technol*, 15(2), 184–190.
- Ajdelsztajn L, Jodoin B, Schoenung J M (2006c), 'Synthesis and mechanical properties of nanocrystalline Ni coatings produced by cold gas dynamic spraying', *Surf Coat Tech*, 201(3–4), 1166–1172.
- Arai S, Endo M, Kaneko N (2004), 'Ni-deposited multi-walled carbon nanotubes by electrodeposition', *Carbon*, 42, 641–644.
- Bakshi S R, Singh V, Balani K, *et al.* (2008), 'Carbon nanotube reinforced aluminum composite coating via cold spraying', *Surf Coat Technol*, 202, 5162–5169.
- Balani K, Laha T, Agarwal A, *et al.* (2005), 'Effect of carrier gases on microstructural and electrochemical behavior of cold-sprayed 1100 aluminum coating', *Surf Coat Technol*, 195, 272–279.
- Blose R E (2005), Spray forming titanium alloys using the cold spray process, in: Lugscheider E (ed.), *International Thermal Spray Conference*, Basel, Switzerland.
- Calla E, McCartney D G, Shipway P H (2006), 'Effect of Deposition Conditions on the Properties and Annealing Behavior of Cold-sprayed Copper', *J Therm Spray Technol*, 15(2), 255–262.
- Dod (2008), Department of Defense Manufacturing Process Standard, 'Materials Deposition, Cold Spray', MIL–STD–3021.
- Eesley G L, Elmoursi A, Patel N (2003), 'Thermal properties of kinetic spray Al-SiC metal-matrix composite', *J Mater Res*, 18(4), 855–860.
- Feng Y, Yuan H L, Zhang M (2005), 'Fabrication and properties of silver-matrix composites reinforced by carbon nanotubes', *Mater Charact*, 55, 211–218.
- Gartner F, Stoltenhoff T, Schmidt T, *et al.* (2006), 'The cold spray process and its potential for industrial applications', *J Therm Spray Technol*, 15(2), 223–232.
- Gonzalez-Nunez M A, Nunez-Lopez C A, Skeldon P, *et al.* (1995), 'A nonchromate conversion coating for magnesium alloys and magnesium-based metal matrix composites', *Corros Sci*, 37(11), 1763–1772.
- Grujicic M, Saylor J R, Beasley D E, *et al.* (2003), 'Computational analysis of the interfacial bonding between feed-powder particles and the substrate in the cold-gas dynamic spray process', *Appl Surf Sci*, 219(3–4), 211–227.
- Hall A C, Cook D J, Neiser R A, *et al.* (2006), 'The effect of a simple annealing heat treatment on the mechanical properties of cold-sprayed aluminium', *J Thermal Spray Technol*, 15233–238.

- Han J H, Lee S W, Lee E A, *et al.* (2006), 'Photocatalytic properties of TiO₂ coatings prepared by cold spray process', *Mater Sci Forum*, 510–511, 130–133.
- Irissou E, Legoux J G, Arsenault B, *et al.* (2007), 'Investigation of Al–Al₂O₃ Cold Spray Coating Formation and Properties', *J Therm Spray Technol*, 16(5–6), 661–668.
- Karthikeyan J (2004), Cold Spray Technology: International Status and USA Efforts, internal report, ASB Industries Inc.
- Karthikeyan J (2006), 'Evolution of cold spray technology', *Adv Mater Process*, 164(5), 66–67.
- Karthikeyan J, Kay C M, Lindeman J *et al.* (2000), Cold spray processing of titanium powder. In: Berndt C C (ed.), *1st International Thermal Spray Conference*, USA, 255–262.
- Kim H J, Lee C H, Hwang S Y (2005), 'Fabrication of WC–Co coatings by cold spray deposition', *Surf Coat Technol*, 191(2–3), 335–340.
- Kim K T, Cha S I, Hong S H, *et al.* (2006), 'Microstructures and Tensile Behavior of Carbon Nanotube Reinforced Cu Matrix Nanocomposites', *Mater. Sci. Eng.*, A 430, 27–33.
- Kim P, Shi L, Majumdar A, *et al.* (2001), 'Thermal transport measurements of individual multiwalled nanotubes', *Phys Rev Lett* 87(21), 215502–1–215502–4.
- King P C, Zahiri S H, Jahedi M Z (2007), 'Rare Earth–Metal Composite Formation by Cold Spray', *J Therm Spray Technol*, 17(2), 221–227.
- Klinkov S V, Kosarev V F, Sova A A, *et al.* (2008), 'Deposition of multicomponent coatings by Cold Spray', *Surf Coat Technol*, 202, 5858–5862.
- Kroemmer W, Heinrich P (2006), 'Cold spraying – Potential and New Application Ideas', in Marple B R, Hyland M M, Lau Y C, Lima R S and Voyer J (eds), *International Thermal Spray Conference*, Seattle, Washington.
- Laha T, Agarwal A, McKechnie T, *et al.* (2004), 'Synthesis and characterization of plasma spray formed carbon nanotube reinforced aluminum composite', *Mater Sci Eng A*, 381, 249–258.
- Lee H Y, Jung S H, Lee S Y, *et al.* (2006), 'Fabrication of cold sprayed Al–intermetallic compound coatings by post annealing', *Mater Sci Eng A*, 433(1–2), 139–143.
- Lee H Y, Jung S H, Lee S Y, *et al.* (2007), 'Alloying of cold-sprayed Al–Ni composite coatings by post-annealing', *Appl Surf Sci*, 253(7), 3496–3502.
- Li T F (2003), *High Temperature Oxidation and Corrosion of Metals*, Chemical Industry Press, Beijing. (in Chinese)
- Li C J, Li W Y (2003), 'Deposition characteristics of titanium coating in cold spraying', *Surf Coat Technol*, 167(2–3), 278–283.
- Li C J, Li W Y (2004), 'Microstructure evolution of cold-sprayed coating during deposition and through post-spraying heat treatment', *Trans Nonferrous Met Soc China*, 14(S2), 49–54.
- Li W Y (2005), 'Study on the Effect of Particle Parameters on Deposition Behavior, Microstructure Evolution and Properties in Cold Spraying', *Thesis of Xi'an Jiaotong University*. (in Chinese)
- Li C J, Li W Y, Wang Y Y (2005), 'Formation of metastable phases in cold-sprayed soft metallic deposit', *Surf Coat Technol*, 198, 469–473.
- Li W Y, Li C J (2006), 'Effect of annealing treatment on the microstructure and properties of cold-sprayed Cu coating', *J Thermal Spray Technol*, 15, 206–211.
- Li W Y, Guo X P, Verdy C, *et al.* (2006), 'Improvement of microstructure and property of cold-sprayed Cu–4 at.%Cr–2 at.%Nb alloy by heat treatment', *Scripta Mater*, 55(4), 327–330.

- Li W Y, Zhang C, Wang H T, *et al.* (2007a), 'Significant influences of metal reactivity and oxide film of powder particles on coating deposition characteristics in cold spraying', *Appl Surf Sci*, 253(7), 3557–3562.
- Li W Y, Zhang C, Guo X P, *et al.* (2007b), 'Deposition characteristics of Al-12Si alloy coating fabricated by cold spraying with relatively large powder particles', *Appl Surf Sci*, 253(17), 7124–7130.
- Li W Y, Zhang C, Guo X P, *et al.* (2007c), 'Fabrication and characterization of Ti and Ti-6Al-4V coatings by cold spraying and microstructure modification by heat treatment', *Adv Eng Mater*, 9(5), 418–423.
- Li W Y, Zhang G, Guo X P, *et al.* (2007d), 'Characterizations of Cold-sprayed TiN Particle-reinforced Al Alloy-based Composites – from Structures to Tribological Behaviour', *Adv Eng Mater*, 9(7), 577–583.
- Li C J, Yang G J, Gao P H *et al.* (2007e), 'Characterization of Nanostructured WC-Co Deposited by Cold Spraying', *J Therm Spray Technol*, 16(5–6), 1011–1020.
- Li W Y, Zhang C, Guo X P, *et al.* (2008a), 'Effect of standoff distance on coating deposition characteristics in cold spraying', *Mater Design*, 27, 297–304.
- Li W Y, Zhang G, Zhang C, *et al.* (2008b), 'Effect of Ball Milling of Feedstock Powder on Microstructure and Properties of TiN Particle-reinforced Al Alloy-based Composites Fabricated by Cold Spraying', *J Therm Spray Technol*, 17(3), 316–322.
- Liu F C, Liang W, Li X R, *et al.* (2008), 'Improvement of corrosion resistance of pure magnesium via vacuum pack treatment', *J Alloys Compd.* 461, 399–403.
- Lutjering G, Williams J C (2003), *Titanium*, Springer-Verlag, Berlin, Heidelberg, New York.
- Maev R G, Leshchynsky V (2006), 'Air gas dynamic spraying of powder mixtures: Theory and application', *J Therm Spray Technol*, 15(2), 198–205.
- Marrocco T, McCartney D G, Shipway P H (2006a), 'Comparison of the Microstructure of Cold Sprayed and Thermally Sprayed IN718 Coatings', in Marple B R, Hyland M M, Lau Y C, Lima R S, Voyer J (eds), *International Thermal Spray Conference*, Seattle, Washington.
- Marrocco T, McCartney D G, Shipway P H, *et al.* (2006b), 'Production of titanium deposits by cold-gas dynamic spray: Numerical modelling and experimental characterization', *J Therm Spray Technol*, 15(2), 263–272.
- Marx S, Paul A, Kohler A, *et al.* (2006), 'Cold spraying: Innovative layers for new applications', *J Therm Spray Technol*, 15(2), 177–183.
- McCune R C, Donlon W T, Popoola O O, *et al.* (2000), 'Characterization of Copper Layers Produced by Cold Gas-Dynamic Spraying', *J Therm Spray Technol*, 9(1), 73–82.
- Morgan R, Fox P, Pattison J, Sutcliffe C and O'Neill W (2004), 'Analysis of cold gas dynamically sprayed aluminium deposits', *Mater Lett*, 58, 1317–1320.
- Ning X J, Jang J H, Kim H J, *et al.* (2008), 'Cold spraying of Al–Sn binary alloy: Coating characteristics and particle bonding features', *Surf Coat Technol*, 202, 1681–1687.
- Novoselova T, Fox P, Morgan R, *et al.* (2006), 'Experimental study of titanium/aluminium deposits produced by cold gas dynamic spray', *Surf Coat Technol*, 200, 2775–2783.
- Ogawa K, Ito K, Ichimura K, *et al.* (2008), 'Characterization of Low-pressure Cold-sprayed Aluminum Coatings', *J Therm Spray Technol*, 17(5–6), 728–735.
- Overfelt R A, Anderson C D, Flanagan W F (1986), 'Plasma Sprayed Fe76Nd16B8 Permanent Magnets', *Appl Phys Lett*, 49(26), 1799–1801.
- Papyrin A (2001), 'Cold Spray Technology', *Adv Mater Process*, 159(9), 49–51.
- Pawlowski L (1995), *The Science and Engineering of Thermal Spray Coatings*. NY: John Wiley and Sons.

- Price T S, Shipway P H, McCartney D G, *et al.* (2007), 'A method for characterizing the degree of inter-particle bond formation in cold sprayed coatings', *J Therm Spray Technol*, 16, 566–570.
- Sansoucy E, Marcoux P, Ajdelsztajn L, *et al.* (2008), 'Properties of SiC-reinforced aluminum alloy coatings produced by the cold gas dynamic spraying process', *Surf Coat Technol*, 202, 3988–3996.
- Schmidt T, Gärtner F, Assadi H, *et al.* (2006), 'Bonding mechanism in cold gas spraying', *Acta Mater.* 54, 729–742.
- Spencer K, Zhang M X (2009), 'Heat treatment of cold spray coatings to form protective intermetallic layers', *Scrip Mater*, 61, 44–47.
- Stoltenhoff T, Kreye H, Richter H J (2002), 'An Analysis of the Cold Spray Process and Its Coatings', *J Therm Spray Technol*, 11(4), 542–550.
- Van Steenkiste T H, Gorkiewicz D W (2004), 'Analysis of Tantalum Coatings Produced by the Kinetic Spray Process', *J Therm Spray Technol*, 13(2), 265–273.
- Van Steenkiste T H, Smith J R, Teets R E (2002), 'Aluminum coatings via kinetic spray with relatively large powder particles', *Surf Coat Technol*, 154(2–3), 237–252.
- Van Steenkiste T H, Smith J R, Teets R E, *et al.* (1999), 'Kinetic spray coatings', *Surf Coat Technol*, 111, 62–71.
- Wang H R, Li W Y, Ma L *et al.* (2007), 'Corrosion behavior of cold sprayed titanium protective coating on 1Cr13 substrate in seawater', *Surf Coat Tech*, 201(9–11), 5203–5206.
- Wang H T, Li C J, Yang G J, *et al.* (2008), 'Cold spraying of Fe/Al powder mixture: Coating characteristics and influence of heat treatment on the phase structure', *Appl Surf Sci*, 255, 2538–2544.
- Weinert H, Maeva E, Leshchynsky V (2006), Low Pressure Gas Dynamic Spray Forming Near-net Shape Parts, in Marple B R, Hyland M M, Lau Y C, Lima R S and Voyer J (eds), *International Thermal Spray Conference*, Seattle, Washington.
- Wolfe D E, Eden T J, Potter J K *et al.* (2006), 'Investigation and characterization of Cr3C2-based wear-resistant coatings applied by the cold spray process', *J Therm Spray Technol*, 15(3), 400–412.
- Wu J W, Yang J G, Fang H Y, *et al.* (2006) 'The bond strength of Al-Si coating on mild steel by kinetic spraying deposition', *Appl Surf Sci*, 252(22), 7809–7814.
- Xu Y, Hutchings I M (2006), 'Cold spray deposition of thermoplastic powder', *Surf Coat Tech*, 201(6), 3044–3050.
- Yamauchi M, Seki J, Sakita E *et al.* (1991), 'Corrosion resistant composite layer on magnesium alloys', *Adv Compos Mater*, 1(1), 3–10.
- Yoon S, Kim H J, Lee C (2006), 'Deposition behavior of bulk amorphous NiTiZrSiSn according to the kinetic and thermal energy levels in the kinetic spraying process', *Surf Coat Technol*, 200(20–21), 6022–6029.
- Yu M F, Laurie O, Dyer M J *et al.* (2000), 'Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load', *Sci*, 287, 637–640.
- Zahiri S H, Antonio C I, Jahedi M (2009), 'Elimination of porosity in directly fabricated titanium via cold gas dynamic spraying', *J Mat Process Technol*, 209(2), 922–929.
- Zhao L D, Bobzin K, Ernst F *et al.* (2006), 'Feasibility study of brazing aluminium alloys through pre-deposition of a braze alloy by cold spray process', *Adv Eng Mater*, 8(8), 751–753.
- Zhou Z J, Ning C D (1993), *Properties of Titanium and Its Applications*, Higher Education Press, Beijing (in Chinese).

Physical vapour deposition of magnesium alloys

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Abstract: Ion beam assisted deposited (IBAD) coatings offer corrosion protection comparable to that offered by many conversion coatings in mild corrosive environments. The wear resistance of these coatings is, however, far superior and is comparable to that of the hard coatings deposited on steel substrates. Furthermore, thick alumina coatings can electrically isolate magnesium components and thus minimize the risk of galvanic corrosion in complex assemblies. These coatings are still at the research and development stage. Duplex IBAD coatings can offer both wear and corrosion protection. Complex components can be treated in a relatively short time using an innovative Plasma Immersion Ion Implantation and Deposition (PIIID) technology.

Key words: RIBAD, IBAD, PIIID, IBSD, magnesium, AM50.

9.1 Introduction

There are many advantages offered by magnesium and its alloys due to their unique characteristics. The automotive industry has recently crossed the threshold from using magnesium in a protected environment (predominantly interior applications) to an unprotected exterior environment. Traditionally, magnesium applications have included interior components such as steering column brackets, instrument panels, seat frames, steering wheels, dashboards, and sunroof track assemblies. More recent applications extend magnesium's domain to roof panels, hoods, rear deck lids, wheels, intake manifolds, cylinder head covers, oil pans, starters/alternators, and engine blocks.

Considering its characteristic of low density, its extensive use in vehicles would obtain major reductions in weight and corresponding fuel savings. In fact it is estimated that the overall weight savings derived from the use of magnesium alloys without drastic changes in design, could be of around 10%. In turn, this weight saving would lead to a fuel saving in the order of 20–30%. A new passenger car generates, on average, some 150 g/km of CO₂. With magnesium technology, this value could be reduced to around 100–120 g/km. Considering the large number of vehicles in use, this weight saving would lead to a significant reduction of carbon dioxide released to the atmosphere, reducing the impact on global warming, in agreement with the Kyoto treaty.

One of the most important goals for the automotive industry of the near future is therefore to extend the use of Mg alloys to other bulky components

of the car, including external parts such as frames and panels (Friedrich and Schumann, 2002).

The main technological disadvantages of magnesium with respect to competing materials in the automotive industry (mainly polymers and aluminium) are its poor corrosion and tribological properties. Parts such as wheels, which have an aesthetic function, would require hard and scratch-resistant undercoats for paint or lacquer finishes. On the other hand, for active components such as pistons, cylinder blocks, and turbine components, wear, erosion, and corrosion resistance are mandatory if magnesium alloys are to be used. In such situations, the corrosion and wear resistance requirements are to say the least, challenging (Skar *et al.*, 2005, pp. 22–23).

9.2 Surface engineering of magnesium alloys

Surface engineering enables the modification of a material's surface without drastically affecting the properties of its bulk. This emerging branch of engineering was defined by (Bell, 1992, p. 2380) as ... 'the application of traditional and innovative surface technology to engineer components and material, in order to produce a composite material with properties unattainable in either the base or the surface material'. With these new techniques, it is possible to select a material for its bulk properties, and afterwards engineer its surface to achieve the required set of tribological properties (Morton, 1992).

Surface treatments are primarily applied to magnesium parts to improve their appearance and corrosion resistance (Avedesian and Barker, 1999, pp. 143–161). The type of surface treatment used is dependent on the service conditions, aesthetics, alloy composition, size, and the shape of the component to be treated. In the past couple of decades, a large number of surface treatments for magnesium and its alloys have emerged, but only a handful have actually achieved commercial importance. Those commonly used in industry are: (i) Oils and waxes; (ii) chemical-conversion coatings; (iii) anodized coatings; (iv) paints and powder coatings and (v) metallic plating.

9.2.1 Chemical conversion treatments

Chemical conversion treatments are, by far, the most common and diverse surface treatments for magnesium alloys. These treatments are used, either on their own, or as a surface preparation for subsequent coating. The bare magnesium surface is inherently alkaline. The surface must therefore be pre-treated to render it more compatible with paints and other organic coatings, and thus enhance coating adhesion.

Due to their inherent porosity, the protection offered by stand-alone

conversion coatings is limited, but it is sufficient for safeguarding magnesium items during transport and storage. Conversion coatings are also used for the protection of components that operate in relatively mild conditions, such as housings for electronic components and parts for domestic appliances, intended for indoor use.

The essential active ingredient in the vast majority of the chemical-conversion treatments of magnesium and its alloys is the hexavalent chromium ion, Cr^{6+} . This substance has been found to be highly carcinogenic, and is an extremely deleterious contaminant for natural ecosystems. Much effort has been dedicated towards finding effective substitutes for chromate treatments. Several commercial phosphate treatments, and simple phosphate formulations, have emerged in recent years as paint bases for high purity die-cast alloys, such as the AZ91D, AM50A, AM60B, and AS41B. However, regrettably, the original chromate treatments still offer superior corrosion protection as standalone coatings. This is particularly true for components used in severely corrosive environments and sand castings, intended for use in aerospace and military application (Avedesian and Barker, 1999, p. 145).

9.2.2 Anodic treatments

Anodic treatment, also known as anodizing, is conducted by applying a DC or an AC current to the component to be treated, which is immersed in the anodizing solution. During the process, the component's surface is stimulated to react rapidly with the solution, resulting in the formation of an oxide-based coating, in various steps. A general discussion on anodizing of light alloys can be found in Chapter 4 of this book.

The anodic coatings resulting from acid magnesium anodizing are mainly composed of magnesium oxide, chromate, fluoride, and phosphate. Anodic coatings or anodizing coatings on magnesium are difficult to dye as they are non-porous films. The anodic coatings formed on magnesium are strongly alkaline-resistant but only weakly resistant to acid and neutral salt media because of the nature of magnesium and its compounds. On the positive side, the coatings provide a fair adhesive base for subsequent painting. Although they are harder than the substrate magnesium metal, anodic coatings on magnesium alloys are softer and have lower wear resistance than those obtained on aluminium alloys. One possible way to address the above limitation is plasma electrolytic oxidation (see Chapter 6)

9.2.3 Electroplating and organic coatings

Magnesium alloys can be electroplated by many commercial plating systems, provided proper pre-plating operations are conducted. However, the only metals that can be plated directly on magnesium are zinc and nickel. Zinc and

nickel under-coats serve as surface preparation for cadmium, copper, brass, nickel, chromium, gold, silver, and rhodium coatings. With the exception of gold plating, metal coatings have found little commercial applications. This is because they offer limited protection against wear and corrosion, and also because of the high processing costs. Gold plating is still used in space applications because of its extreme stability in all operating environments, resistance to tarnish and radiation, high superficial electrical conductivity, low infrared emissivity, and resistance to cold welding in high vacuum. Metal plated wrought alloys give better and more reproducible corrosion resistance than metal plated cast alloys. This has been attributed to the surface porosity and inclusions found in cast alloys (Avedesian and Barker, 1999, p. 157).

Organic coatings are also used on magnesium alloys to provide corrosion protection and for decoration. Organic finish paints range from single coats applied, on a phosphate or a chromate treatment, to complex multicoat™ systems involving anodizing, epoxy surface sealing, priming, and one or more topcoats. Surface sealing with epoxy resin was developed, as a first step in the finishing of castings for the aerospace and military applications. This sealing is an important step to increase the corrosion performance of the complex finishing systems required in aggressive environments (Avedesian and Barker, 1999, p. 159).

9.2.4 Conventional physical vapour deposition techniques

Heightened environmental concerns in recent years have made plasma processes increasingly important in the surface engineering of magnesium alloys. Physical vapour deposition (PVD) involves the atomization of a condensable material by the application of heat, energetic beam, or electric arc in a vacuum chamber. The vaporized material is allowed to condense onto the substrate under accurately controlled conditions. PVD processes generally require very high vacuum conditions and a substrate temperature ranging from 200–550°C. The range of metals that can be deposited by PVD is limited only by their compatibility with the substrate. A reactive gas or a combination of gases can be leaked into the chamber during deposition to react with the condensable material to generate compound coatings such as TiN, CrN, and TiCN coatings. Using multiple vapour sources it is also possible to deposit complex or layered coatings with specific physical, electrical, or magnetic properties. Controlling the pressure inside the chamber is very important as it has a significant effect on coating integrity; thus the deposition of compound coatings is much more difficult to control.

As their name implies, PVDs are not thermodynamically driven processes and can therefore operate at relatively low temperatures. Coating composition and structure are almost entirely controlled by ‘surface effects’. This

allows for a great deal of flexibility but also introduces a number of serious limitations. The most notorious of these limitations are the ‘line-of-sight’ and the adatom limited lateral mobility. The line-of-sight problem limits the complexity of the substrate that can be uniformly coated and introduces the need for complex and expensive sample manipulators. Together with the reduced adatom lateral mobility, it is also responsible for the formation of pinholes in the growing film and impaired coating densification at low operating temperatures. This is clearly a problem if such coatings are to be applied on magnesium and aluminium alloys, many of which cannot be exposed to temperature above 150°C for prolonged periods of time. If not properly controlled, this eventually leads to the building up of large tensile stresses on the coating surface, resulting in adhesion failure. Furthermore, these porous coatings have inferior mechanical properties and provide little corrosion protection, and in many cases actively contribute to aggravate the corrosion problem of light alloys.

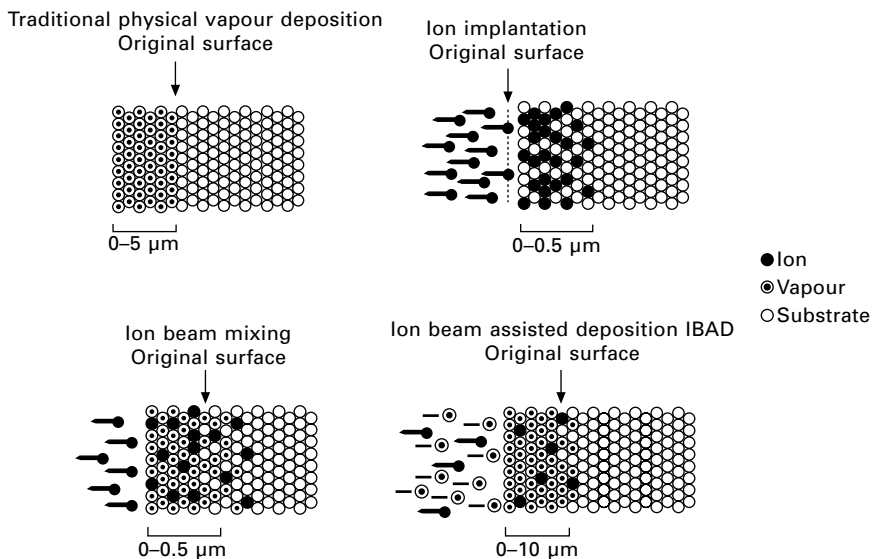
9.3 Ion beam assisted deposition (IBAD) and reactive ion beam assisted deposition (RIBAD)

Ion beam assisted deposition (IBAD), also referred to by some scientists as ion beam enhanced deposition (IBED), is a combination of two surface treatment processes, namely, vacuum deposition and ion implantation (Klingenberg *et al.*, 2002, pp. 164–169). The deposition process is usually accountable for the material build-up, while the ion flux imparts the kinetic energy required to achieve adhesion and the required coating properties (Deutchman and Partyka, 2002). If a reactive gas is used to feed the ion source, the process is referred to as Reactive Ion Beam Assisted Deposition or RIBAD for short. The kinetic energy imparted by the ion beam activates a number of processes on the surface of the growing film. Surface atoms are displaced, enhancing migration of atoms along the surface and thereby increasing the coating density, even at low deposition temperatures. The ion beam also provides the required stitching (ion beam mixing) of the coating to the substrate at a low temperature (Itoh, 1989, pp. 170–179), making this process applicable to a wide range of materials (Bradley *et al.*, 1986; Friedrich and Urbassek, 2003; Hydro Magnesium, 2005). Furthermore, accurate tuning of the ion to condensable flux ratio (I/C), enables the control of coating stoichiometry, structure, and residual stresses (Anders, 2000, pp. 177–209).

The main difference between the IBAD deposition technique and other ion-assisted deposition processes is that, in the former, the energetic ion source and the condensable material flux source are separated into two distinct devices. Thus, in IBAD, these two parameters can be controlled independently. In comparison, other plasma-based deposition techniques such as DC and RF magnetron sputtering, and other Plasma Enhanced Physical

Vapour Deposition (PEPVD) techniques do not allow this flexibility. This is because, in these technologies, the condensable material and ion fluxes are extracted from the same plasma source. This feature gives the IBAD process more control over the deposition parameters, when compared to other deposition processes (Emmerich *et al.*, 1992b). Another important difference is the operating pressure. Plasma assisted coatings usually operate between 0.1 – 1300 Pa, which is the pressure required to sustain a plasma. In contrast, IBAD techniques usually operate in high vacuum, between 1×10^{-6} and 1×10^8 mbar. The need to operate at such a low pressure is mainly due to physical limitations of the hardware and mean free path restrictions (Mändl *et al.*, 1996, pp. 252–254). As IBAD techniques operate in the collision-free pressure regime, the evaporant and the ion beam travel in straight lines (line-of-sight) to the substrate. This is a serious limitation of the traditional IBAD process, which restricts the complexity of the parts that can be treated. However, a newly emerging ion implantation technology, namely Plasma Immersion Ion Implantation and Deposition (PIIID) is likely to solve this and a number of other problems encounter in IBAD, and elevate this process to the same level of industrial importance as anodizing.

There are two principal ways to carry out the IBAD process – the coating can be deposited under simultaneous or alternating ion bombardment. In the first case, low energy ion sources with no mass separation are used, such as the broad-beam Kaufman type. In the second case, a higher energy is required, depending on the thickness deposited between each irradiation interval (Fig. 9.1). The increment in thickness on each successive pass is,

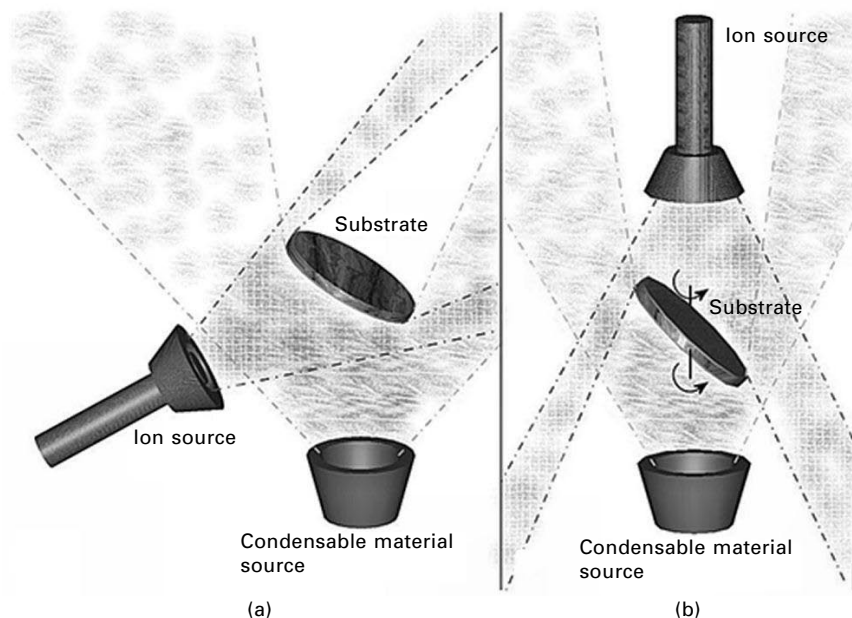


9.1 Ion beam deposition processes.

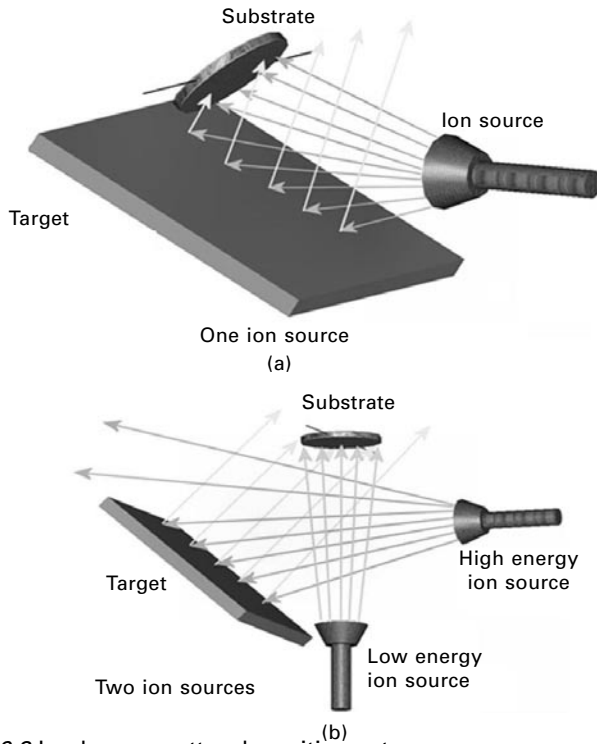
usually a few tens of nanometers. In both cases, the typical energy range used for IBAD/RIBAD is 100 eV – 30 KeV. When higher energies are used, decomposition of the deposited compounds occurs and the coating structure is damaged. This is particularly the case in the RIBAD process (Emmerich *et al.*, 1992a), where the ion beam species form solid compounds with the incoming vapour particles (condensable material). Figure 9.2a illustrates an IBAD/RIBAD deposition process in which a solid is vaporized thermally and condenses onto the substrates, which is stationary, while in Fig. 9.2b the substrate is being manipulated to minimize the line-of-sight problem.

9.3.1 Ion beam sputter deposition (IBSD)

If the source of condensable material is obtained by ion beam sputtering of atoms from a target, the process is known as ion beam sputter deposition (IBSD). Figure 9.3a, shows a single-ion source setup, while Fig. 9.3b shows a two-ion source configuration. To compensate for the extremely low deposition rates, sputtering deposition requires an ultra-high vacuum, to limit coating contamination from the residual gas. The high kinetic energies of the adatoms (10–300eV) in IBSD impart excellent adhesion and coating densification, resulting in superior wear and corrosion protection, (Valvoda, 1998 pp. 61–65). These high kinetic energies allow deposition of dense



9.2 IBAD/RIBAD setup.



9.3 Ion beam sputter deposition setup.

and hard coatings at temperatures lower than any other physical deposition process (Wasa and Hayakawa, 1992, pp. 65–78).

Clearly, the two-ion source configuration offers greater flexibility and control over coating structure and stoichiometry (Ingat *et al.*, 2004, pp. 124–134). Then again, multiple evaporation and ion sources may be required for the synthesis of compound coatings in the the IBAD/RIBAD processes. A configuration of two separately-controlled ion sources has achieved a relative degree of success in the United States. One institution using this system in the early 1980s was the US Naval Research Laboratory, which developed a series of processes suitable for high-temperature aerospace applications (Emmerich *et al.*, 1992a).

The most important process parameters, for the IBAD, IBSD, and RIBAD processes are the impinging fluxes of ions and neutrals ratios, base and operating pressure, the ion energies, and the substrate temperature (Ensinger *et al.*, 1992; Zhou and Wadley, 1999, pp. 42–57). These parameters determine the film stoichiometry, physical structure, and growth rate. Within the limits of the available hardware, these parameters are usually easily controllable.

9.4 Effects of ion bombardment

9.4.1 Effect of ion bombardment on film structure

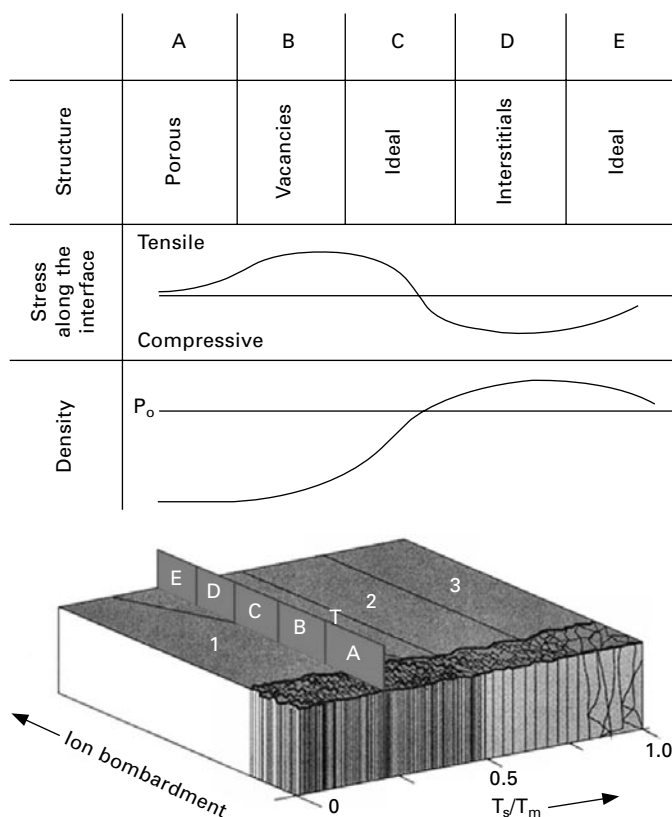
The physical properties of thin films are most strongly related to their morphology. Thermal and electrical conductivity, permeability, colour, toughness, and hardness properties are all very much dependent on morphology, and to a lesser extent on the chemistry of the coating. Ion beam bombardment has a profound effect on the structure of deposited films, at low and medium substrate temperatures. It is therefore reasonable to expect that ion bombardment will also influence the physical properties of the coatings produced by such processes. Ion bombardment enhances the lateral mobility of adatoms, and as a result, has a strong influence on coating density. The increased coating density, in turn, modifies the internal stresses and the mechanical properties of the resulting coating.

Müller (1978, pp. 1796–1799) showed that the internal stresses of a film are directly related to its density. He demonstrated that tensile stresses will be set up across the voids, if the deposited structure contains voids and has a lower than theoretical density. Conversely, if the bulk density of the coating is higher than the theoretical value, compressive stresses will result. Density and stress can therefore be qualitatively correlated to ion bombardment. This reasoning is only applicable to processes conducted at a substrate temperature represented by the structure–zones diagram, as pertaining to Zones 1 and T, Fig. 9.4b.

With increasing ion bombardment, the film becomes more compacted and its density increases. At the same time, the tensile stresses are reduced, up to a point where they are completely neutralized, as the coating density reaches the nominal density stage, C in Fig. 9.4. If the ion beam intensity is too high, the excess particles implanted into the solid bulk create self interstitials and interstitial defects in the coating. This will eventually result in coating densities that are higher than nominal (ρ_0). If the concentration of defects is further increased, the strain energy induced becomes high enough to induce plastic deformation of the substrate, or the coating may peel off the substrate surface in order to relieve the internal stresses. Metal films cannot exceed the theoretical density because of their atom mobility. Conversely, covalently bonded coatings can substantially exceed the theoretical density, giving rise to metastable structures stabilized by chemical bonds.

Region C of Fig. 9.4 is of particular interest for practical applications, as the internal stresses of the coatings produced in this regime are at a minimum. This is usually referred to as the ‘stress’ annealing regime. Brighton and Hubler (1978, pp. 527–533) postulated that in Region C each of the atoms in the growing film is involved, at least once, in a collision cascade.

The formation of high compressive stresses, as the coating grows, might promote the formation of dense metastable phases. Probably the most typical



9.4 Effect of ion bombardment on density and internal stress.

example of this is the deposition of amorphous carbon. Ion bombardment induced stresses have been shown to result in the formation of a significant percentage of sp^3 bonds in the final coating, resulting in a significant increase in hardness and wear resistance (Anders, 2000, pp. 193–194). The graphite and diamond phases are separated by the Berman–Simon line. At sufficiently high pressure, diamond, rather than graphite, becomes the thermodynamically stable phase (Yin and McKenzie, 1996, pp. 95–100). Using the IBAD deposition process, it is then possible to deposit coatings with various percentages of sp^3 coordination (Gago *et al.*, 2000, pp. 8174–8180).

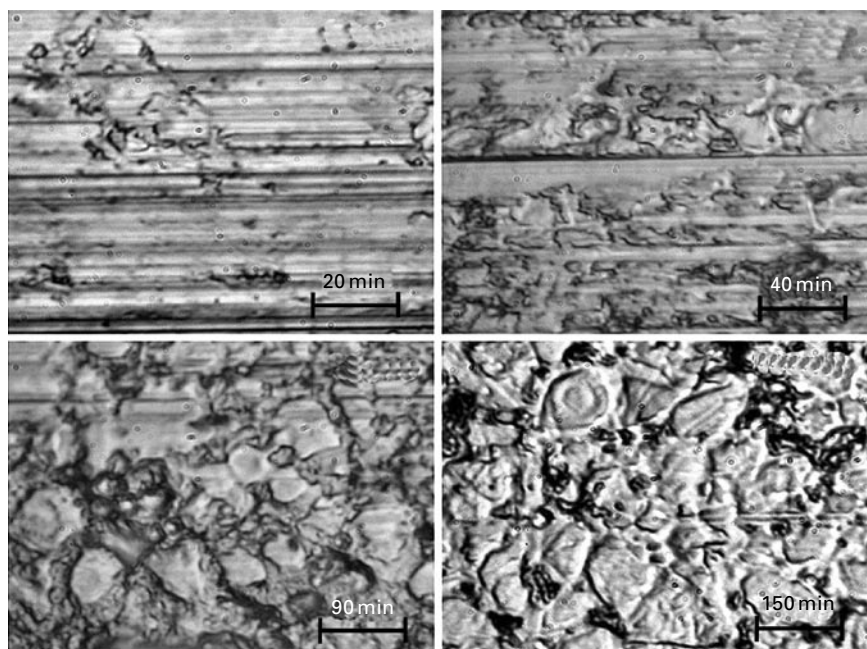
Since ion beams travel in straight lines, the angle at which they collide with the surface is not changed for the whole duration of the deposition process. Thin films deposited under ion bombardment, therefore, tend to exhibit preferential crystal orientation or texture. Using experimental data from various authors, Bradley *et al.* (1986, pp. 4160–4164) developed a model that describes the growth of thin film with texture, under the influence of ion bombardment. To minimize the shadowing effect, complex components

require extensive manipulation during the deposition process. This results in lengthier processing time and requires a greater capital expenditure.

9.4.2 Sputter cleaning of the magnesium substrate

The first step in any coating process is surface preparation of the substrate. In practically all PVD processes, substrate cleanliness is crucial for coating adhesion. Substrates are usually subjected to a number of cleaning steps before they are introduced into the deposition chamber. Metals substrates tend to absorb significant quantities of water vapour and oxygen; therefore, the final cleaning procedure for such substrates is usually conducted *in situ*, just before deposition is started. This involves bombardment of the surface of the substrate with high energy ions in order to sputter-clean the surface. This is particularly so for magnesium alloys, whose superficial oxide film is weakly adherent. Ion beam sputtering polycrystalline magnesium alloy substrate can lead to extensive roughening of the substrate surface leading to poor coating performance.

Pre-sputtering an AM50 magnesium substrate surface and its effect on the the performance of $0.5\ \mu\text{m}$ Al_2O_3 coatings on dry sliding is illustrated in Fig. 9.5. This investigation revealed that pre-sputtering for 10–20 minutes



9.5 Optical micrographs of shallow ($0.5\ \mu\text{m}$) Al_2O_3 coated substrates pre-implanted for periods varying between 20–150 minutes.

results in a very rapid increase in coating endurance because the weak oxide film is cleaned and the generation of a large number of point defects on the specimen's surface later act as nucleation sites supporting film growth. An increase in pre-sputtering time leads to a marked reduction in coating properties, reaching a minimum at 75 minutes of pre-sputtering. This is believed to be due to the preferential sputtering resulting in induced surface roughening. It was observed that the material at the grain boundaries sputtered preferentially, leaving relatively deep cracks in the substrate surface (Fig. 9.5).

The mechanisms leading to the formation of surface roughness were investigated by Friedrich and Urbassek (2003, pp. 315–323), who used a series of molecular dynamic simulations to investigate the effect of the presence of ledges and interfacial defects on the sputtering yield. Amongst their findings, these investigators reported that at room temperature, the sputtering yield of metals irradiated with particles having energies in the KeV range and impinging at sharp angles, is significantly higher in the vicinity of interfacial defects, further increasing the surface roughness. This result is consistent with the findings reported above.

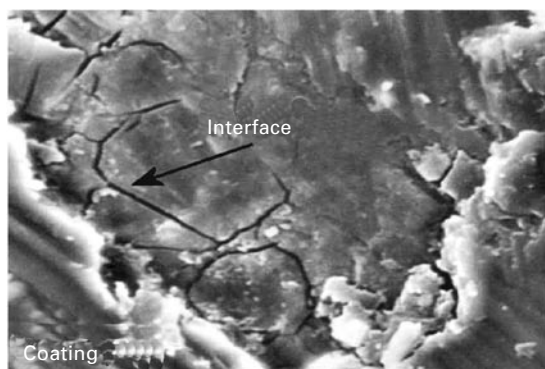
To understand the reason why the material at the grain boundaries is being sputtered at a much faster rate than the material in the central region of the grain, one has to consider the structural and chemical differences between these two regions. The most obvious difference is that at the grain boundary there are more atomic vacant sites, resulting in a less ordered crystal structure and weaker bonding. The difference in chemical composition between the core and the grain boundaries is even more important. This is particularly the case in the Mg-Mn-Al magnesium alloy system referred to as the AM series. In this series of magnesium alloys, segregation of the heavy elements Mn and Fe is brought about by the preferential growth of the Mn-Al-Fe, along the grain boundaries.

Research conducted at Hydro Magnesium (Hydro Magnesium, 2005, pp. 1–12) showed that in the case of AM50, as well as other Mg-Al-Mn alloys, corrosion starts at the Mg rich areas, which are at the centre of the grains, and then it propagates to the grain boundaries in the form of pits where it is stopped by the Al rich phase, situated along the grain boundaries. Data published by the above-mentioned company shows that in AM50 alloys, these precipitates contain Fe and Mn atoms, in the form of complex aluminates at the grain boundaries. These intermetallic compounds, AlMn_xFe_y , have a cubic structure and contain 15–35% Fe (55.84 amu) and 15–35% Mn (54.94 amu). The presence of such a high concentration of heavy elements in a light metal matrix gives rise to a process known as yield amplification during sputtering. Sputter yield amplification was described by Berg and Katardjiev (1999, pp. 1916–1925) as a process which takes place when thermodynamic processes are suppressed because of the low processing temperature.

Heavy elements, because of their large atomic mass, absorb considerable kinetic energy from the relatively smaller impinging ions. This kinetic energy is subsequently dissipated in the surface atomic layers. When this energy is transmitted to the nearby Al (26.98 amu) or Mg (24.31 amu) atoms, they acquire enough kinetic energy to enter the vapour phase and are, hence, sputtered. This is confirmed by simulation and experimental data published by the International Nuclear Data Committee at the 13th meeting of the A+M Data Centres and ALADDIN Networks (Botero, 1995). In this session, it was shown that when a solid is irradiated with a high energy ion beam, there is a strong relation between the sputtering yield and the impact cross-section of the particles.

Accelerated sputtering takes place only in regions rich in Fe and Mn, which have higher impact cross-section, resulting in the roughening of the surface. The loss of Al and Mg leads to precipitates containing more Fe and Mn, rendering the substrate more susceptible to galvanic corrosion. Berg and Katardjiev (1999, pp. 1916–1925) explain how a few percentage impurity content of atoms that are significantly heavier than those of the host, lead to an increase in sputtering rate; up to two orders of magnitude higher than that of the pure substance.

In Fig. 9.5 it can be seen that following pre-implantation for 150 minutes, most of the Mn-Fe precipitates on the surface, protrude out of the coating, with much of the surface in their vicinity heavily eroded. Also, the microstructure of the surface is clearly visible, with the grain boundary regions preferentially sputtered. The presence of Al rich phase on the substrate surface was confirmed by XRD analysis. The Fe and Mn rich phase, AlMn_xFe_y , appears as dark coagulates on the surface. The sputtered Al and Mg generate sharp voids, which can be seen in Fig. 9.6. As the sputtering time exceeds 90 min, the sharp edges become rounded, rendering, the void less damaging; thus the minor improvement in coating endurance, Fig. 9.5.



9.6 Deep cracks at the grain boundaries of the substrate surface exposed after alumina coating is worn in the wear track.

9.5 RIBAD deposition of titanium nitride (TiN) on magnesium alloys

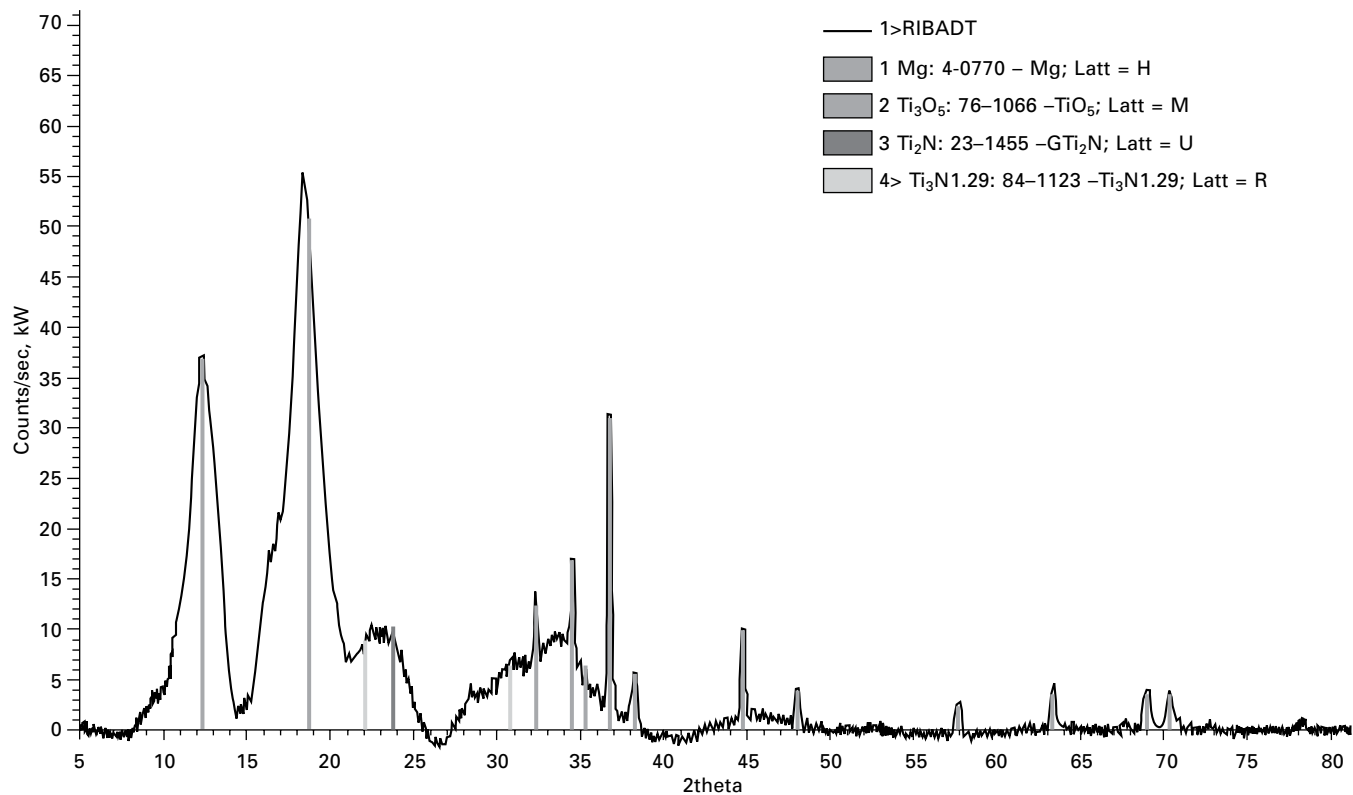
TiN has been deposited on AM50 magnesium alloy substrates using the incremental deposition technique. Various layers of $0.1\text{ }\mu\text{m}$ Ti were deposited and post-implanted with 45 KeV N^+ at room temperature. During each deposition cycle, residual molecules inside the chamber were incorporated in the growing film, such that each layer contained a substantial quantity of nitrogen and oxygen molecules, even prior to post-implantation. This can be clearly seen in Fig. 9.7, which illustrates an X-ray diffraction measurement taken on a RIBAD titanium layer, prior to post-implantation. This diffractograph shows peaks of $\text{TiN}_{0.26}$ and titanium oxide.

The mechanical properties of the coatings change with post-implantation time. Figure 9.8 illustrates the change in coating hardness and wear rate with post-implantation times ranging between 40 minutes ($2.7 \times 10^{16}\text{ N}^+\text{cm}^{-2}$) and 840 minutes ($5.7 \times 10^{17}\text{ N}^+\text{cm}^{-2}$). The substrate temperature was maintained at 25°C throughout the deposition process. From this graph it can be seen that with the deposition parameters used, the optimum post-implantation time is 220 minutes. The corresponding hardness is 26.8 GPa and the resultant wear rate is at its lowest value of $2.51 \times 10^{-12}\text{ mm}^3\text{Nm}^{-1}$.

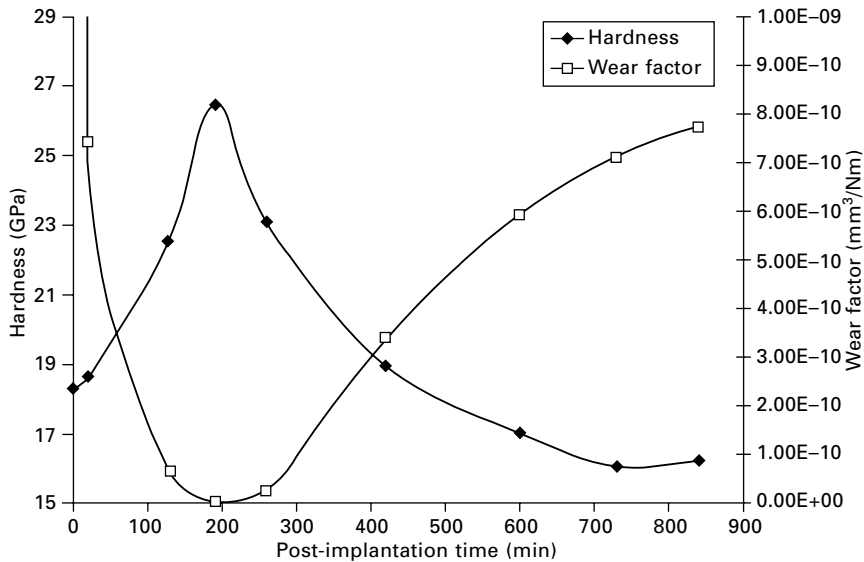
The effect of post-implantation dose on the TiN coating structure can be easily visualized by conducting a series of Scanning (electron) Tunnelling Microscopy (STM) scans. Figure 9.9 (on page 310) shows a series of scans conducted on TiN coatings with increasing nitrogen ion implanted dose ($2.7 \times 10^{16}\text{ N}^+\text{cm}^{-2}$ – $4.08 \times 10^{17}\text{ N}^+\text{cm}^{-2}$). Despite the low deposition temperature, the structure of all coatings is dense and is composed of equiaxed grains of various sizes.

Extending the post-implantation time results in a very rapid increase in hardness, reaching a maximum at a post-implantation dose of $8.1 \times 10^{16}\text{ N}^+\text{cm}^{-2}$, as indicated from Fig. 9.8. This increase in hardness results from the recrystallization of the coating surface. Increasing the post-implantation dose from $8.1 \times 10^{16}\text{ N}^+\text{cm}^{-2}$ to $1.62 \times 10^{17}\text{ N}^+\text{cm}^{-2}$, gives rise to a gradual increase in grain size and a corresponding reduction in hardness. The nitrogen content of the surface, measured by EDX, did not exceed 54 at%. When the nitrogen content exceeded 52 at%, the coatings experienced blistering after several months of storage at room temperature, implying that the nitrogen composition in the sub-surface could be much higher, a feature typical of ion implantation.

The sputtering yield of nitrogen in samples having nitrogen contents higher than the stoichiometric composition, is much higher than that of titanium. Thus, much of the excess nitrogen in the near surface region is re-emitted into the vacuum. Schneider *et al.* (1997, pp. 1084–1088) has reported a similar behaviour for the reactive sputter deposition of alumina



9.7 X-ray diffraction from RIBAD TiN with no post-implantation.



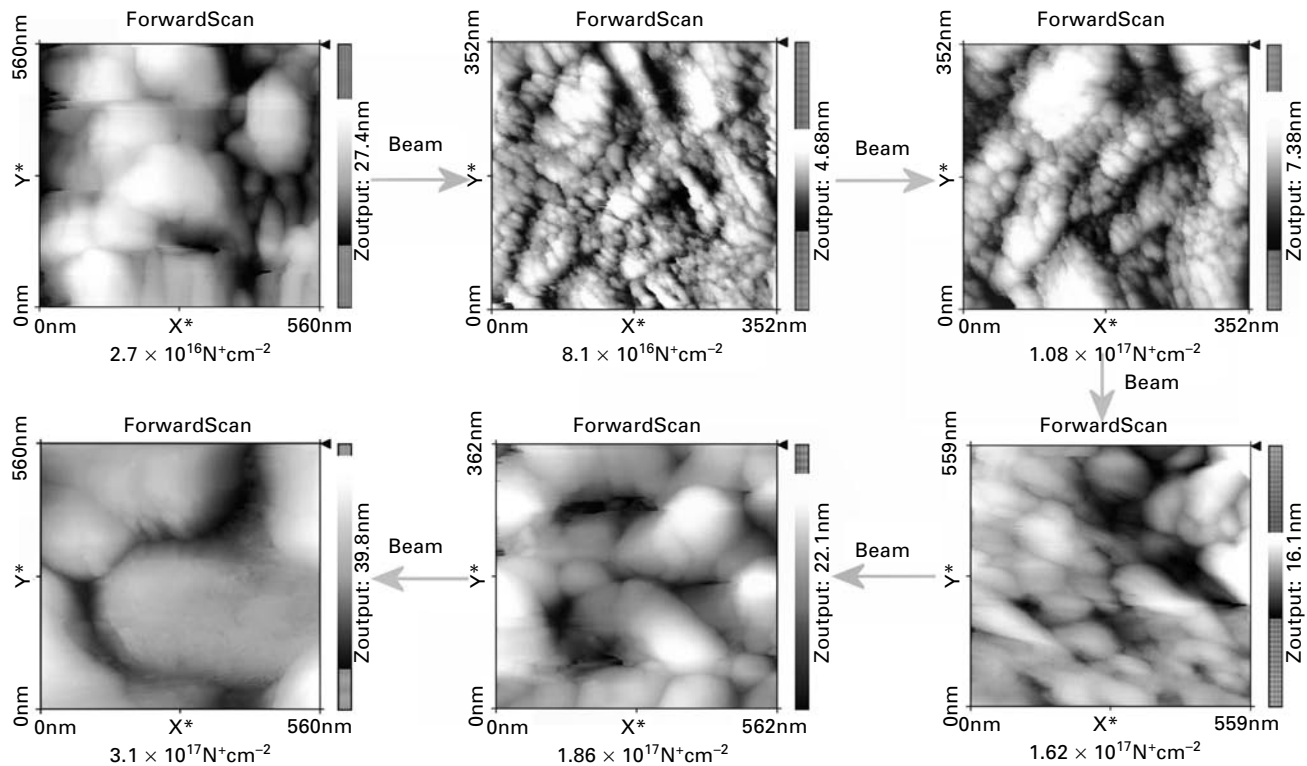
9.8 Effect of post-implantation time on the surface hardness and wear resistance of RIBAD TiN coatings.

under oxygen bombardment. Fu *et al.* (1997) also investigated the effect of ion beam energy on the grain size, hardness and wear resistance of RIBAD TiN. They reported increased grain size, and a progressive decrease in hardness, with increasing ion beam energy. They also observed a gradual reduction in wear resistance with increasing ion beam energy. These results concord with the findings reported by the author.

Shin *et al.* (2002, pp. 807–812) also observed grain growth of RIBAD deposited TiN from 10–100 nm, as the ion beam energy was increased from 0 to 200 eV. Fukumoto *et al.* (1999, pp. 205–209) have implanted N⁺ in pure titanium substrates using a 150 KeV ion beam. They also reported TiN grain growth with increasing N⁺ dose. However, the actual sizes of the TiN precipitates in this case were not reported.

9.6 Sliding wear and aqueous corrosion of Mg alloys

The poor tribological properties of magnesium and, in particular, its poor corrosion resistance, are the main reasons for the decline in the use of magnesium alloys in the automobile industry experienced in the 1970s. Strict legislations, such as Corporate Average Fuel Economy (CAFE), Directive 70/220/EEC (light vehicles) and 88/77/EC (heavy vehicles), as well as recent amendments to those directives, have proven to be a sufficient incentive for the revival of magnesium and its alloys in the automotive industry. Despite



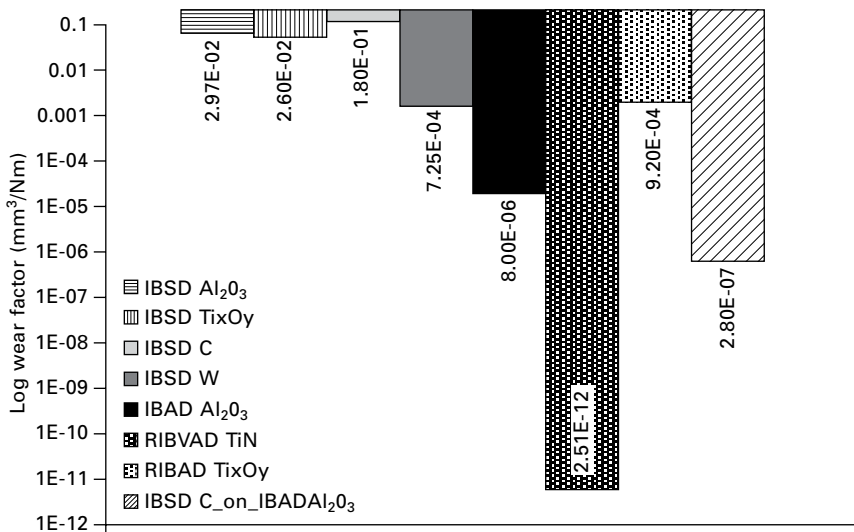
9.9 Effect of N_2^+ Ion implantation dose on RIBAD Ti micro structure $2.7 \times 10^{16} \text{N}^+ \text{cm}^{-2} - 3.1 \times 10^{17} \text{N}^+ \text{cm}^{-2}$.

the considerable improvement in the corrosion resistance of modern, high-purity magnesium alloys, the galvanic corrosion problem can be solved only by proper coating systems. Nevertheless, defects in a coating deposited on a magnesium substrate would result in enhanced localized attack.

This was pointed out by Blawert *et al.* (2004, pp. 397–408) in an extensive report on the trends for use of Mg in the automotive industry. Gadow *et al.* (2000) also stated that the intrinsic poor tribological behaviour is the only impediment for the wider use of magnesium base alloys in a range of domestic applications. Further evidence to this is provided by Hoche *et al.* (2003, pp. 1018–1023), who indicated that the poor corrosion resistance, low capacity for strengthening, poor ductility and, especially, the unsatisfactory wear behaviour of magnesium and its alloys are the main reasons why they are used only for static (passive) components.

9.6.1 Wear resistance of coated AM50 substrates

The wear rate of the various 1 μm thick coatings on AM50 magnesium substrates is compared in Fig. 9.10. The vertical axis of this graph is the log of the coating material volume worn away, divided by the sliding distance and the applied normal load. Thus for a specific coating, the deeper its corresponding inverted rectangle is in Fig. 9.10, the more resistant this coating is to wear, under the specific testing conditions. The coatings discussed in this chapter are described in Table 9.1.



9.10 Wear resistance of various coatings, subjected to the pin-on-disc test.

Table 9.1 Coatings under investigation

Coatings	IBSD Al ₂ O ₃	IBSD Ti _x O _y Al	AM50	IBSDC	RIBAD Ti _x O _y	PVD TiN	C on Al ₂ O ₃	IBAD Al ₂ O ₃	IBSD W	IBAD TiN	
Thickness (μm)	1	0.98	na	na	0.86	1.02	5.3	0.84 + 1	1.12	1	1.08
Deposition technology	IBSD	IBSD	na	na	IBSD	RIBAD/Step	PVD	EB/IBAD	EB/IBAD	IBSD	EB/RIBAD
Deposition temperature (°C)	20	20	na	na	20	50	300	20	20	20	50
Substrate Material	AM50	AM50	Pure Al	AM50	AM50	AM50	AM50	AM50	AM50	AM50	AM50
Ion Beam	Ar	O ₂	na	na	Ar	O ₂	N ₂	Ar	Ar	Ar	N ₂
Backfill Gas	none	none	na	na	none	none	N ₂ + Ar	none	none	none	N ₂

As can be seen from the chart, ion beam sputtered aluminium oxide, titanium oxide and carbon coatings have very high wear rates compared with those of sputtered W and ion beam assisted deposition coatings. Also, from the same figure, it can be concluded that by far the best performing coating is RIBAD TiN, resulting in a wear factor of $2.51 \times 10^{-12} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. This is followed by IBAD alumina (I/C 0.3) which resulted in a wear factor of $8 \times 10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$. The far right pyramid, in this chart, represents the wear rate of $1 \mu\text{m}$ sputtered carbon on top of a $5 \mu\text{m}$ IBAD alumina (I/C = 0.3) coating. This composite coating wears at a rate of $2.8 \times 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, and shows, therefore, an improvement over that of IBAD alumina on its own.

All the coatings in Fig. 9.10, were deposited at 25°C in the same deposition chamber which could attain a base pressure of 0.2 Pa. The wear factor of the base material is not included as it is not possible to represent it using this scale. The poor performance of all the ion beam sputter deposition (IBSD) coatings can be attributed to the high residual gas pressure combined with the extremely low deposition rate, and is not an intrinsic property of IBSD coatings. The high partial pressure results in a continuous build-up of physisorbed gas molecules on the substrate surface, which hinder coalescence of the growing coating island, leading to a high concentration of nanometric voids inside the coating. This results in much lower hardness and density as compared to the theoretical value for the respective coating material. The only exception is the sputter deposition of W, which has a very high hardness, even though the coating density is only 0.8 of the theoretical value. This is believed to be due to the difference in mass between the residual gas molecules, $195 (\text{H}_2\text{O} (18 \text{ amu}), \text{O}_2 (32 \text{ amu}), \text{ and nitrogen } (28 \text{ amu}))$ and that of W (184 amu). As a result, W particles lose little kinetic energy during binary collisions with residual gas particles on the surface. Konczos *et al.* (1998, Chapter 5), in their discussion of the effect of residual gas pressure in deposition systems, mention the effects of adsorbed gases on the growing film surface. They affirm that at room temperature, residual reactive gases occupy the reactive sites of the substrate surface and ‘act as a source of mechanical stresses to pin grain boundaries and vacancies’. In turn, this results in poorly adherent films, which are either amorphous or have very small grains. At higher temperatures, according to Konczos *et al.* (1998), the incorporated gases give rise to mechanical stresses in the coatings, and significantly modify both their electrical and optical properties.

Despite the high residual gas pressure and the low deposition rate used, the coating adhesion and wear resistance reported by Ignatenko *et al.* (2005, pp. 148–151), are significantly better than those of RIBAD TiN deposited by Lloyd and Nakahara (1977, pp. 655–659). on the same substrates. At first sight, Ignatenko’s results appear also to be in contrast with the results obtained by the author, in which the deposition by IBSD of TiN resulted

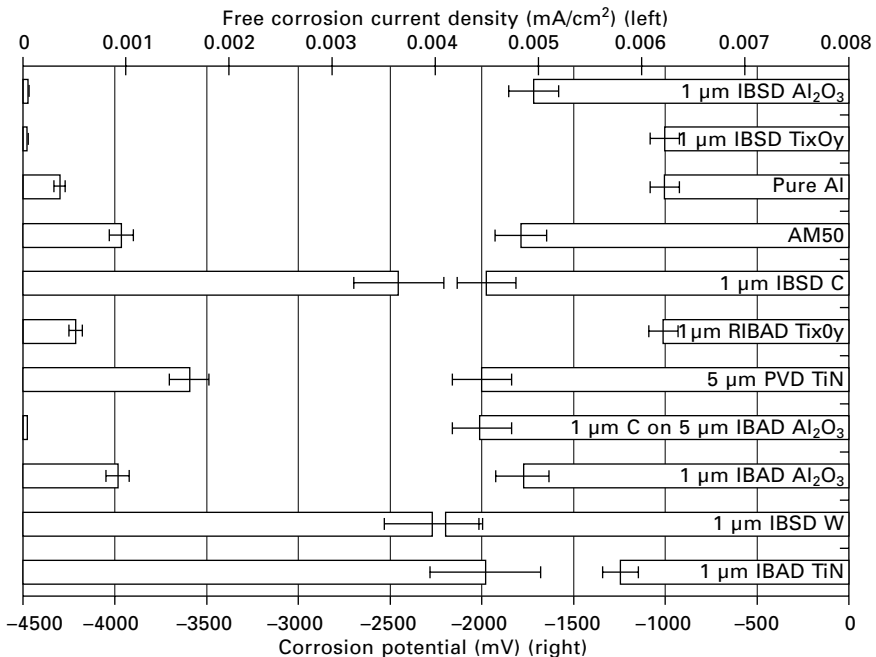
in a loosely bound mixture of titanium oxides with exceedingly poor mechanical properties (Fig. 9.10). Still, this difference originates mainly from the difference in the operating parameters used. While in the first case the substrate temperature was not allowed to exceed 30°C and no substrate bias was used, Ignatenko *et al.* applied a deposition temperature of 500°C and a substrate bias of -200V. This is believed to be responsible for the considerable improvement in the coating hardness and adhesion to such an extent that it actually outperformed the RIBAD TiN deposited by Lloyd and Nakahara using similar conditions. Unfortunately magnesium substrates cannot be treated at such a high temperature as this results in the sublimation of magnesium. Petrov *et al.* (2003) showed that low density coatings result when metal films are deposited with an impurity arrival rate much higher than that of the metal itself. They also stated that, for alumina deposited under these conditions, adequate mechanical properties cannot be achieved at deposition temperatures lower than 500°C in the case of ion beam bombardment, and 800°C when no ion beam irradiation is applied. The findings of the author's investigation concur with the findings of Petrov *et al.* (2003), whose conclusions are based on experimental data gathered from work carried out by a number of researchers over several decades. Thus for the successful application of IBSD coatings on magnesium substrates (below 500°C), the condensable flux ratio must be considerably higher than the residual gas molecule impingement rate. This can be achieved by using very high sputtering rates (i.e. using very high ion beam currents), and using very low deposition pressures $< 1 \times 10^{-6}$ Pa.

Magnesium oxide present on the substrate is a weak link in the coating system, and is thought to be responsible for poor coating adhesion. Busk (1986, pp. S497–S499) describes this oxide as unstable, due to a misfit between the lattices of the cubic oxide and that of the hexagonal metal, resulting in a Pilling–Bedworth factor of less than one. In addition, when exposed to humid atmospheres, magnesium oxide reacts to form hydroxide, further compromising adhesion. While investigating plasma surface treatment of magnesium alloys, Hoche *et al.* (2003, pp. 1018–1023) demonstrated that the presence of magnesium oxide at the interface of a hard coating is detrimental for the coating hardness and adhesion. They suggest that the weak bond of the MgO with the parent metal inhibits the formation of compressive stresses in hard coatings deposited on top of the MgO, resulting in lower hardness and adhesion and therefore poor tribological properties. Kurth *et al.* (2006, pp. 931–940) investigated the oxide formation on magnesium at reduced pressures and low temperatures (0–200°C). In their paper they report that previous attempts to grow thicker MgO layers at elevated temperature invariably resulted in cracks in the oxide film, consequently leading to poor adhesion and poor corrosion protection. In contrast, work conducted by Stippich *et al.* (1998, pp. 29–35) has shown that magnesium oxide can

be grown, under controlled conditions, to form a protective layer. In their work they explain that IBAD deposited MgO, using 5–15 KeV Ar⁺ and an I/C of 0.2, can generate a range of useful crystal structures that can offer moderate corrosion protection on their own but, more importantly, can be used to provide support for better protective surface layers. This was amply demonstrated by Hoche *et al.* (2005c, pp. 223–229) who reported the performance of three coating systems for magnesium substrates, namely 9 μm CrN, 2.1 μm TiN and 0.5 μm MgO + 3 μm Al₂O₃. In their new setup, they used an RF magnetron source to sputter the condensable material while feeding the reactive gas at very low pressure. The hardnesses of the TiN and Al₂O₃ coatings deposited with this method were 42.86 GPa, and 22.07 GPa, respectively, which are surprisingly high.

9.6.2 Corrosion resistance of coated AM50 substrates

The free corrosion current density and the corrosion potential with respect to the standard hydrogen electrode (SHE), of the various coated AM50 samples considered above, are plotted in Fig. 9.11 for comparison. From this chart,



9.11 Free corrosion potential (right) and free corrosion current density (left) of AM50 substrates coated with 1 μm of various coatings, in 5% NaCl solution at 20°C, after 20 min immersion holding time.

it is clear that IBSD Al_2O_3 and Ti_xO_y offer the best corrosion protection, followed closely by the IBSD C deposited on IBAD Al_2O_3 composite coating. The worst corrosion protection is that offered by RIBAD TiN. Sputter deposited W and C show somewhat similar behaviour to that of RIBAD TiN. From this chart, it is evident that these coatings have a negative effect on the corrosion properties of the underlying AM50 magnesium alloy. Thus, compared to the uncoated AM50 and pure aluminium substrates (which are included for reference), most of the coated surfaces result in a higher free corrosion current density. The excellent performance of IBSD coatings in corrosion protection is attributable to their low bulk defect density.

In a similar investigation, Hoche *et al.* (2005ab, pp. 559–567, 623–631) concluded that a high defect concentration, particularly in the case of conducting coatings, has a negative effect on the integrity of magnesium alloys exposed to corrosive environments. This is also in accordance with the results reported by Ignatenko *et al.* (2005, pp. 148–151) who attribute the improved corrosion resistance of IBSD coated magnesium alloys, compared to IBAD coatings deposited on the same substrates, to the higher electrical resistance of the former coatings and relatively low defect concentration.

According to Petrov *et al.* (2003), the deposition of PVD Ti at room temperature (zone 1 of the SZM) tends to form a fine fibre texture in which growth along the length of the fibre is more dominant than nucleation. This results in the formation of a porous coating. The researchers have also demonstrated that the deposition of metals with an impurity arrival rate much greater than that of the metal flux results in severely limited adatom mobility, lack of texture and absence of bulk porosity. This does not mean that there is no porosity, but in this case it is distributed in fine nanometric pores across the whole matrix, with no interconnectivity.

These results would explain the wide difference in corrosion performance between RIBAD TiN and IBSD coatings experienced in the former investigation. In the case of RIBAD TiN, Ti atoms are evaporated by means of an electron beam gun at room temperature. For each deposition cycle, the arrival rate of Ti could be adjusted to minimize the effect of contamination. This, according to Petrov *et al.* (2003) results in fine grained coatings with high porosity, which appears to explain the poor corrosion characteristics experienced. On the other hand, in the case of the IBSD coatings, the metal/impurity arrival rate was severely limited by the maximum ion beam current limiting the metal flux to 9×10^{13} atoms per square centimetre each second. This is very low, compared with the arrival rate of the impurity particles. The high impurity concentration in the growing film is responsible for the disruption of texture, and also for the absence of bulk porosity (porosity large enough to expose the substrate surface), which in turn promotes good corrosion performance in these coatings.

Coatings deposited by electron gun evaporation contained significantly

more large defects than those produced by sputtering. Even when evaporating at the lowest controllable evaporation rate, numerous globules (sputters) are collected on the substrate surface. Though, most of the globules are small compared to the coating thickness, some inclusions can be big enough to lead to pinholes, shadowing effects, and cracks in the coating. Similar defects have also been reported by Mattox (1998, p. 476) and Carvalho *et al.* (2003, pp. 273–280).

Altun and Sen (2005, pp. 193–200) used DC magnetron sputtering to deposit AlN on various AZ series magnesium alloys. In their publication, they point out the inability of the AlN coatings to protect the underlying substrates because of the large number of defects, pores, and cracks which, according to Altun *et al.*, are impossible to avoid. Hollstein *et al.* (2003, pp 261–268) also affirm that pinhole defects are process related, and that these are more prominent in depositions conducted at low temperature because of adsorbed gases and higher nucleation rates. They demonstrated that the porosity density in the PVD coatings can be reduced by depositing thicker coatings. Similar behaviour was also reported by Hoche *et al.* (2005ab, pp. 559–567, 623–631). In this case, this group reported increased corrosion, resulting from defective conductive PVD coatings giving rise to highly accelerated corrosion rates; 100X for TiN coated substrates and 2000X for CrN coated substrates, with respect to the uncoated material when exposed to a 5% NaCl salt spray test.

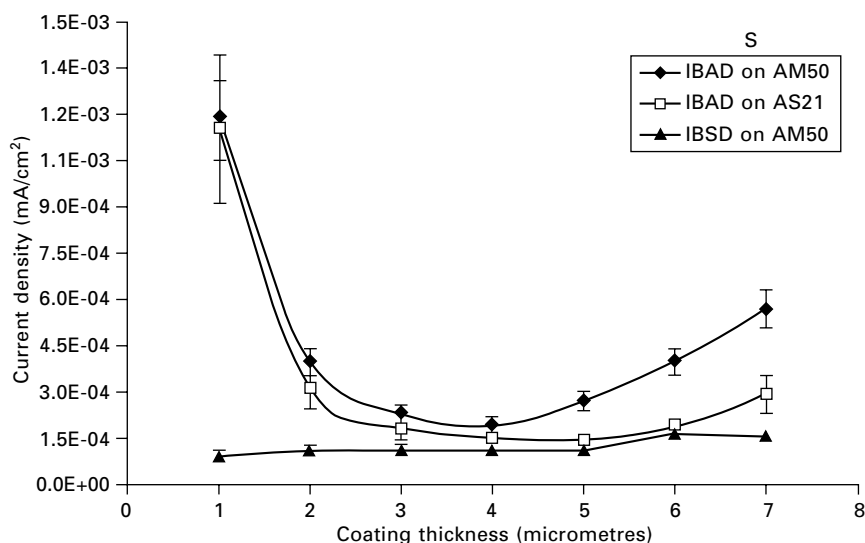
From Fig. 9.11, it is evident that the non-conductive RIBAD coatings do not accelerate corrosion. In this chart, RIBAD Ti_xO_y and IBAD Al_2O_3 , have a current density almost identical to that of the uncoated AM50 substrate. In fact, these coatings offer a small degree of protection, despite having the same defect concentrations typical of the other PVD coatings. RIBAD Ti_xO_y coatings investigated in this study showed superior corrosion resistance compared with IBAD Al_2O_3 coatings, even if the two coatings exhibited similar defects. This is believed to stem from the layered structure of the latter.

Hoche *et al.* (2005c, pp. 223–229) studied the galvanic corrosion properties of different PVD coatings on AZ91. They found that the rate of corrosion of TiN coated substrates containing pinholes was higher than that of the uncoated substrate. Hoche *et al.* attributed this enhanced corrosion to the fact that the conductive TiN surface acts as a stable cathode, dissipating the electrons liberated by the oxidation of magnesium. The investigators also demonstrated that the non-conductive 2 μm Al_2O_3 coatings deposited on 1 μm thick plasma anodized magnesium layer, greatly outperforms thicker TiN and CrN coatings, which are both conductive. Both TiN and CrN coatings were shown to be gradually debonded from the surface by the dissolution of the interface material, after which the samples attained the same performance as the uncoated substrate. Conversely, the results

reported by Hollstein *et al.* (2003, pp. 261–268) are in net disagreement with those reported by Hoche *et al.* Using polarization experiments, Hollstein *et al.* concluded that TiN deposited on AZ31 magnesium alloys, provided a corrosion protection comparable to that of numerous other PVD coatings. The observed improvement in corrosion resistance reported by Hollstein *et al.* for TiN, may in fact be due to the greater coating thickness used, namely 5 μm .

The effect of coating thickness on the free corrosion current density of alumina coated substrates, for both IBAD Al_2O_3 and IBSD Al_2O_3 coatings on AM50 and AS21, is illustrated graphically in Fig. 9.12. From this figure, it can be inferred that the performance of IBSD alumina is practically independent of coating thickness. In comparison, the performance of IBAD Al_2O_3 on both substrate materials is greatly dependent on the coating thickness. These coatings show a rapid improvement in corrosion resistance as the coating thickness increases to 4 μm . Increasing the coating thickness up to 5 μm leads to minor changes in free corrosion current. However, further thickening of the coating has a rapidly increasing detrimental effect on corrosion resistance.

As discussed previously, the improvement in corrosion protection with thickness of the IBAD coating is mainly due to the reduction in coating surface porosity, physically connected to the substrate. The increase in free corrosion current observed in coatings having a thickness greater than 5 μm



9.12 Free corrosion current density of AM50 and AS21 substrates coated with Al_2O_3 coatings of various thickness, in 5% NaCl solution at 20°C, after 20 min immersion holding time.

is thought to be due to arcing-induced defects, due to the charging of the alumina coating, which leads to the formation of large defects. Since alumina is a dielectric material, when these coatings are bombarded by the ion beam a charge build-up is generated on the surface. As the coating thickness is increased, less current is able to leak through the coating. When the electric field reaches the breakdown voltage, arcing takes place. The damage caused by arcing seriously compromises the performance of the coating. A separate investigation has revealed that, for optimal mechanical protection of the underlying magnesium substrates, IBAD alumina coatings must be thicker than $7\text{ }\mu\text{m}$.

During the deposition of IBSD alumina, the deposition flux is scattered by colliding with the residual gas in the chamber and on the surface of the substrate. This residual gas hinders coating densification and, to a larger extent, crystallization, but it is also responsible for the formation of a stress-free featureless coating with very little porosity. Also, this coating is not prone to arcing as the substrate surface is never exposed to the ion beam.

9.7 Conclusion

It is evident from the work reported that it is possible to deposit an extensive range of coatings on magnesium alloy substrates using ion beam assisted deposition techniques. The extreme nature of magnesium alloys makes the application of this technology to these substrate rather problematic. A case in point is the fact that pre-sputtering of the AM series magnesium alloys can lead to surface roughening, which has a negative effect on the mechanical properties of the coated surface. However, through scientific investigation of each system, the deposition parameters for a specific alloy system can be pinpointed with relative ease.

The combination of low deposition temperature and high residual gas pressure results in a low adatom mobility during ion beam sputter deposition at low temperatures. It was shown that, under these conditions, the coatings produced are highly amorphous and have poor mechanical properties. Despite their low density, the IBSD oxide coatings provide good corrosion resistance, far superior than that offered by traditional conversion coatings, even for oxide coating thicknesses below $3\text{ }\mu\text{m}$. The mechanical properties of IBSD Al_2O_3 and Ti_xO_y can be substantially improved by upgrading the vacuum system. This phenomenon provides the ideal conditions for engineering a base coating layer with specific properties designed to provide corrosion protection and enhanced mechanical support to a hard topcoat. Such a topcoat could be applied selectively, in order to reduce processing costs. Plasma immersion ion implantation is a promising candidate for this application.

Conversely, IBAD coatings were found to contain many defects which lower their resistance to corrosive solutions. These coatings can, however,

be substantially improved, either by increasing the coating thickness or by depositing additional coatings with minimal surface porosity. It was demonstrated that conductive coatings, such as carbon in the form of graphite, titanium nitride and tungsten, and in particular titanium nitride, significantly accelerate corrosion by setting up galvanic corrosion. The last gives rise to severe pitting or filiform corrosion, which will eventually detach the coating completely from the surface.

Alumina coatings with 10–30% crystallinity can be deposited onto magnesium substrates, even at room temperature. The transparent coatings have a matrix average hardness of 13GPa with embedded hard alpha alumina crystals (28GPa). For optimal wear resistance of Al_2O_3 coatings deposited on AM50 substrates, an I/C ratio of 0.3 should be used. The mechanical properties of these coatings could be further improved by applying a substrate bias, in order to minimize shadowing effects.

IBAD alumina coatings offer corrosion protection comparable to that offered by many conversion coating in mildly corrosive environments. However, the wear resistance of these coatings is by far superior and is comparable to that of the hard coatings deposited on steel substrates. Increasing the coating thickness can substantially improve both the corrosion and mechanical protection provided by these coatings. Arcing defects can be easily avoided, by using either a pulsed DC or an RF substrate bias, measures which would also enhance the properties of IBSD coatings. Thick alumina coatings would also electrically isolate magnesium components which could later be used in complex assemblies, minimizing the risk of galvanic corrosion.

Finally, various investigators have shown that it is possible to deposit duplex coatings that exhibit wear and corrosion resistance using a two cycle process in one chamber. The first step involves the deposition of a thick layer of dense and adherent modified MgO coating, which provides a smooth transition of mechanical properties. This coating would cater for the corrosion properties and provide adequate mechanical support for the topcoat. On top of this coating, a thinner but harder topcoat is deposited.

9.8 References

- Altun H, Sen S (2005), *Surface and Coating Technology*, Volume 197, 193–200.
- Anders A (2000), *Handbook of Plasma Immersed Ion Implantation and Deposition*. Wiley-Interscience, ISBN: 0-471-24698-0.
- Avedesian M M, Barker H (1999), *Magnesium and Magnesium Alloys*, ASM Specialty Handbook, The Materials Information Society, ISBN: 0-87170-657-1.
- Bell T (1992), *Journal of Physics D: Applied Physics*, 25, A297–A306.
- Berg S, Katardjiev I V (1999), *Journal of Vacuum Science & Technology A, Vacuum, Surfaces, and Films*, Volume 17, Issue 4, 1916–1925.
- Blawert C, Hort N, Kainer K U (2004), *Trans. Indian Inst. Metal.*, August, 397–408.
- Botero J (1995), International Nuclear Data Committee, (INDC) IAEA Advisory Group

- Meeting on 'Technical aspects of atomic and molecular data processing and exchange'. *13th Meeting of the A+M Data Centres and ALADDIN Networks*. 10–11 July 1995, IAEA Headquarters, Vienna, Summary Report, December 1995.
- Bradley R M, Harper J M E, Smith D A (1986), *Journal of Applied Physics*, Volume 60, 4160–4164.
- Brighton D R, Hubler K (1987), *Nuclear Instruments and Methods in Physics*, B28, 527–533.
- Busk R.S (1986), *Magnesium Products Design*, CRC Press, ISBN-10: 0824775767.
- Carvalho N J M, Kooi B J, De Hosson J T M (2003) *2002 IFHTSE/ISEC Surface Engineering Congress*, Columbus, OH, USA, ASM. 2003, 273–280.
- Deutchman A H, Partyka R J (2002), 'Ion Beam Enhanced Deposited (IBED) Tribological Coatings for Non-Ferrous Alloys', *Proceedings from the 1st International Surface Engineering Congress and the 13th IFHTSE Congress*, 7–10 October 2002, Columbus Ohio.
- Emmerich R, Enders B, Ensinger W (1992b), 'Ion Beam Assisted Deposition of Thin Films and Coatings: Part 2', *Surface Modification Technologies VI*, November 2–5, ISBN: 0-87339-217–5.
- Emmerich R, Enders B, Ensinger W (1992a), 'Ion Beam Assisted Deposition of Thin Films and Coatings: Part 1', *Surface Modification Technologies VI*, November 2–5, ISBN: 0-87339-217–5.
- Enginger W (1992), *Review of Scientific Instruments*, Volume 63, Issue 4, April, 2380.
- Enginger W, Enders B, Emmerich R (1992), 'Ion Beam Assisted Deposition of Thin Films and Coatings: Part III', *Surface Modification Technologies VI*, ISBN: 0-87339-217–5, November 2–5
- Friedrich A, Urbassek H M (2003), *Journal of Surface Science*, Volume 547, 315–323.
- Friedrich H, Schumann S (2002), Mineral Processing and Extractive Metallurgy, *IMM Transactions*, Section C, Volume 111, Number 2, August, 65–71(7).
- Fu Y, Zhu X, Xu K, He J (1997), 'Ion Bombardment on the Mechanical Properties of IBAD TiN Films, Part 1', *Surface Modification Technologies*, Volume X. Published by the American Society of Materials. ISBN: 1861250223.
- Fukumoto S, Tsubakino H, Inoue S, Liu L, Terasawa M, Mitamura T (1999), *Materials Science and Engineering*, Volume A263, 205–209.
- Gadow R, Gammel F J, Lehnert F, Scherer D, Skar J I (2000) 'Corrosion protection of magnesium diecastings using silicone-modified organic coatings', *10th International Metallurgy and Materials Congress and Trade Fair*, 24–28 May, Istanbul.
- Gago R, Jimenez I, Climent-Font A, Albella J M, Caceres D, Vergara I, Terminello L J, Banks J C, Doyle B L (2000), *Journal of Applied Physics*, Volume 87, Issue 11, 8174–8180.
- Hoche H, Blawert C, Broszeit E, Berger C (2005a), *Proceedings of the 6th International Conference Magnesium Alloys and their Applications*, ISBN: 3-527-30975-6, Chapter 99, April, 623–631.
- Hoche H, Blawert C, Broszeit E, Berger C (2005b), *Proceedings of the 6th International Conference Magnesium Alloys and their Applications*, ISBN: 3-527-30975-6, Chapter 89, April, 559–567.
- Hoche H, Blawert C, Broszeit E, Berger C (2005c), *Surface and Coating Technology*, Volume 193, 223–229
- Hoche H, Scheerer H, Probst D, Broszeit E, Berger C (2003), *Surface and Coating Technology*, Volume 174–175, 1018–1023.
- Hollstein F, Wiedemann R, Scholz J (2003), *Surface and Coating Technology*, Volume 162, 261–268.

- Hydro Magnesium (2005), Corrosion and finishing of magnesium alloys, September, <http://www.hydro.com/magnesium/en/services/publications/>
- Ignatenko P I, Klyakhina N A, Badekin M Y (2005), *Journal of Inorganic Materials*, Vol. 41, Number 2, 148–151. Translated from *Neorganicheskie Materialy*, Vol. 41, Number 2, 2005, 193–196.
- Ingat S, Sallamand P, Grevey D, Lambertin M (2004). *Applied Surface Science*, 225, Numbers 1–4, 124–134.
- Itoh T (1989), *Beam Modification of Materials 3. Ion Beam Assisted Growth*. Elsevier, ISBN: 0444872809.
- Klingenberg M, Arps J, Wei R, Demaree J, Hirvonen J (2002), *Surface and Coatings Technology*, Volumes 158–159, September, 164–169.
- Konczos G, Bársony I, Deák P (1998), *Introduction to Materials Science and Technology*. A Textbook of the Technical University of Budapest. For PhD. students in physics.
- Kurth M, Graat P C J, Carstanjen H D, Mittemeijer E J (2006), *Surface and Interface Analysis*, Volume 38, 931–940.
- Lloyd J R, Nakahara S (1977), *Journal of Vacuum Science and Technology*, Volume 14, Issue 1, 655–659.
- Mändl S, Brutscher J, Günzel R, Höller W (1996), *Nuclear Instruments and Methods in Physics Research B*, Volume 112, 252–254.
- Mattox D M (1998), *Handbook of Physical Vapor Deposition (PVD) Processing. Film Formation, Adhesion, Surface Preparation and Contamination Control*. Noyes Publications, Park Ridge, NJ, ISBN: 0-8155-1422-0.
- Miessler G L, Tarr D A (2003), *Inorganic Chemistry*, 3rd edition. Prentice Hall, ISBN: 0130354716
- Morton P H (1992), *Surface Engineering and Heat Treatment, Past, Present, and Future*, Institute of Metals, London. ISBN: 0901716014.
- Müller K-H (1978), *Journal of Applied Physics*, Volume 62, 1796–1799.
- Petrov I, Brana P B, Hultman H, Greene J E (2003), *Journal of Vacuum Science and Technology A*, Volume 21, Number 5, September–October.
- Schneider J M, Sproul W D, Voevodin A A, Matthews A (1997), *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, Volume 15, Issue 3, 1084–1088.
- Shin H J, Cho Y J, Won J Y, Kang H J, Baeg C H, Hong J W, Wey M Y (2002), *Nuclear Instruments and Methods in Physics Research*, Volume B, 190, 807–812.
- Skar J I, Isacson M, Zheng T (2005), ‘Corrosion performance of die cast magnesium in field exposure and accelerated laboratory tests’, *Magnesium Automotive and End User Seminar (EFM)*, Aalen, Germany, September, 22–23.
- Stippich F, Vera E, Wolf G K, Berg G, Friedrich Chr (1998), *Surface and Coatings Technology*, Volume 103–104, 29–35.
- Valvoda B (1996), *Surface and Coatings Technology*, Volume 80, No 1–2, 61–65.
- Wasa K, Hayakawa S (1991), *Handbook of Sputter Deposition Technology, Principles, Technology and Applications*. Noyes Publications, Park Ridge, NJ, ISBN: 0-8155-1280-5.
- Yin Y, McKenzie D R (1996), *Thin Solid Films*, Volume 280, Issue 1–2, 95–100.
- Zhou X W, Wadley H N G (1999), *Surface Science*, Volume 431, 42–57.

Plasma-assisted surface treatment of aluminium alloys to combat wear

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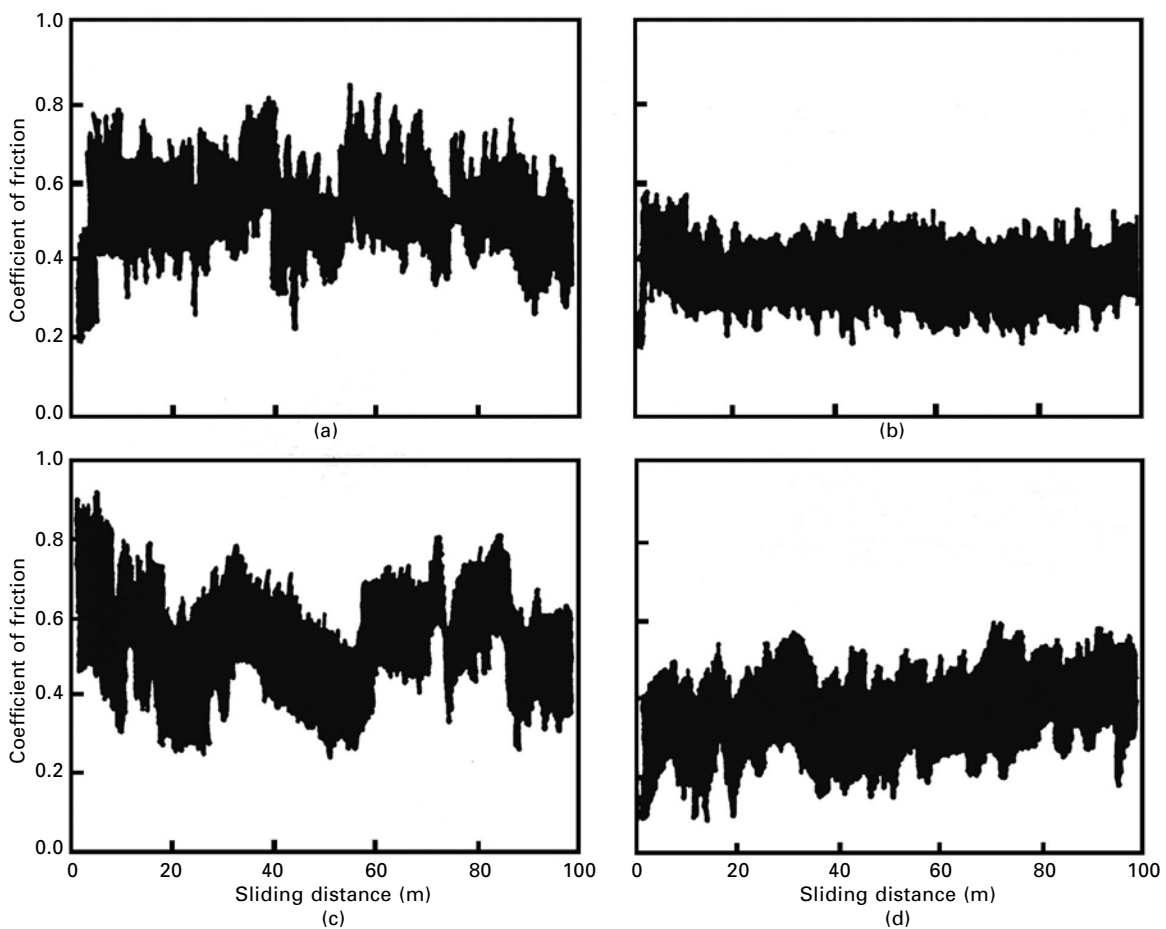
Abstract: Application of plasma to those metals with a stable, tenacious oxide film is a key factor in surface treatment to ensure sufficient adhesion of a coating to the substrate and acceptable performance of the coating. This chapter introduces typical metal and ceramic coatings produced by plasma-assisted processes on aluminium to enhance tribological properties. Hard ceramic coatings below a certain thickness have no beneficial effect, but thick coatings or the addition of a metal interlayer on aluminium will increase significantly their wear resistance. Use of duplex treatments incorporating PVD titanium, and subsequent plasma nitriding, is described and the results of wear tests are presented. Dominant factors, including coating adhesion to aluminium and load-bearing of the coated surface, are related to the role of plasma, and the suitability of these coatings for aluminium substrates is discussed.

Key words: aluminium alloys, wear, plasma-assisted coatings, plasma nitriding, surface oxide.

10.1 Introduction

Aluminium forms the basis of the most important group of light alloys in terms of application range in aerospace, automotive and general engineering. Its usefulness arises from low density, high corrosion resistance of the pure metal and good mechanical properties when suitably alloyed and heat treated (Polmear, 1995).

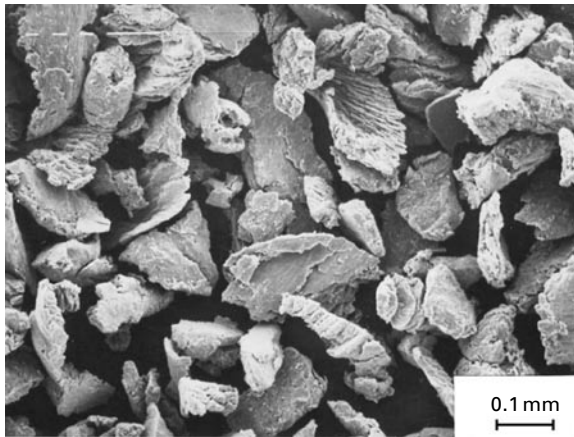
Aluminium alloys are, however, relatively soft and a fundamental problem is their intrinsically poor tribological properties, as detailed in Chapter 2. It has been observed that running aluminium against steel produces, after an initial low frictional value, large fluctuations in the frictional resistance (Ashrafizadeh, 1997). Typical coefficient-of-friction traces during pin-on-disc testing at a moderate sliding speed and a relatively small load are shown in Fig. 10.1. The initial friction is low at all speeds and loads, but only for a very short distance. During this stage, there is little chance of adhesive wear because oxide film is present on the sliding surfaces. (Breakdown of the oxide film due to inadequate support from the rather soft aluminium substrate would cause a sudden increase in the coefficient of friction.) As sliding continues, the mean frictional force falls gradually, settling to an almost steady value with more moderate fluctuations. Careful examination of the friction traces indicates that this uniform part is, in fact, composed of



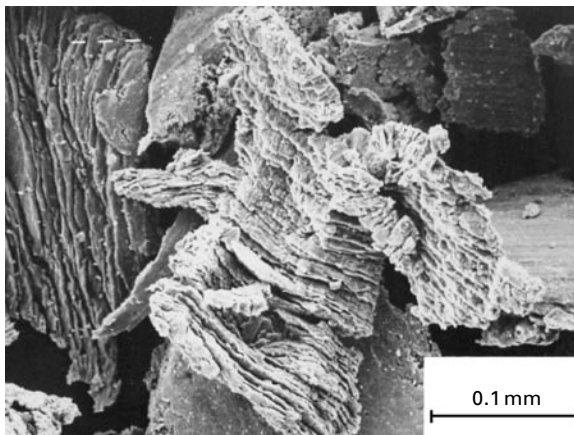
10.1 Variation of friction coefficient with sliding distance for uncoated aluminium alloy; (a) load 2 N, speed 5 cm/s, (b) load 2 N, speed 25 cm/s, (c) load 18 N, speed 5 cm/s, (d) load 18 N, speed 25 cm/s.

some peaks and troughs which are, to some extent, regularly repeated. With further increase in sliding distance, adhesion of aluminium to steel increases because there are more newly formed clean surfaces. The subsequent fracture of the welded junctions generates relatively large pieces of wear debris, Fig. 10.2.

Study of the friction traces by several authors has demonstrated that aluminium alloys have severe stick–slip motion during sliding (Sarkar and Clarke, 1980; Ashrafizadeh, 1993). Examination of the pin surface, Fig. 10.3, has revealed severe adhesive wear, accompanied by metal transfer from aluminium substrate to steel counterface. The fact that metallic wear

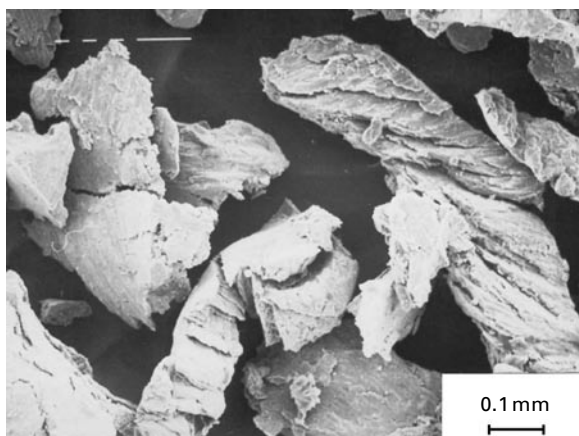


(a)

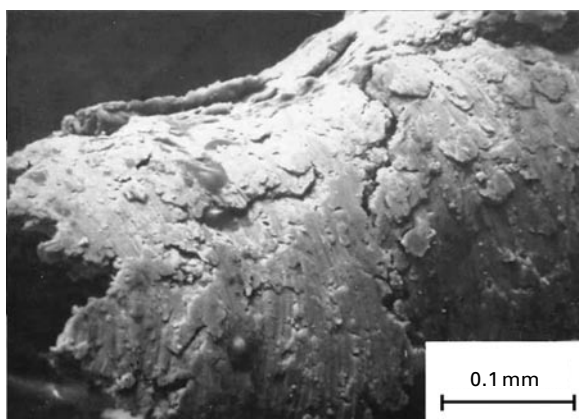


(b)

10.2 Wear debris of uncoated aluminium alloy after sliding against 52100 steel; (a) and (b) load 2 N, speed 25 cm/s, (c) and (d) load 18 N, speed 5 cm/s.



(c)

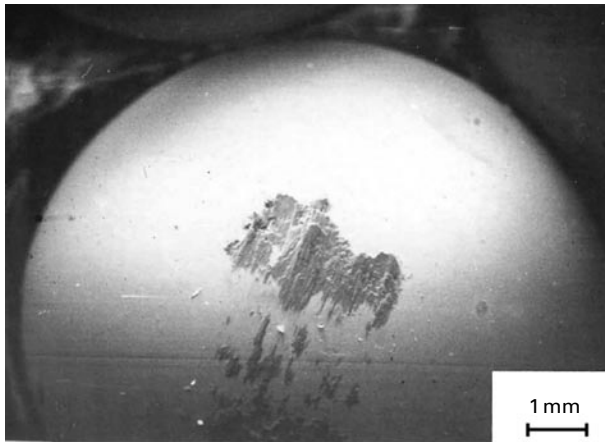


(d)

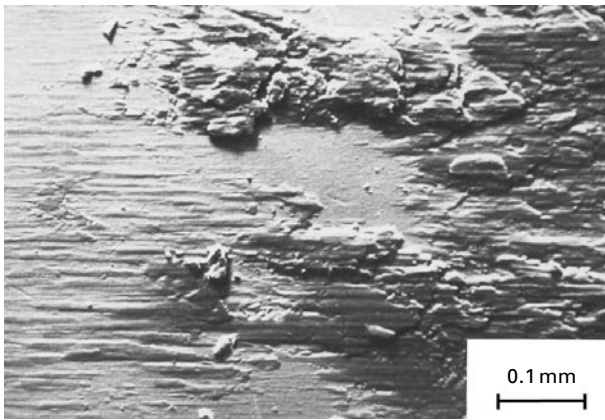
10.2 Continued

occurs from the very beginning of sliding indicates that the mild–severe transition must have been at a much lower contact pressure. In other words, a very small normal load is sufficient to break the oxide film and to cause yielding of aluminium material. Adhesion and metal transfer, followed by the formation of metallic debris, are the controlling mechanisms which result in the relatively high wear of aluminium alloys during sliding contact against steel. Surface protection through surface treatment is therefore essential if these alloys are to be used efficiently in applications where boundary contact with a counterface is unavoidable.

Although high temperature surface treatments normally used in ferrous alloys are not possible for aluminium, the wear resistance can be improved by deposition of soft or hard coatings on the surfaces prone to wear. With soft coatings, the aim is to interpose low shear strength films between the



(a)



(b)

10.3 Steel ball after sliding against uncoated aluminium alloy showing severe adhesive wear; (a) appearance of steel surface after pin-on-disc test, (b) details of metal transfer.

asperities and reduce the opportunity for adhesion. Hard coatings, on the other hand, produce hard surfaces that resist wear by resisting the deformation and fracture processes. Many techniques are available; plasma nitriding (Spies and Wilsdorf, 1998), anodic oxidation treatment (Kawai, 2002) (Chapters 4 and 5), electro-deposition of chromium (Gawne and Gudyanga, 1984), diffusion coatings (Gregory, 1978), sputter coatings (Ramalingam *et al.*, 1981), metal and hard coatings by PVD (Ashrafizadeh *et al.*, 1987), ion implantation (Bunshah and Suri, 1979), laser surface alloying (Schaeffer *et al.*, 1980) (Chapter 13), thermal spray coating (Edrisy *et al.*, 2001) (Chapters 7 and 8) and reactive evaporation (Bunshah, 1981) have been experienced since the development of surface engineering. In addition, nitriding of

aluminium has been carried out by a variety of plasma-assisted processes (Evans *et al.*, 2002). Despite many improvements reported, most of these processes are still at the stage of research and development. This chapter will focus on plasma-assisted treatments for enhanced wear performance; metal and ceramic coatings, and duplex surface treatment incorporating physical vapour deposition and plasma nitriding are considered, and the influence of dominant factors on friction and wear behaviour is discussed.

10.2 Effect of plasma on surface oxide film

When a freshly-formed aluminium metal surface is exposed to the atmosphere, it immediately becomes covered with a thin film of oxide. An important and beneficial feature of this oxide film is that its molecular volume is stoichiometrically 1.5 times that of the metal used up in oxidation (Wernick *et al.*, 1987). This means that the oxide film is under compressive stress and will not only cover the metal continuously, but can cope with a certain amount of substrate deformation without rupturing. The rapid formation of such an oxide film of alumina on the surface makes aluminium and its alloys relatively stable in most environments and inhibits bulk reaction. The natural oxide film formed in air is very adherent to the aluminium surface, leading to a high degree of protection of the metal. The oxide is the basis of that group of coatings which involves the technique of anodic oxidation in its varied forms. This protective film is stable in aqueous solutions of pH range 4.5 to 8.5, and becomes probably the most corrosion-resistant coating when suitably thickened and strengthened by electrochemical means.

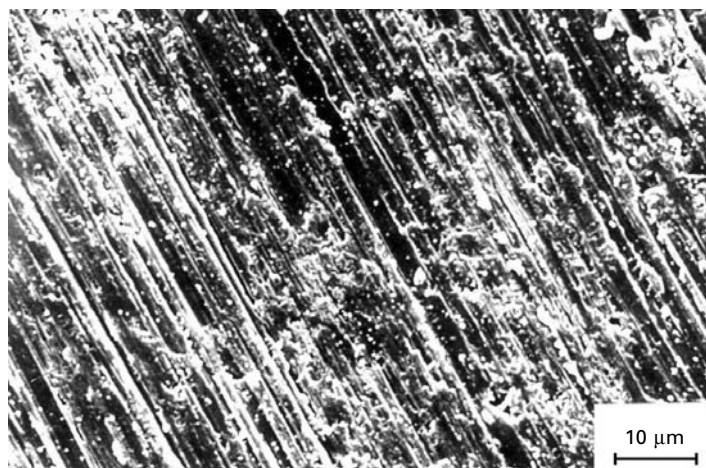
On the other hand, the tenacity of this thin layer is a serious adverse factor in the production of other finishes and coatings, as it must be removed before the alternative coating can be successfully applied. Strong acids or alkalis must be used to remove the oxide from the surface wherever a clean, oxide-free, metallic surface is necessary for subsequent processing. Even after using special techniques to effect this, a very thin but tenacious oxide film, 2–3 nm thick (Wernick *et al.*, 1987), covers the surface as soon as the metal is exposed to the atmosphere. For this reason, to obtain good coating adhesion on aluminium substrates, an *in-situ* treatment must be practised to remove the oxide film before deposition commencement.

When a glow discharge forms on aluminium, ion bombardment of the surface results in a number of effects, including sputtering, defect production, surface morphology change, temperature rise, physical mixing, and diffusion, all of which can enhance the properties of the coating produced (Bland *et al.*, 1974). The negative glow is often referred to as a plasma, and a true plasma can be described as a partially ionized gas containing ions, electrons, and charged and neutral atoms and molecules which are uniformly distributed (Manory, 1990). Plasma leads to sputtering; a momentum transfer process

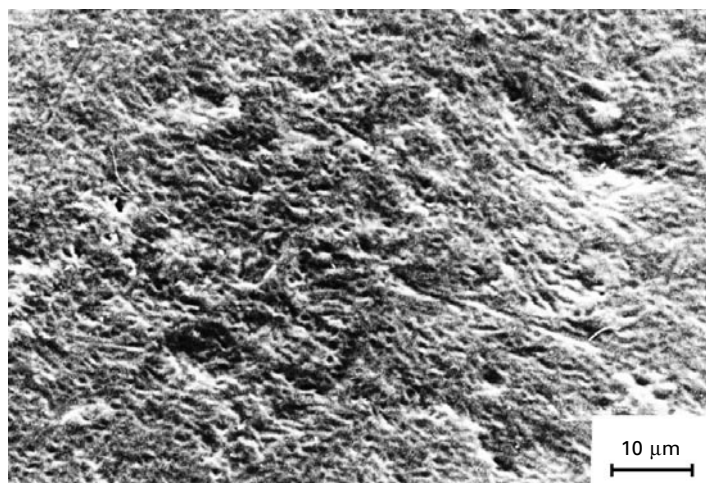
in which an incoming particle creates a collision cascade that intersects the surface, causing the ejection of an atom. Sputtering of a surface leads to removal of surface material, hence it is called sputter cleaning; a characteristic of plasma-assisted processing. This *in-situ* process effectively removes the thin oxide film from the aluminium surface, producing an atomically clean surface for coating deposition.

Exposure of oxide surfaces to an inert gas discharge has long been used to clean surfaces prior to film deposition. The cleaning mechanism is poorly defined since the surface is being bombarded with ions, electrons and high energy neutrals, as well as with radiation from the plasma (Bunshah, 1982). In a series of tests performed on aluminium alloys, sputter cleaning was maintained for 30 minutes in high purity argon at a pressure of 3.3 Pa and a cathode voltage of 3 KV. (Higher voltages caused some instability in the discharge by producing small arcs.) Under the former conditions, the discharge current became stable after a few minutes and then decreased to a steady value. The steady current density was around 0.1 mA.cm^{-2} and, at the end of the sputter cleaning procedure, the substrate temperature was above 100°C . The appearance of the substrate surface after a long sputter cleaning is compared with the initial surface in Fig. 10.4. Although the profilometer readings may not indicate significant changes in the measured average roughness, the change of surface texture is quite clear. The cleaned surface appears nodular, to some extent, with deep grooves, owing to preferential sputtering of some particles (Figueroa *et al.*, 2003). Further examination of this sputter-cleaned surface would demonstrate the influence of ion bombardment on coating adhesion; not only the oxide barrier is removed to allow intimate contact and inter-diffusion, but also a uniform roughness is formed on the surface which will cause mechanical keying and improved adhesion.

In order to study the effectiveness of the cleaning procedure, aluminium surfaces were examined before and after sputter cleaning by using Auger electron spectroscopy. Typical AES spectra are shown in Fig. 10.5. The re-formation of natural oxide film on the aluminium surface was avoided by depositing a thin film of nickel. This film was then removed in the Auger chamber via ion etching prior to analysis. Both oxygen and aluminium in Al_2O_3 show a decreased intensity on the sputter-cleaned surfaces. The Al-metal line, on the other hand, grows and reaches a stable level. The oxygen line, however, did not disappear totally, even after lengthy sputtering. This situation could be attributed to the cleanliness of the Auger chamber and the sensitivity of aluminium for the immediate formation of oxide film on the surface. It follows that the first step in plasma processing is to obtain a very low base pressure in order to reduce any residual oxygen in the chamber. The next step is to eliminate the alumina layer from the substrate surface in such a way as to avoid backscattering of sputtered material and



(a)

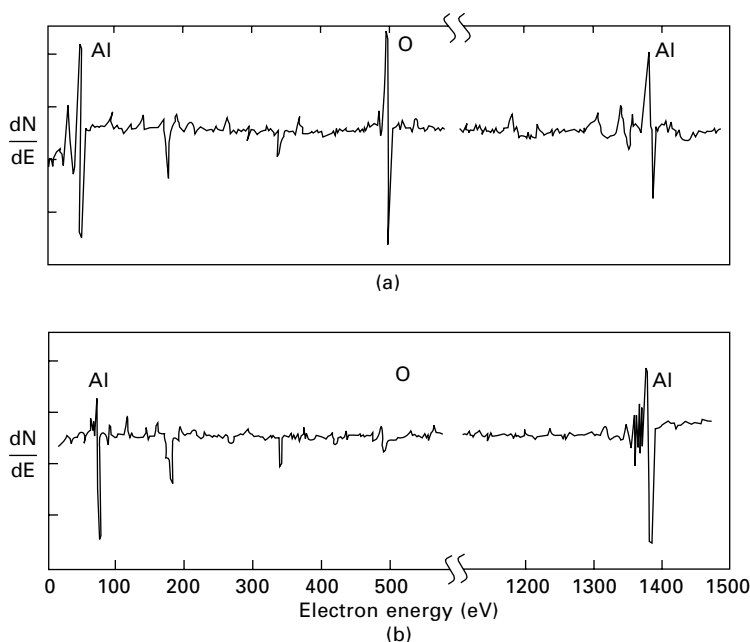


(b)

10.4 SEM micrographs of aluminium surface; (a) after grinding, (b) after sputtering in argon.

to prevent reoxidation of the surface. Therefore, to carry out an effective sputter cleaning procedure on aluminium, a low initial contaminant level should be achieved and a low-pressure discharge in a clean vacuum system should be maintained in order to flush away sputtered contaminants.

Sputter cleaning is usually carried out in pure argon or in an atmosphere of a mixture of argon and hydrogen. For the plasma nitriding process, nitrogen is added, too. The presence of gases other than argon may have a profound influence on the discharge characteristics. Nitrogen is probably the reactive gas in widest commercial use, primarily for the production of nitride



10.5 AES spectra of the aluminium surface; (a) before sputter cleaning, (b) after sputter cleaning.

coatings. The ionization potentials and collision cross-sections for electron impact ionization of nitrogen and argon are comparable and therefore the bombardment energy characteristics and ionization efficiencies are expected to be broadly similar for these gases.

10.3 Plasma nitriding of Al alloys

Since the industrial development of plasma nitriding (Edenhofer, 1974), there has been an increased interest in applying the process to aluminium alloys for which conventional gaseous thermochemical treatments have not been successful.

Plasma nitriding, also referred to as ion nitriding, is performed to improve the wear and fatigue resistance of ferrous materials and some titanium alloys (Ashrafizadeh, 2003; Kashaev *et al.*, 2005). Processing is accomplished in an air-tight vacuum chamber where the workpiece made the cathode and the chamber walls the anode. An applied potential across the cathode workpiece and chamber wall creates a plasma in the abnormal glow discharge range, with good electrical conductivity, consisting of ions, electrons, and charged and neutral atoms and molecules. Under these conditions, a uniform purple glow is established around the cathodic work pieces and the sputtering action

of the glow discharge heats and cleans the surfaces of the components. The addition of nitrogen to the chamber initiates and sustains the nitriding action, with an enhanced mass transfer to the surface of the metal. In iron and steel, this leads to a rather deep nitrogen diffusion and this is considered a major advantage in the plasma nitriding process (Hosseini and Ashrafizadeh, 2009).

Intensive investigations during the 1980s demonstrated that plasma nitriding of aluminium alloys is possible provided an efficient sputter cleaning stage is performed to remove the natural oxide layer and very pure nitrogen is used. Otherwise, oxide film formed before and/or during plasma treatment on the surface of the aluminium alloy will act as a barrier to the diffusion of nitrogen into the metal. Other studies later explored the possibility of aluminium nitriding even without prior sputter cleaning (Reinhold *et al.*, 1998). Experimental results reported by Spies *et al.* (2001) proved that the formation of aluminium nitride is possible on aluminium surfaces covered with an Al_2O_3 film, and other investigators successfully carried out plasma nitriding of aluminium and its alloys without argon presputtering (Visuttipitukul *et al.*, 2003).

Initial attempts to form aluminium nitride on the surface of aluminium substrates appeared in the literature as a European patent (Tachikawa *et al.*, 1985). As aluminium readily reacts with oxygen to form oxide films, the inventors tried to carry out the process in an oxygen-free atmosphere. After evacuating the chamber to 0.133 Pa, the substrates were heated in a glow discharge using an inert gas such as argon. This glow discharge, in addition to raising the temperature, produced a clean surface to facilitate the diffusion of nitrogen. The treatment was continued by replacing the inert gas with nitrogen or ammonia at a pressure above 13.3 Pa. Several aluminium alloys were nitrided at temperatures of 300 to 650°C; temperatures below 450°C did not produce a significant hardening effect, whereas 600°C and above caused spalling of the surface layer. Nitrided layers of several micrometres thickness were produced at temperatures between 450 and 550°C. Hardness values of 1000 HV and above were reported for the black AlN layers, with some improvements in wear resistance.

Several problems must be noted when considering nitriding aluminium alloys. The first major problem in the nitriding of aluminium is the stable oxide film which acts as a barrier to reaction between the aluminium surface and nitrogen. Although the sputter cleaning process is expected to remove the oxide film directly before plasma nitriding, it is practically impossible to avoid reoxidation and to maintain an atomically clean surface during the treatment. This has been attributed to the very low oxygen potential needed for Al_2O_3 formation (Stock *et al.*, 1994). The second problem is concerned with the process temperature – the nitriding temperature is rather close to the solidus temperature of aluminium alloys. Therefore, a critical control of

temperature is required during plasma nitriding since even minor overheating may lead to local melting of the component. Other problems arise due to the large differences in the physical properties between aluminium and aluminium nitride (Table 10.1); large differences in coefficients of thermal expansion produce high values of residual stress, which can lead to cracking and spalling for thick aluminium nitride layers. Therefore, in order to produce crack-free surface aluminium nitride layers, their thickness must not exceed about $3\text{ }\mu\text{m}$ (Spies and Spies *et al.*, 2010). Finally, AlN has a high electrical resistance and as its thickness is increased, the current density will decrease unless the plasma parameters are effectively adjusted.

Various techniques, in addition to simple dc plasma, have been employed to modify the nitriding process for aluminium and its alloys. Pulsed dc discharge, thermionic assisted dc, high frequency plasma, microwave discharge plasma, electron beam excited plasma, plasma source ion implantation and plasma immersion ion implantation (PIII) have been successfully applied to aluminium alloys, Table 10.2. PIII appears, to be particularly advantageous in that it can produce an AlN layer at the surface with a thickness up to $15\text{ }\mu\text{m}$ at 500°C (Richter *et al.*, 2000). This is a process where the plasma is generated in a suitable size vacuum chamber, immersing the workpiece from all sides (Mandl *et al.*, 1996). By applying negative high-voltage pulses to the sample, positively charged ions are extracted from the plasma through the plasma sheath and implanted into the whole surface at the same time, thereby reducing the process time for large components (more details of PIII can be found in Chapter 11).

From a technological point of view, the selection of a particular aluminium alloy for plasma nitriding, the temperature uniformity in the batch and the surface quality obtained are the crucial points. The nitridability of the aluminium alloys in Fig. 10.6 shows that the growth rate of the nitride layers increases with increasing magnesium content of the alloy. Obviously, layer thickness is a key factor in load bearing ability of the surface and must be considered when designing a nitriding process for industrial aluminium parts. The actual improvement in wear resistance is yet another point of concern; the

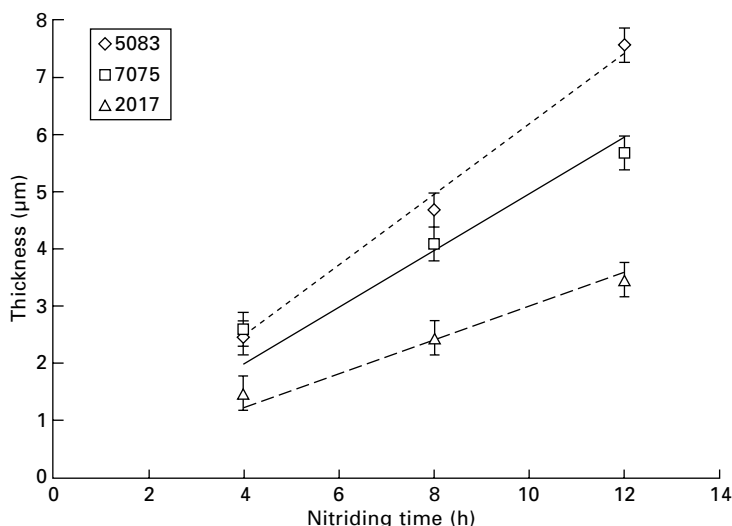
Table 10.1 Physical properties of Al and AlN

Property	Al	AlN
Melting point, K	933	2572
Density ρ , g cm^{-3}	2.7	3.26
Young's modulus E , GPa	72	400
Hardness HV (load, N)	20–30 (100)	1530 (1)
Thermal expansion coefficient α , 10^{-6}K^{-1}	23	5.0*
Thermal conductivity η , $\text{W m}^{-1}\text{K}^{-1}$	226	320
Electrical resistivity $10^{-8}\text{ }\Omega\text{m}$	2.5	$>10^{19}$

* 600–1300 k

Table 10.2 Techniques and process parameters for plasma nitriding of aluminium alloys

Process	Conventional d.c.		Pulsed d.c.	Pulsed d.c. +r.f.	Thermionically assisted d.c. triode	Thermionic arc	Microwave + ECR ion	Plasma immersion ion implantation
Base pressure (Pa)	10^{-3}	2.66	10^0 – 10^{-4}	10^{-3} – 10^{-4}	2×10^{-3}	6×10^{-4}	2×10^{-4}	–
Sputter cleaning time (h)	1	3	–	–	0.5	1.5	0.5	–
Pressure (Pa)	90	133.3	–	200	3.3	0.4	1.0	–
Bias voltage (V)	600	200	–	400–600	2000	80	1000	–
Gas	Ar	N ₂	–	Ar ₂ H ₂	Ar	Ar ₂ H ₂	Ar	–
Nitriding time (h)	≤20	20–70	4–12	d.c./r.f.≤2	2–10	2–18	0.5	3
Pressure (Pa)	505	533.3	200–300	350/350	2.7	0.8	1	0.14
Bias voltage (V)	?	200	460–600	600/200	2000	50	1000	40 000
Temperature (°C)	450	550	400–460	480	300	340–460	500	300–500
Gas	N ₂	N ₂ –H ₂	N ₂	N ₂	N ₂	N ₂ ,Ar	N ₂	N ₂
AlN layer thickness (μm)	≤5	3–5	2–8	≤18	ca. 0.1	≤10	Very thin	≤0.05



10.6 Growth of the AlN layer as a function of the effective nitriding time at 400°C for aluminium alloys of different magnesium content (2017: 1.6%Mg, 7075:2.6%Mg, 5083: 4.5%Mg) (Spies *et al.*, 2010).

formation of AlN on the surface changes the chemistry and the condition of the contact, thereby changing the wear mechanism, for example, from severe adhesive and abrasive to mild abrasive wear (Visuttipitukul and Aizawa, 2005). Nevertheless, the large difference between physical and mechanical properties of aluminium and AlN, together with the low thickness of the layer, limit the application of plasma-nitrided components to light sliding contacts. Thicker modified layers obtained by special nitriding techniques or duplex processing are necessary to produce a supporting layer of high load-bearing capacity with substantially better wear properties.

10.4 Physical vapour deposition (PVD) of aluminium alloys

Ion plating, as one of the physical vapour deposition techniques, has been used to produce coatings on aluminium alloys for obvious advantages. It is defined as a deposition process in which the item to be coated is subjected to a flux of high energy ions both before and during deposition (Mattox, 1973). A film results only when the deposition rate is greater than the removal rate. Typical properties obtainable in this process include the following:

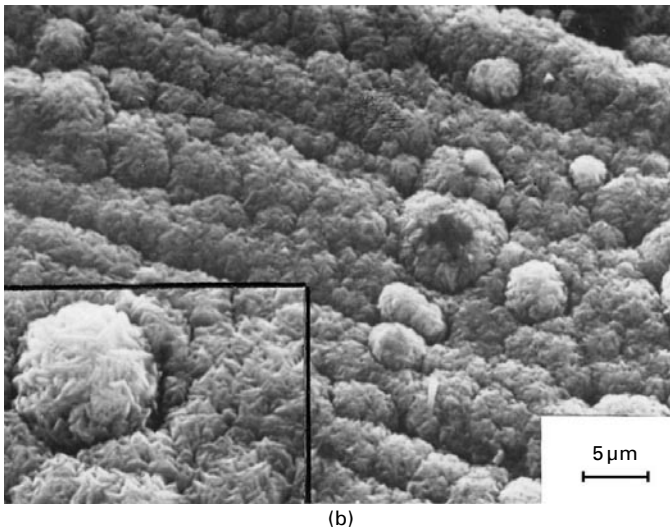
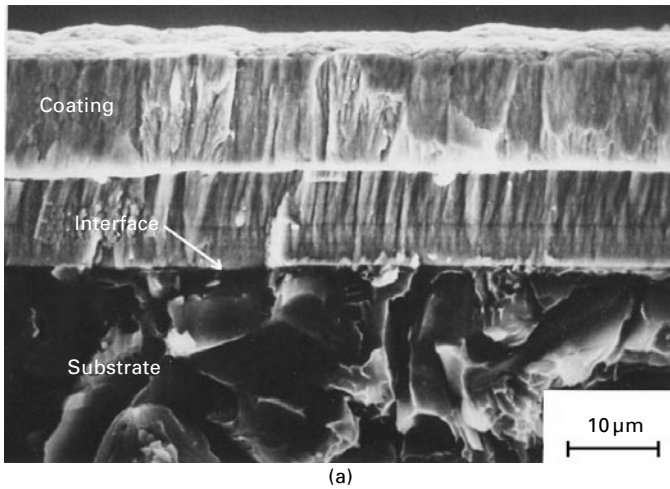
- Improved coating adhesion, due to the ability to ‘sputter clean’ and pre-heat substrates by energetic ion and neutral bombardment of the substrate surface.

- Uniform coating thickness through gas-scattering effects and the ability to rotate or displace samples relative to the vapour source during deposition.
- Avoidance of a final machining or polishing stage after coating as, in most cases, the coating replicates the original surface finish.
- Controlled coating structure due to the effect of bombardment in obviating columnar growth and encouraging deposited atom mobility.
- Controllable deposition rates, using a wide variety of vapour sources including resistance heated, electron beam, induction, etc.
- Usually there are no effluents or pollutants, as in most cases there are no harmful by-products or toxic chemical solutions used.
- High purity deposits through the use of a controlled vacuum environment and pure source materials.
- Lower deposition temperatures, as direct energization of the coating species provides many of the benefits previously achievable only on hot substrates. For example, lower substrate temperatures can be used for ceramic deposition compared with chemical vapour deposition.
- Deposition of a wide range of coating and substrate materials, including metals, ceramics and compounds.

A laboratory-size ion plating system has been employed to produce various metal and ceramic coatings on an aluminium alloy to improve tribological behaviour. Selected metals were chromium, copper, nickel and titanium; and ceramics included TiN and CrN. The structure and properties of these coatings are presented in the next sections.

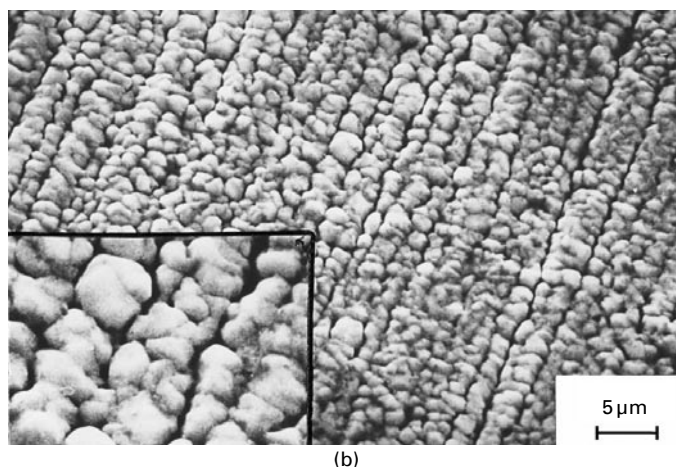
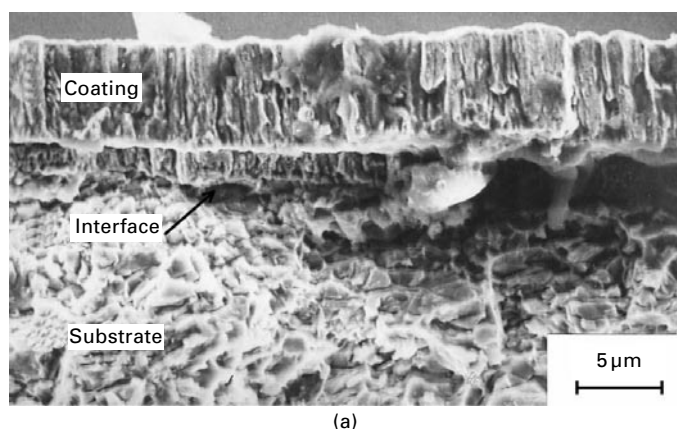
10.4.1 Metal coatings

The morphology of metal coatings is evident from Figs 10.7–10.11, which represent typical scanning electron micrographs of both fracture sections and coating surfaces. The micrographs indicate that coating morphology, in general, depends on the process temperature and gas pressure, as correlated to the M-D structural zone model (Movchan and Dimchishin, 1969), Fig. 10.12. The crystallites are separated by voids which are weak; this reduces the cohesive strength of the coating. As the negative bias was increased and the argon pressure was reduced, the structure became less porous and more nearly like a columnar growth. The structure obtained at a power density of 0.3 W.cm^{-2} (i.e. a current density of 0.1 mA.cm^{-2}), is made under conditions those typical of used for the deposition of metal coatings. Its pebble-like top, Fig. 10.8 (b), appears bright metallic in the $5 \mu\text{m}$ layers but darker and less rounded in the thicker coatings. The interface between substrate and coating is not very sharp as the result of some diffusion, producing a graded interface. Further, it is evident that the initial layer of copper is finer and, to some extent, denser than the top-most sections.



10.7 SEM micrographs of chromium coating on aluminium alloy; (a) fracture section, (b) coating surface.

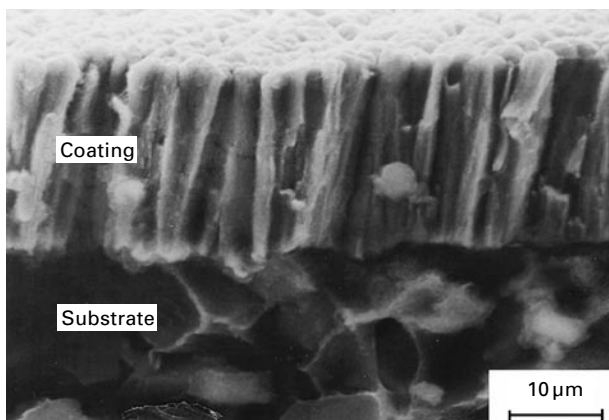
The structure of the ion plated chromium in Fig. 10.7 consists of fibrous grains but they are more densely packed. The boundaries seem less porous and stronger than those of copper deposited under the same conditions (except that the temperature was about 50°C higher in the case of chromium). The rod-shaped columns show similarity to those of Zone T in the structural model (Fig. 10.12) and the surface morphology is smoother. There are no cracks in the films, but there are occasional large nodules (with diameters of up to 5 μm), as can be seen in Fig. 10.7 (b). The nodules are a common feature of sputtered and ion plated films.



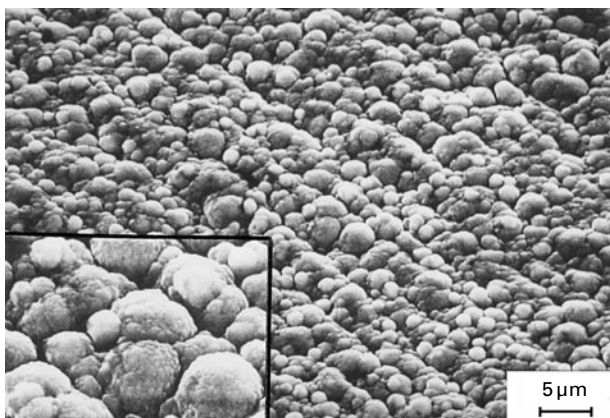
10.8 SEM micrographs of copper coating on aluminium alloy; (a) fracture section, (b) coating surface.

Both nickel, Fig. 10.9, and titanium, Fig. 10.10, are similarly columnar with porous boundaries, a characteristic of ion plated coatings. The structure of nickel is finer and its surface appearance is spherical rather than dome-shaped. Both of these coatings were produced by electron beam ion plating but titanium had a higher evaporation rate, leading to a coarser, more porous coating with a higher surface roughness. The fact that copper and chromium were evaporated by resistive heating, and nickel and titanium by electron beam, produced a difference in that electron beam caused more ionization of the vapour in addition to the glow discharge effects.

The effect of chamber pressure on the coating morphology can be seen from Fig. 10.11, which depicts the structure of titanium coatings produced by evaporation in high vacuum and in argon gas, without application of



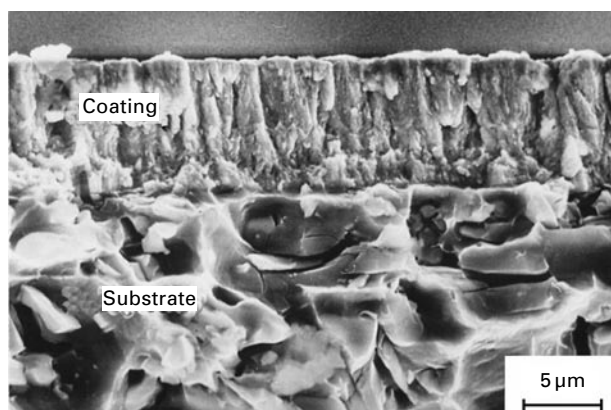
(a)



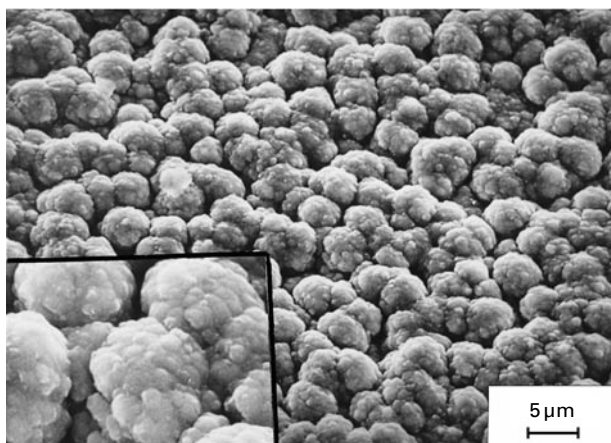
(b)

10.9 SEM micrographs of nickel coating on aluminium alloy; (a) fracture section, (b) coating surface.

glow discharge. At the rather low temperature of deposition, which was attained only by radiation from the molten source, the typical structure of vapour depositions can be observed. Comparison of micrographs (a) and (b) clearly demonstrates that the presence of argon, at a pressure of 3.3 Pa, changes the structure from a rather dense, smooth morphology to a porous, sponge-like structure. This is accompanied by a decrease in surface hardness from 540 to 306 HK, but an increase in the throwing power due to gas scattering. It is well established that coatings formed by PVD techniques at low temperatures consist of tapered, nodular or columnar growth, with porous boundaries of low cohesive strength as a result of the limited mobility of depositing atoms. Such structures are usually attributed to geometric shadowing effects. The structure of ion plated coatings is affected both by



(a)

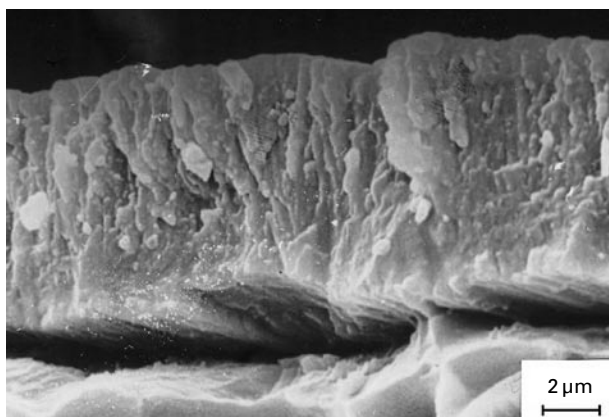


(b)

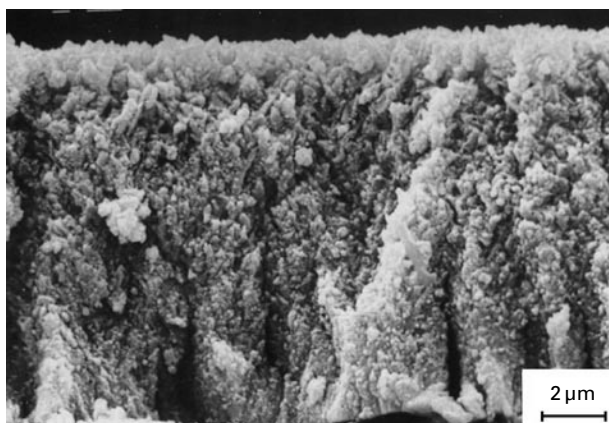
10.10 SEM micrographs of titanium coating on aluminium alloy; (a) fracture section, (b) coating surface.

gas pressure and ion bombardment, as well as by substrate temperature. The T/T_m dependence of the structure itself is determined largely by the interplay of three mechanisms; shadowing, adatom diffusion, together with surface and volume recrystallization, and grain growth (Thornton, 1975). As far as aluminium substrates are concerned, there is limitation to increasing the process temperature, but higher ionization levels may be employed to assist in obtaining a coating of rather dense structure.

The hardness and average wear rate of coatings is summarized in Table 10.3, and the variation of friction coefficient with sliding distance for typical metal coatings is presented in Fig. 10.13. Amongst the metallic coatings studied, ion plated chromium had higher wear resistance and copper films a steady, low coefficient of friction. All the coatings improved the wear



(a)

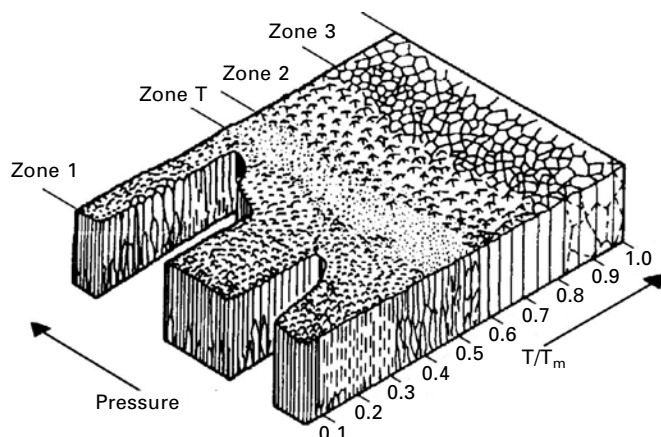


(b)

10.11 Fracture sections of titanium coatings on aluminium alloy without glow discharge; (a) evaporation in vacuum, (b) evaporation in argon gas.

behaviour of the aluminium base alloy; however, nickel and titanium showed adhesion problem in sliding against steel. Being rather soft, aluminium alloys deform readily beneath the coated layer, thereby minimizing the effect of the layer. Good correlation exists between wear resistance and the onset of coating breakdown as determined by the coating thickness and the bearing pressure. The thickness, in particular, has a significant effect on the wear resistance; the coating must be thick enough to overcome the influence of the substrate deformation.

Ion plating principles have been used to produce adherent aluminium coatings as an alternative to cadmium plating. The process is referred to as 'ion vapour deposition' (IVD) or 'ivadizing'. IVD aluminium is a soft, ductile



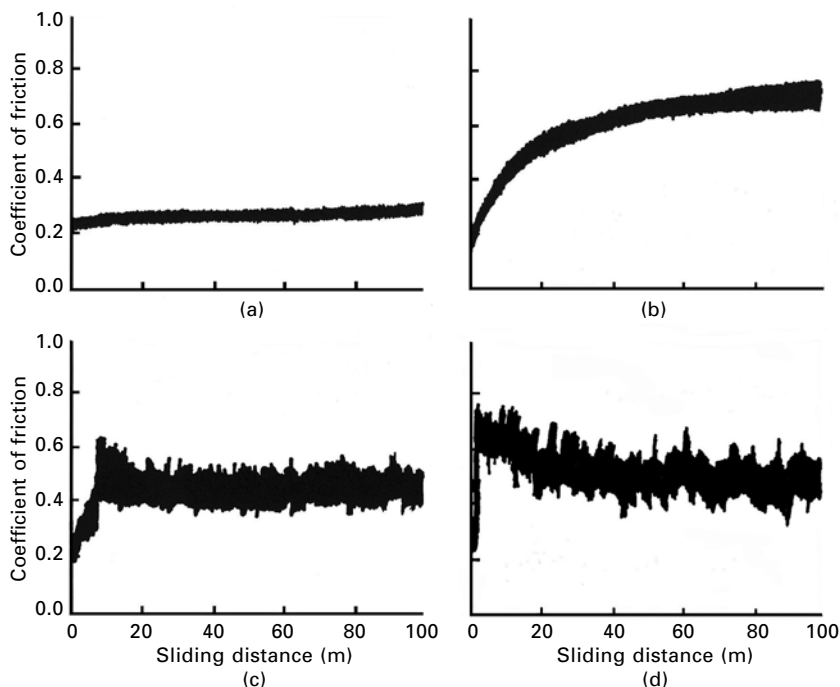
10.12 Thornton model of structural zones in sputter coatings (Thornton, 1975).

Table 10.3 Properties of ion plated coatings on aluminium alloy

Coating	Thickness (μm)	Surface hardness (HK)	Average wear rate ($\text{mg}\cdot\text{m}^{-1}$)
Chromium	6	620	0.05
Chromium	19	738	0.01
Copper	6	208	0.05
Copper	21	192	0.02
Nickel	5	285	0.2
Nickel	18	348	0.03
Titanium	5	420	0.1
Titanium	20	508	0.02
CrN	5	1080	0.01
Cr, CrN	6.5	1100	0.0
Cr, CrN	19.5	1152	0.0
TiN	2	1237	> 0.3
TiN	5	1582	0.0
TiN	8	1830	0.0
Ti, TiN	5.2	1362	0.0
Ti, TiN	5.5	1630	0.01 ⁺
Ti, TiN	20.5	1900	0.01 ⁺
Substrate	Uncoated	140 BHN	> 0.5

+ indicates a weight gain.

coating and has properties nearly identical to pure aluminium. The coating is applied to steels, as well as to high-strength aluminium alloy structures, without any detrimental effect on mechanical strength (Muehlberger, 1983) or fatigue life. IVD aluminium can be used at temperatures of up to 500°C, provides galvanic protection to aluminium alloys, and does not present any ecology problem. But it is not designed for tribological purposes.

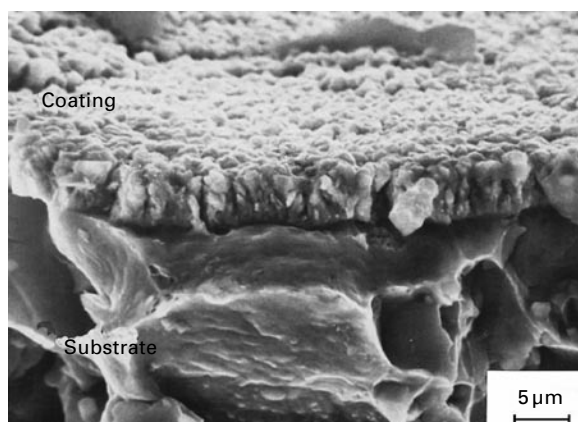


10.13 Variation of friction coefficient with sliding distance for typical metal coatings on aluminium alloy; (a) copper, (b) chromium, (c) nickel, (d) titanium.

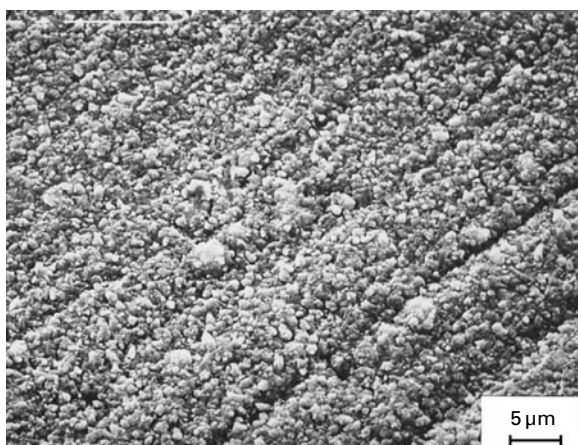
10.4.2 Ceramic coatings

Titanium nitride and chromium nitride have been successfully produced on aluminium alloy by using a triode ion plating to intensify the glow discharge (Ashrafizadeh and Bell, 1990). TiN coatings deposited at a similar power density, Fig. 10.14, show a more distinct columnar growth, which corresponds to Zone 2 of the structural zone model. Commercially produced TiN on aluminium alloy has a fracture which is almost featureless, probably because of the very fine grain size. This coating, produced at 500°C by arc ion plating, is much thinner and has a different surface appearance, composed of some spits and unreacted particles. There are also some fine cracks in the matrix structure. The increase in temperature causes sufficient bulk diffusion to produce a structure approaching that of a Zone 3 type.

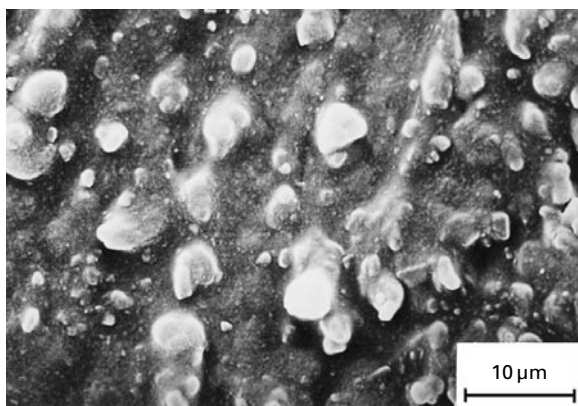
Scanning electron micrographs of the coating topographies indicate surface nodularity to varying degrees. The sections reveal that ion plated coatings are in intimate contact with the aluminium substrate, reproducing the initial surface irregularities, particularly at lower thickness levels. As the process temperature was experienced below 250°C, there was no significant change in the substrate microstructure after coating.



(a)



(b)



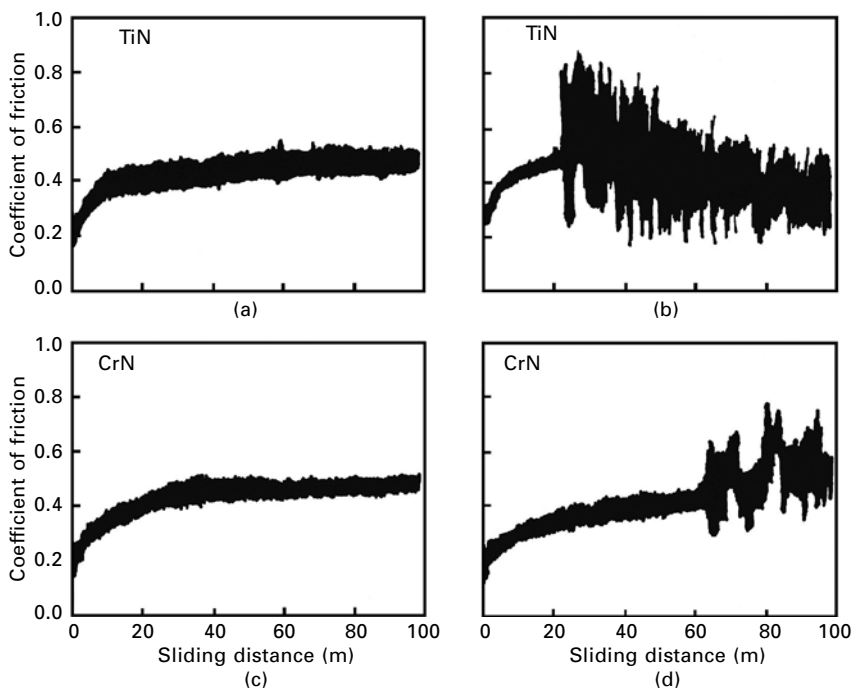
(c)

10.14 SEM micrographs of titanium nitride coatings: (a) e.b. ion plating, fracture section, (b) e.b. ion plating, coating surface, (c) droplets in arc ion plated TiN.

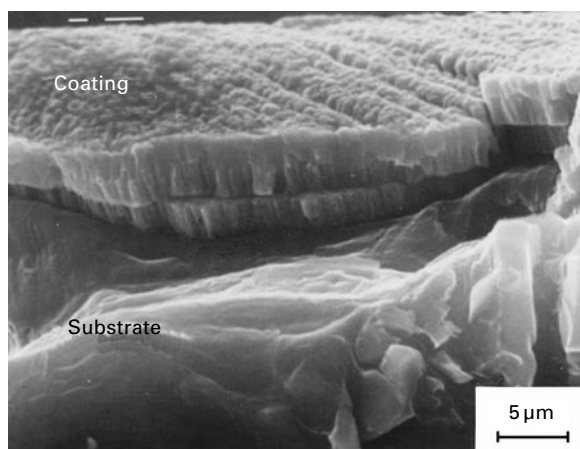
Variations of the coefficient of friction for the ceramic coated specimens at a sliding speed of 5 cm/s are shown in Fig. 10.15. The ceramic coatings showed a low value of friction initially, which gradually increased as the steel ball was abraded. The harder films deposited under high current density had a slightly higher coefficient of friction compared to less dense films of equivalent thickness.

Referring to Table 10.3, it may be seen that ceramic coatings have high values of hardness and very low rates of wear. Titanium nitride perform much better than the metal coatings in terms of low friction and wear. The 8 μm coating of TiN gives complete wear protection to the substrate when sliding 300 m against the steel ball under a load of 27 N. This is the result of high hardness combined with chemical stability of this ceramic coating. A particularly beneficial feature is the very low solubility of titanium nitride with steel even at high temperatures. When a metallic layer with a hardness value intermediate between those of the aluminium alloy and the ceramic coating was used, lower thicknesses were also effective in controlling the amount of wear.

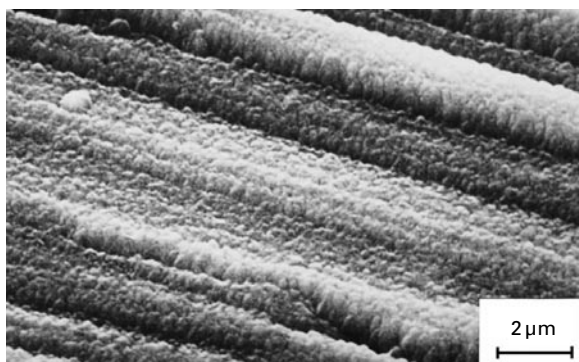
The Cr-N coatings deposited on aluminium alloy were dense, with a non-uniform surface which appears as a series of grooves (Fig. 10.16).



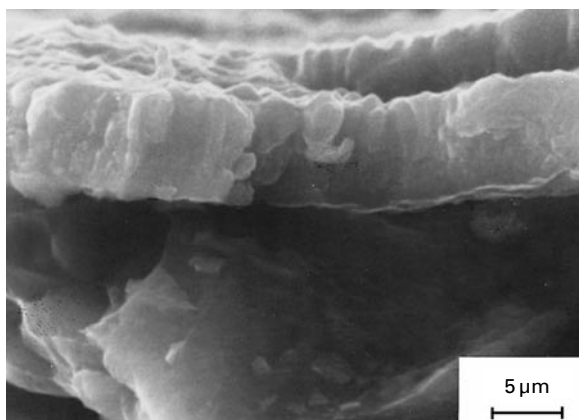
10.15 Variation of friction coefficient with sliding distance for typical ceramic coatings on aluminium alloy; (a) 5 μm TiN, (b) 2 μm TiN, (c) 5 μm CrN, (d) powdery CrN with high nitrogen content.



(a)

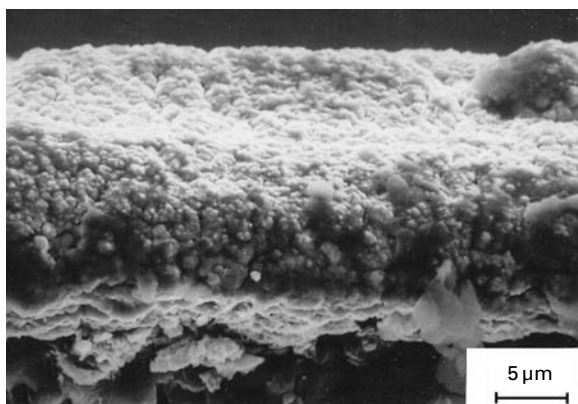


(b)



(c)

10.16 SEM micrographs of chromium–nitrogen deposits on aluminium alloy; (a) CrN fracture section, (b) CrN coating surface, (c) dense structure with low nitrogen content, (d) powdery structure with high nitrogen content.



(d)

10.16 Continued

The intense bombardment caused the formation of a high density of nuclei and hence a small grain size, without any sign of pores or cracks. The results confirm that it is possible to produce dense coatings by ion plating on substrates whose bulk temperature is kept rather low. The morphology changes, however, from a dense columnar one, which is the case for other chromium nitrogen deposits, to a powdery form at nitrogen levels of 50% or more. The results of the chromium–nitrogen coatings produced at about 30%N₂ indicate some advantage of nitrogen-containing phases over pure chromium metal in adhesive wear applications. In particular, the CrN phase appears to offer better performance in the absence of metal chromium and/or powdery chromium–nitrogen mixtures.

Ceramics have virtues in adhesive wear situations because of their tendency not to react with metals (Wachtman and Haber, 1986). The thermal energy liberated in the tribological contact regions might be sufficient to modify the plastic properties so that the steel possesses the capacity to flow, whilst TiN is under elastic contact behaviour. Thin films of titanium nitride did not last for a long sliding distance, even at relatively small loads. Coating breakdown occurred, leading to high adhesive wear similar to that of the uncoated substrate. This was thought to be due to substrate collapse below the hard TiN film. Coatings of 5 μm thickness and above, in contrast, gave nearly perfect wear protection to the substrate. Thicker TiN coatings performed very well in all sliding tests (Table 10.3). Under conditions of mild wear, the debris was in the form of a fine black powder, which was probably iron oxide, since the steel ball was abraded leaving a scratched flat surface.

TiN coatings routinely produced had (200) orientations of varying degrees and a dense, non-porous, columnar structure. The change in texture was accompanied by changes in hardness and wear resistance. The improvement has been attributed, in part, to an increase in coating densification which

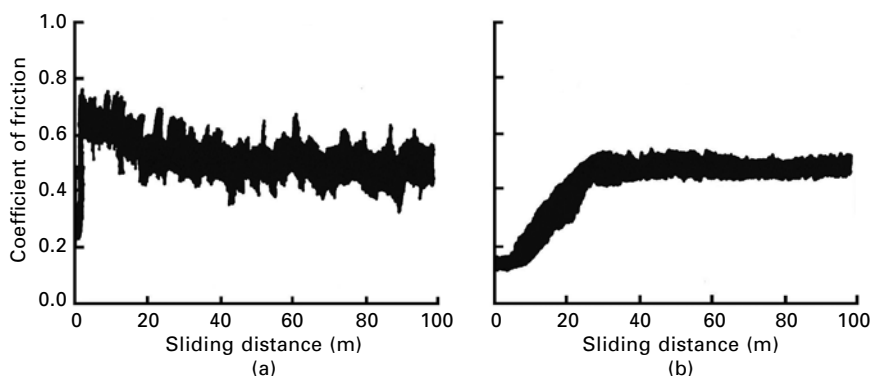
occurs under the higher ion bombardment conditions giving the (200) texture. It was clear that hard coatings on the relatively soft aluminium alloy substrate would break up under rather heavy loads. TiN films produced at a lower current density proved to be slightly better in this respect. It is probable that the presence of unreacted titanium in the latter produced a higher toughness; the lower hardness could also be one indication of this phenomenon.

10.5 Duplex surface treatment

Ion plating and subsequent plasma nitriding were applied to aluminium alloy in an investigation to improve the tribological properties of such alloys (Ashrafizadeh, 1992). Coatings of titanium, deposited onto the aluminium substrate, were subjected to a series of plasma nitriding cycles in order to form a graded interface and hard metal compounds on the surface. The results indicated that a significant improvement could be achieved when titanium films of adequate thickness are nitrided to produce hard compounds on the surface, above the aluminium–titanium interface. The properties obtained in this duplex treatment were much better than those obtained by either nitriding or ion plating.

Titanium coatings were deposited in two thicknesses, 5 and 20 μm , and subsequently, plasma nitriding was carried out in a nitrogen–hydrogen atmosphere at a steady pressure of 270 Pa. Two treatment temperatures, 500 and 550°C, were employed throughout, with a constant time of 20 hours. No considerable nitriding was observed at, or below, 450°C. At the end of the process cycle, the power was switched off and the specimens were slowly cooled to room temperature in the nitriding chamber.

Plasma nitriding was found to produce very attractive properties in terms of low friction (Fig. 10.17). Nitriding of thinner films does not seem to be



10.17 Comparison of friction traces for two surface treatments of aluminium alloy; (a) titanium coating, (b) duplex treated (PVD titanium and plasma nitrided).

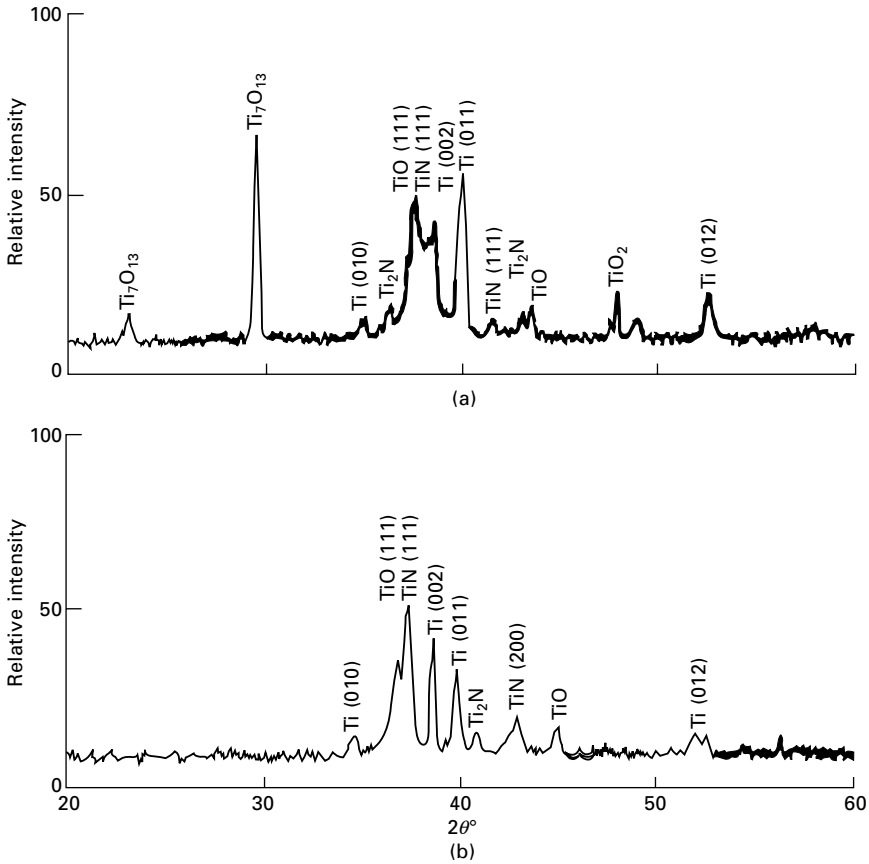
very beneficial since the films were mostly removed by the sputtering action of the process. The nitrided 20 μm titanium coating, on the other hand, performed very well in pin-on-disc wear testing. In particular, the specimen plasma nitrided at 500°C had negligible wear under various loads (Table 10.4). The formation of nitrides and microhardness, however, were optimum for nitriding at 550°C. This situation indicates that, in addition to surface nitriding, other mechanisms must have been responsible for the decreased wear.

A thin oxide film is always present on the surface of titanium metal. During plasma nitriding, three competing processes can simultaneously affect this oxide film; sputtering of the oxide, deposition of oxygen atoms/ions, and solution of some oxygen followed by diffusion of oxygen into the metal. It is generally accepted that at temperatures of 800°C and above, sputtering and solution dominate over deposition of oxygen and, as a result, the surface is depassivated and nitriding of titanium can proceed. At temperatures below 600°C, on the other hand, the deposition of oxygen predominates, and there is no extensive nitriding. As depassivation of the surface is a key factor in controlling the extent of nitriding, it follows that if the process chamber is free from oxygen, nitriding can proceed at lower temperatures, producing both oxide and nitride within the top layers (Miyagi *et al.*, 1980).

Accurate analysis of the diffraction patterns of the nitrided surface in Fig. 10.18 shows the presence of oxides and nitrides, and one possible explanation for the tribological behaviour of these specimens is the relative amounts of the two phases in terms of the nitriding temperature and the cleanliness of the nitriding atmosphere. There are some similarities between the reaction of nitrogen and oxygen with titanium, and the surface layers may well be a mixed oxy-nitride, denoted as TiX , where X represents a variable mixture of oxygen and nitrogen. The effect of increasing temperature may then be to change the ratio of oxygen and nitrogen in the layer: plasma nitriding at 550°C, as compared to 500°C, produces more nitrides than oxides, a higher hardness, a higher depth of hardening and some diffraction peaks which

Table 10.4 Surface hardness and wear rate of the specimens after duplex treatment

Specimen/Treatment	Hardness	Average wear rate (mg.m^{-1})
Aluminium alloy substrate	140 BHN	> 0.5
5 μm Ti	420 HK	0.1
5 μm Ti, nitrided at 500°C	1592 HK	0.04
5 μm Ti, nitrided at 550°C	1947 HK	0.03
20 μm Ti	508 HK	0.02
20 μm Ti, nitrided at 500°C	1858 HK	0.0
20 μm Ti, nitrided at 550°C	2065 HK	0.01



10.18 X-ray diffraction patterns of duplex treated (PVD titanium and plasma nitriding) aluminium alloy; (a) plasma nitriding at 500°C, (b) plasma nitriding at 550°C.

probably belong to intermetallics at the aluminium–titanium interface, Fig. 10.19.

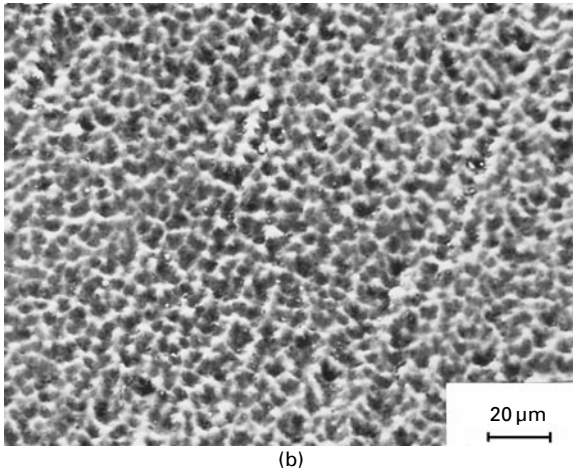
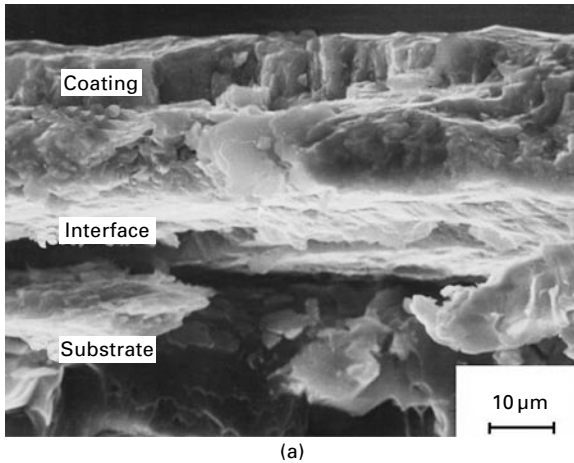
During pin-on-disc wear testing, the oxide–nitride compounds on the plasma nitrided surfaces have the advantage of controlling the damage to the steel counterface and, thus, a lower coefficient of friction and longer sliding under mild wear conditions. Examination of the wear tracks demonstrates the fact that plasma nitriding, in effect, shifts the wear couple from a metal–metal one to a metal–oxynitride one, thus changing the fundamental wear process. Obviously, the nitride provides high hardness and the oxide is intimately associated with low friction and wear. Neither of the titanium coatings nor the plasma nitriding of aluminium could produce comparable properties. It is, then, the formation of hard compounds accompanied by a

graded interface in this duplex treatment that must be responsible for the improved tribological properties.

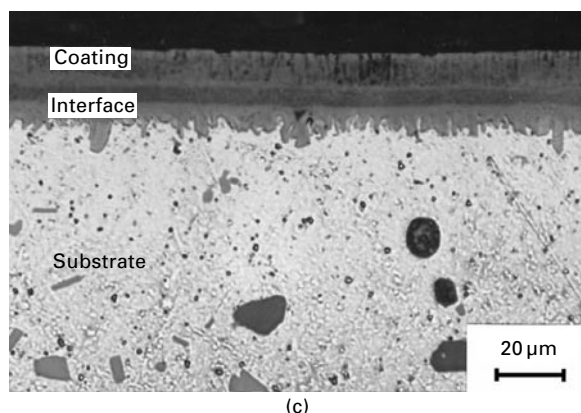
10.6 Load bearing capacity and interface design

10.6.1 Adhesion and load bearing capacity

The first and foremost requirement for the application of coating techniques in tribology is that the deposited films be well bonded to the substrate. Various



10.19 Typical micrographs of duplex treated (PVD titanium and plasma nitrided) aluminium alloy; (a) fracture section, (b) coating surface, (c) coating–substrate interface in a polished and etched section.



10.19 Continued

methods have been developed to measure the adhesion between a substrate and a coating (Rickerby and Matthews, 1991), but each has limitations. The simplest adhesion tests, such as the scotch tape, are purely qualitative and are not designed to quantify adhesion strength except to assert that the adhesion is greater than some arbitrary limiting value. More sophisticated methods have been designed for quantitative measurement of adhesion strength. The scratch test is one that has become widely established as a comparative method and is in widespread use (Valli *et al.*, 1986). But measurement of adhesion of hard coatings to rather soft aluminium substrates has been a problem since the development of modern coatings by physical vapour deposition.

For adhesion evaluation of PVD coatings to aluminium, a modified scratch test has been developed and used to characterize typical coatings, as well as to study the effect of deposition parameters. The adhesion test adopted is very similar to the standard scratch hardness test except for the interpretation of the results (Ashrafizadeh, 2000). The loads listed in Table 10.5 correspond to the 'load-bearing capacity' of the coating-substrate combination. This is the condition just before the critical load where the coating is still adhered to the substrate but may show local removal by internal cohesive failure. The data confirm that thicker coatings have a higher load-bearing capacity than the thinner films. It is also evident that a coating with better mechanical properties and good ductility has the highest load-bearing capacity. Thicker layers have lower adhesion compared to corresponding thinner films; for example, the adhesion index (defined as the slope of the plot of scratch width versus the square root of the applied load) for a 5 μm Ti coating is 0.44 and for 20 μm Ti is 0.19. This is in contrast to the evaluation of adhesion based on the value of critical load, which is higher for thicker layers. In the conventional scratch test, the stress required for coating detachment is transmitted through the coating; thicker layers may well require a greater surface stress to achieve

Table 10.5 Results of the modified scratch adhesion tests

Specimen number	Specimen conditions	Load-bearing (N)	Adhesion index	Type of failure during scratching
Ti-1	5 μm , diode ion plating	0.8	0.44	Film removal
Ti-2	20 μm , diode ion plating	1.9	0.19	Film removal
Ti-3	5 μm + vacuum annealed	0.9	0.35	Film removal
Ti-4	20 μm + vacuum annealed	1.8	0.38	Film removal
Ti	Vacuum deposition	0.5	0.21	Spalling
Ti*	Deposition in argon gas	0.5	0.28	Spalling + film removal
TiN-1	5 μm , triode ion plating	0.5	0.30	Spalling + film removal
TiN-2	8 μm , triode ion plating	0.8	0.24	Spalling + film removal
TiN-3	Commercially produced (e.b.)	0.2	0.43	Spalling + film removal
TiN-4	Commercially produced (arc)	0.3	0.42	Film removal
Ti-I	Ion plating, high discharge	0.3	0.49	Film removal
Ti-II	Ion plating, low discharge	0.5	0.30	Film removal

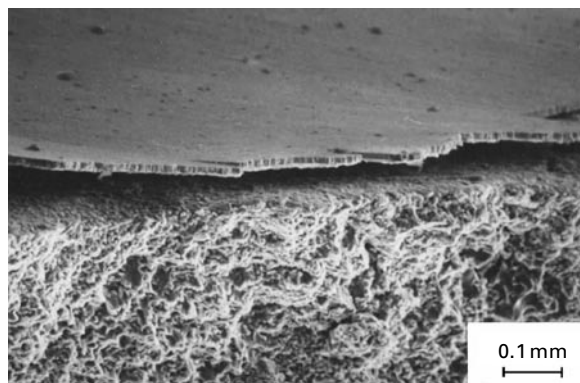
the same shear at or near the interface, thus showing higher critical loads. However, it is not clear whether the apparent increase in critical load with coating thickness represents a real increase or a decrease in adhesion. There is no such contradiction in the modified scratch test; the test is well suited to compare adhesion of hard coatings on aluminium substrates.

The effect of glow discharge and current density on coating adhesion has been studied for various TiN layers on aluminium alloy. The current density for TiN-I was 0.4 mA.cm^{-2} and that for TiN-II was 0.2 mA.cm^{-2} . The higher adhesion of the former is mainly attributed to a less porous structure, which strengthens the interface by effectively increasing the area of contact, though other factors such as sputtering and higher deposition temperature are involved. TiN coatings all had good adhesion to the substrate. The commercially produced films had relatively low load bearing capacity although they were very adherent to the substrate. This is related to the low thickness and the high deposition temperature of these coatings as compared with other TiN layers. In general, titanium nitride coatings have shown good adhesion to aluminium base alloys; adhesion values as high as 30 MPa have been reported (Rickerby and Matthews, 1991) for sputter deposited TiN on duralumin in pull test measurements.

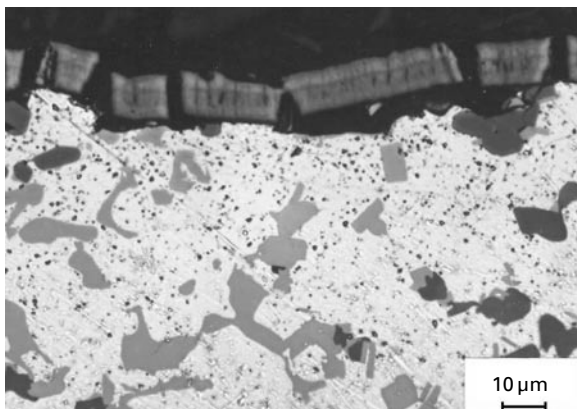
Titanium coatings deposited by vacuum evaporation or in argon, without glow discharge, had very poor adhesion when compared with that of ion plating, and were abruptly delaminated when sliding under load. The sputtering action of argon and metal ions removes barrier layers such as oxide film, adsorbed gases and surface residues which could prevent intimate contact between the titanium coating and the aluminium substrate. A titanium coating, prepared

by vacuum evaporation, after peel off in sliding, is shown in Fig. 10.20. This specimen had high weight loss and a high coefficient of friction, similar to that of uncoated aluminium. Poor adhesion strength caused debonding at the coating–substrate interface, with subsequent formation of rather large pieces of titanium which formed as loose debris at the early stages of the wear test.

Another important coating property, related to adhesion, is the load bearing capacity. High normal loads produce high bearing pressures, which are transmitted to the specimen through the coating. For ductile and strong materials, sliding interaction transmits the bearing pressure deep into the material, leading to plastic stress and strain. For brittle materials, the bearing pressure cannot be transmitted through extensive subsurface plastic strain as the stress is sufficient to initiate fracture in the surface and subsurface close to the contact. A chromium coating under high load illustrates the situation: as is shown in Fig. 10.21, the coating is fractured due to deformation and collapse of the underlying substrate. When the coating is thick, so that all stresses and strains diminish inside the layer, the surface can support a load as high as its intrinsic limit. However, if the layer is thin, shear stresses will be present at the interface and these will transfer across the interface into the underlying base material. Since the aluminium substrate is softer, it will deform more easily than the adjacent coating material and the result will be a shear fracture at, or near, the coating–substrate interface. Coating toughness and its adhesion to the substrate are the relevant factors in controlling this kind of fracture. In addition, coating thickness is a decisive factor on the ability of the layer to withstand higher applied stresses and, in effect, to increase the load-bearing capacity of the coated aluminium substrate.



10.20 SEM micrograph of a vacuum evaporated titanium coating on aluminium alloy detached during specimen preparation.



10.21 SEM micrograph of a chromium coating on aluminium alloy fractured under high load due to inadequate support from the substrate.

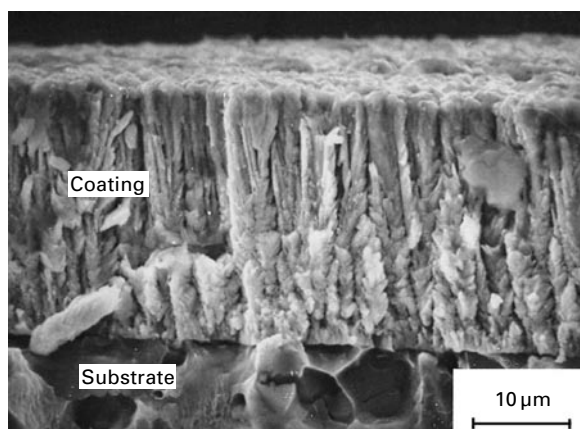
10.6.2 Interface and intermediate layers

The interface between the substrate and coating usually forms a discontinuity in the normally uniform properties and composition. It is, in general, desirable to eliminate or reduce this abrupt mismatch by inducing a graded interface. This is practically possible by interdiffusion and the application of intermediate layers before deposition of the top coating.

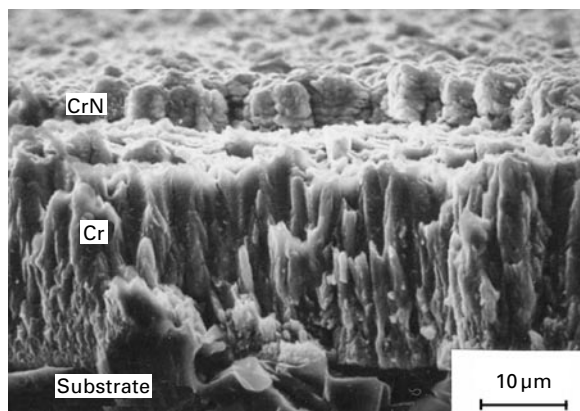
Results of microanalysis and hardness profiles experimentally verify the formation of a graded interface in plasma assisted deposition, which is partly responsible for adherence of the coatings. The graded interface not only provides good adhesion, but also induces a strengthening effect that normally improves the mechanical properties. The presence of a diffusion type interface strengthened by solution hardening and intermetallic particles leads to higher hardness in the interface regions.

Metal intermediate layers can be deposited onto the substrate before deposition of ceramic coatings on aluminium alloy: titanium beneath TiN and chromium beneath CrN are examples. Typical micrographs are shown in Fig. 10.22 where the results of the wear tests indicate the beneficial effects of such layers. While a thin TiN coating does not confer a high wear resistance due to its fracture under load, the presence of a titanium layer between this and the substrate increases the surface hardness to 2190 HK and lead to a high wear resistance in sliding tests. Such composite coatings also show better adhesion to the substrate in scratch testing. A similar situation exists in the case of Cr-CrN duplex coatings which induce better wear resistance than either chromium or chromium nitride.

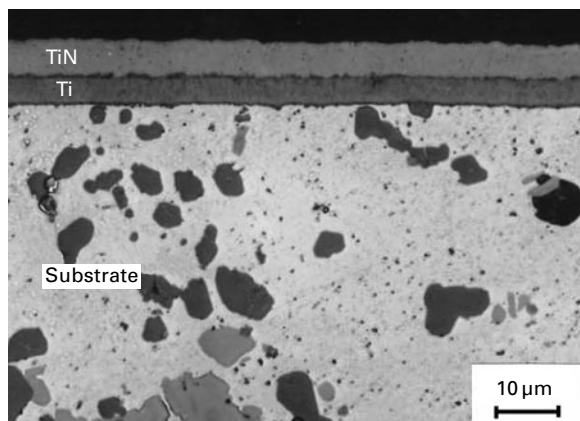
The interface of transition from the substrate material to the coating usually



(a)



(b)



(c)

10.22 Typical micrographs of ceramic coatings with interlayers on aluminium alloy; (a) fracture section of Ti-TiN, (b) fracture section of Cr-CrN, (c) polished and etched section of Ti-TiN.

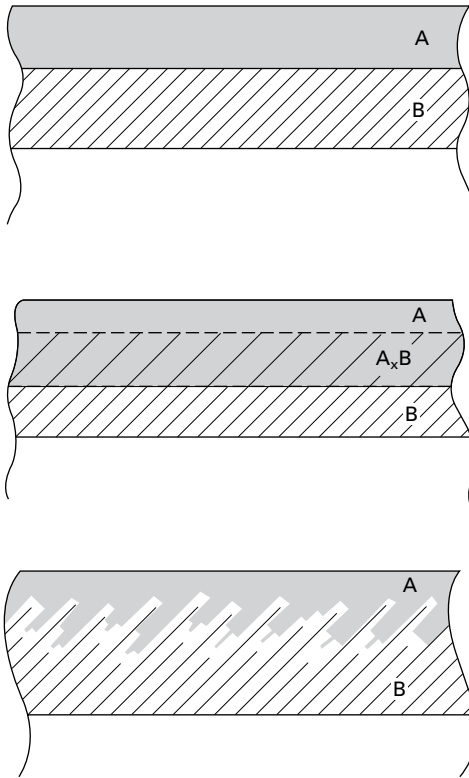
forms a break in the normally uniform crystallinity and/or composition. This abrupt mismatch is reflected in a change in the coefficient of thermal expansion, thermal conductivity and hardness. Plasma assisted processes, in general, provide a gradual composition change or graded interface, but over a very short depth. Intermediate films, on the other hand, spread the interfacial stresses onto a thick, strong metallic layer rather than imposing them on the interface, below which a fracture can rapidly propagate. The effect of the intermediate layer, then, is to introduce a graded transition over a depth much longer than that produced by a graded interface, from the substrate properties to those of the coating.

The other important effect of an intermediate layer is to increase the load bearing capacity of the coated substrate. In the case of aluminium alloys, this means less deformation under a given load and, thus, higher wear resistance. The improvement is likely to be due, at least in part, to the improved load support afforded by the intermediate layer, since both chromium and titanium are harder than the substrate. This effect is much more influential than interposing a thin intermediate layer just to reduce the differential thermal expansion, which may result in adhesive failure of some coatings at the interface (Holmberg and Matthews, 1994).

As is sketched in Fig. 10.23, interfaces, compound formation, and inter-diffusion are the three possible forms. These can occur separately or most likely in various combinations, depending on the coating–substrate compatibility. It is usually difficult to characterize an interface located below the surface, particularly in the case of rather thick, well adherent coatings. Nevertheless, the results of analyses, and microhardness and microscopical studies give good indications on the nature of the intermediate layers formed at the interface regions.

In the case of ion plated chromium, both compound formation and inter-diffusion are the controlling mechanisms at the interface, since X-ray diffraction has indicated some peaks of CrAl_7 . Formation of this compound as a polycrystalline film has been reported after heat treating Al–Cr couples at 300–400°C, and deep penetration of ion plated chromium in aluminium substrates has been confirmed by AES studies (Poate *et al.*, 1978).

Annealing up to 500°C did not produce any continuous intermetallic phases in titanium coatings, although high values of hardness were obtained as a result of inter-diffusion. This is advantageous, whereas a brittle phase is detrimental to the coating–substrate properties. Thus, it appears that plasma processing without formation of intermetallic layers can improve the tribological properties of the coating–substrate combination by increasing hardness and adhesion. Formation of a continuous layer of brittle phases, on the other hand, has a damaging effect by reducing effective adhesion of the coating to the aluminium substrate.



10.23 Schematic representation of interface between coating A and substrate B: (a) uniform sharp interface, (b) compound formation, (c) interdiffusion with concentration gradient.

10.7 Summary

In a tribological contact situation, soft and hard coatings may be used to reduce friction/wear. With soft coatings, the aim is to confine friction losses to a thin film of low shear strength interposed between the contacting surfaces. Such films not only reduce the coefficient of friction, but also limit the variation in friction that is undesirable in some applications. Soft films, however, wear gradually and the protection is eventually lost. Hence, the greatest contribution surface layers can make in tribology is through hard coatings (Komvopoulos *et al.*, 1987).

It is well established that a wear resistant coating must have; (i) good adhesion to the substrate, (ii) high hardness, and (iii) the ability to withstand deformation of the substrate (Kramer, 1983). Coating adhesion is not considered a problem in plasma-assisted processes provided the sputter cleaning stage is well performed to remove the oxide film and to produce a graded interface.

The other two requirements are not totally independent from one another: higher hardness, in general, is accompanied by less ductility and therefore lower capacity for plastic deformation. It is therefore important to develop coatings with sufficient toughness. Since wear resistance is achieved through a combination of high microhardness with sufficient ductility, a compromise is sometimes necessary to be made between these two factors. Some evidence suggests that titanium nitride coatings with lower hardness impart better wear resistance on aluminium alloy substrate compared with harder coatings of the same thickness.

Choice of the coating primarily depends on the proposed application and the counterface material. For applications where intermediate bearing pressures are involved, ion plated chromium may be suitable and, when low friction is required, metallic copper is preferred. On the other hand, for sliding situations against a hard material, titanium nitride of a thickness above 5 μm , or a lower thickness together with a titanium interlayer, appear to be appropriate coatings for aluminium alloys. A duplex process, incorporating PVD titanium and plasma nitriding, may be applied to impart both a moderate coefficient of friction and high wear resistance to aluminium substrates. Duplex treatments have the advantage of higher load bearing capacity, which is a key factor in coating development for aluminium substrates. This appears to be the future trend in surface engineering of aluminium alloys for tribological applications.

10.8 References

- Ashrafizadeh F (1992), Duplex surface treatment of aluminium alloys, *Int. Conf. Heat & Surface* 92, Kyoto, 341–344.
- Ashrafizadeh F (1993), Surface Treatment of Aluminium Alloys to Combat Wear, *Light Metals Processing and Applications*, Quebec, The Metallurgical Society of CIM, 615–626.
- Ashrafizadeh F (1997), Tribological evaluation of copper-coated aluminium, *Surface Engineering*, 13(1), 41–44.
- Ashrafizadeh F (2000), Adhesion evaluation of PVD coatings to aluminium substrate, *Surf & Coat Technol*, 130, 186–194.
- Ashrafizadeh F (2003), Influence of plasma and gas nitriding on fatigue resistance of plain carbon (Ck45) steel, *Surf & Coat Technol*, 173–174, 1196–1200.
- Ashrafizadeh F and Bell T (1990), Hard Coatings on Aluminium Alloys by PVD, *Surface Engineering Practice*, England, Ellis Horwood Publishers, 46–59.
- Ashrafizadeh F, Young J M and Bell T (1987), PVD treatment of aluminium alloys, *Proc. 2nd Int. Conf. Surface Engineering*, The Welding Institute, Stratford, UK, 51.1–51.13.
- Bair S, Ramalingam S and Winer W O (1980), Tribological experience with hard coats on soft metallic substrates, *Wear*, 60, 413–419.
- Bland R D, Kominiak G J and Mattox D M (1974), Effect of ion bombardment during deposition on thick metal and ceramic deposits, *J. Vac. Sci. Technol.*, 11(4), 671–674.

- Bunshah R F (1981), The activated reactive evaporation process, developments and applications, *Thin Solid Films*, 80, 255–261.
- Bunshah R F (1982), *Deposition Technologies for Films and Coatings*, USA, Noyes Pub.
- Bunshah R F and Suri A K (1979), Friction and wear of stainless steel, titanium and aluminium with various surface treatments, ion implantation and overlay hard coatings, *Proc. Conf. Ion Plating and Allied Techniques*, IPAT'79, 230–241.
- Edenhofer B (1974), Physical and metallurgical aspects of ionitriding, *Heat Treatment of Metals*, Vol. 1, No. 1, 23–28.
- Edrisy A, Perry T, Cheng Y T and Alpas A T (2001), Wear of thermal spray deposited low carbon steel coatings on aluminium alloys, *Wear*, 251, 1023–1033.
- Evans R, Salifa A, Zhang G, Evans E, Hariharan S I and Young G W (2002), Development of experimental techniques and an analytical model for aluminium nitriding, *Surf and Coat Technol*, 157(1), 59–65.
- Figueroa U, Salas O, Oseguera J, Rodriguez S and Ruiz B (2003), Effect of presputtering on plasma ion nitriding of aluminium substrates, *Surface Engineering*, 19(5), 337–344.
- Gawne D T and Gudyanga T F P (1984), Durability of chromium plating under dry sliding conditions, *Tribology International*, 17(3), 123–128.
- Gregory J C (1978), Low temperature metal diffusion treatments for the improvement of scuffing and wear resistance of ferrous and non-ferrous metal parts, *Heat Treatment of Metals*, 2, 33–38.
- Holmberg K and Matthews A (1994), *Coatings Tribology*, Netherlands, Elsevier.
- Hosseini S R, Ashrafizadeh F (2009), Accurate measurement and evaluation of the nitrogen depth profile in plasma nitrided iron, *Vacuum*, 83, 1174–1178.
- Kashaev N, Stock H R, Zoch H W (2005), *Surf & Coat Technol*, 200, 502–506.
- Kawai S (2002), *Anodizing and Coloring of Aluminum Alloys*, ASM International.
- Komvopoulos K, Saka N and Suh N P (1987), The role of hard layers in lubricated and dry sliding, *Journal of Tribology*, 109, 223–231.
- Kramer B M (1983), Requirements for wear-resistant coatings, *Thin Solid Films*, 108, 117–125.
- Mandl S, Brutscher J, Gunzel R, Moller J (1996), *J. Vac. Sci. Technol.*, B14, 2701.
- Manory R R (1990), Some principles for understanding surface modification of metals by glow discharge processes, *Materials and Manufacturing Processes*, 5(3), 445–470.
- Mattox D M (1973), Fundamentals of ion plating, *J. Vac. Sci. Technol.*, 10(1), 47–52.
- Miyagi M, Sato Y, Mizuno T and Sawada S (1980), Titanium 80 Science and Technology, *Proc. 4th Int. Conf. on Titanium*, 4, 2867.
- Movchan B A and Dimchishin A V (1969), *Phys. Metals and Metallography*, 28, 83.
- Muehlberger D E (1983), *Plating and Surface Finishing*, 70(11), 25.
- Poate J M, Tu K N and Mayer J W (1978), *Thin Films; Interdiffusion and Reactions*, John Wiley.
- Polmear I J (1995), *Light Alloys, Metallurgy of the Light Metals*, 3rd ed., U.K., Arnold Publications.
- Ramalingam S, Shimazaki Y and Winer W O (1981), Magnetron sputtering of non-ferrous aerospace alloys for wear protection, *Thin Solid Films*, 80, 297–303.
- Reinhold B, Naumann J, Spies H J (1998), *Härterei Tech. Mitt.*, 53, 329–336.
- Richter E, Gunzel R, Parasacandola S, Telbizova T, Kruse O, Moller W (2000), Nitriding of stainless steel and aluminium alloys by plasma immersion ion implantation, *Surf & Coat Technol*, 128–129, 21–27.
- Rickerby D S and Matthews A (1991), *Advanced Surface Coatings*, USA, Chapman and Hall.

- Sarkar A D and Clarke J (1980), Friction and wear of aluminium–silicon alloys, *Wear*, 61, 157–167.
- Schaeffer R J, Tucker T R and Ayers J D (1980), *Laser and Electron Beam Processing of Materials*, Academic Press.
- Spies H J, Reinhold B, Wilsdorf K (2001), *Surface Engineering*, 17, 41–54.
- Spies H, Spies H J (2010), Nitriding, surface alloying and duplex surface engineering – a contribution to the surface engineering of aluminium and titanium alloys, *Surface Engineering*, 26.
- Spies H J, Wilsdorf K (1998), *Härterei Tech. Mitt.*, 53, 294–305.
- Stock H R, Chen H Y, Mayr P (1994), *Aluminium*, 70, 220–228.
- Tachikawa H, Suzuki T, Fujita H and Arai T (1985), *Process for ion nitriding aluminium or aluminium alloys*, European Patent 0158271 A2.
- Thornton J A (1975), Influence of substrate temperature and deposition rate on structure of thick sputtered Cu coatings, *J. Vac. Sci. Technol.*, 12(4), 830–834.
- Valli J, Makela U and Matthews A (1986), *Surface Engineering*, 2(1), 49–53.
- Visuttipitukul P, Aizawa T, Kuwahara H (2003), *Mater. Trans. Japan*, 44, 1412–1418.
- Visuttipitukul P, Aizawa T (2005), *Wear*, 259, 482–489.
- Wachtman J B and Haber R A (1986), Ceramic films and coatings, *Chemical Engineering Progress*, 82(1), 39–46.
- Wernick S, Pinner R and Sheasby P G (1987), *The Surface Treatment and Finishing of Aluminium and its Alloys*, 5th edn, Finishing Publications.

Plasma immersion ion implantation (PIII) of light alloys

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Abstract: Plasma immersion ion implantation (PIII) or plasma source ion implantation (PSII), which overcomes the line-of-sight limitation inherent to beam-line ion implantation is an important surface modification technique for light alloys. In this chapter, the processes and advantages of the PIII technique are introduced, which is followed by an up-to-date overview of the progress and current status of PIII surface modification of light alloys including Mg, Al and Ti alloys. The structural changes in light alloys after PIII and the resulting improvements in the corrosion resistance, surface mechanical properties, as well as biological performance of the treated alloys are described. New trends in PIII surface treatments are also discussed.

Key words: light alloys, plasma immersion ion implantation, corrosion resistance, surface mechanical properties, biological performance.

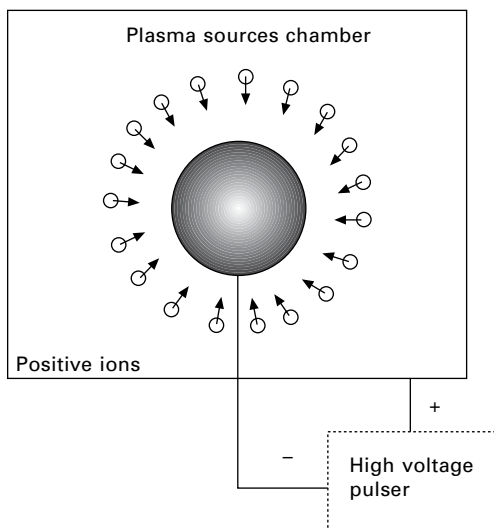
11.1 Introduction

Plasma immersion ion implantation (PIII) or plasma source ion implantation (PSII) is a well established technique based on plasma science. The unique advantage of PIII is processing of samples with a complex shape, because the technique circumvents the line-of-sight restriction encountered in conventional beam-line ion implantation (Conrad, 1987; Tendys, 1988). As the typical implantation depth is quite shallow, generally about several nanometers to micrometers from the surface, PIII does not usually alter the bulk properties of the materials. Hence, this technique has become an important and effective method for the surface modification of various electrically conducting (Conrad, 1987; Liu, 2007a; Kostov, 2004; Poon, 2005) and insulating materials (Zhang, 2006, 2007a; Powles, 2007). One of its important applications is surface modification of light alloys such as Mg-based, Al-based, and Ti-based alloys. In this chapter, the principle and advantages of PIII are introduced. A summary of recent progress in surface modification of light alloys, namely Mg, Al, and Ti alloys by PIII is presented. The structural changes in these light alloys after undergoing PIII and the resulting corrosion resistance, surface mechanical properties, as well as biological performance of the treated alloys are described. New

trends pertaining to PIII surface treatment of light alloys are discussed at the end of the chapter.

11.2 Processes and advantages of plasma immersion ion implantation (PIII)

PIII was first introduced back in the mid-1980s by Conrad *et al.* (1987) and Tendys *et al.* (1988). Initially called plasma source ion implantation (PSII), this technique is now frequently referred to as plasma immersion ion implantation (PIII) in order to distinguish it from conventional beam-line ion implantation. In PIII, the specimens are surrounded by a low temperature plasma and are pulse-biased to a high negative potential relative to the chamber wall, as illustrated in Fig 11.1. The ions generated in the plasma shroud are accelerated across the sheath formed around the specimens and are implanted into the surface of targets according to plasma physics. The ion energy and angle of incidence depend on the scattering mean free path, which is function of the plasma gas pressure, accelerating voltage, and sample topography. Owing to the absence of transport optics and mass selection, PIII can provide a high ion flux. The principle governing the PIII process depends on plasma physics and such details can be found readily in many books and references, such as those listed in the Section 11.8, Bibliography and so they will not be discussed here. In short, the advantages of PIII are described in the following (Chu, 1996):



11.1 Schematic diagram of the PIII process.

- (i) It is not subject to normal thermodynamic constraints such as impurity solubility.
- (ii) The instrumentation is simple and cheaper than traditional ion implanters.
- (iii) The implantation flux can be as high as $10^{16} \text{cm}^{-2} \text{s}^{-1}$ and the implantation energy can vary from 10 to 10^5 eV.
- (iv) Non-planar samples can be implanted with good conformality and uniformity without special target manipulation.
- (v) Multiple processes, such as simultaneous and consecutive implantation, deposition, and etching can be carried out.
- (vi) Insulators can be treated.

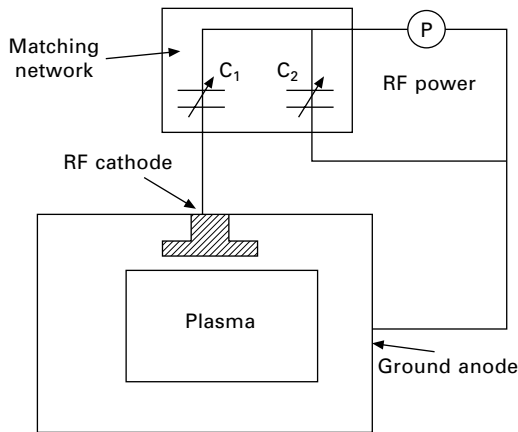
These unique characteristics make PIII very attractive for the modification of the surface properties of a myriad of materials.

11.2.1 Gaseous PIII

Both gaseous and solid ion implantation can be performed by means of PIII, which requires a low temperature and, typically, high-density plasma. In most applications, the plasma is produced by an electrical discharge. According to the nature of the implanted ions, they can be classified into gaseous plasma discharges such as radio frequency (RF) discharge and microwave discharge, glow discharge, and metal plasma discharge, as in the case of vacuum arc discharge.

RF discharge can be classified into two groups according to the coupling of the RF power with the load: capacitive coupling and inductive coupling. The normal setup contains a RF generator, an antenna, and a matching network, as shown in Fig 11.2. Generally, the generator works at a frequency of 13.56 MHz, which is above the ion plasma frequency and below the electron frequency. Thus, electrons respond to the variation in the electric field, but ions experience the average field. The working pressure during discharge ranges from about 10^{-1} to 10 000 Pa (Chu, 1996). The plasma density in the RF glow discharge during low-pressure discharge varies from 10^9 to 10^{11}cm^{-3} and can reach 10^{12}cm^{-3} under medium pressures (1–100 Torr) (Miyake, 2000). In low-pressure discharge, the ion mean free path is typically longer than the sheath dimension at the substrate, giving rise to collisionless conditions. The plasma potential of the RF discharge typically falls into the range of 10–30 V above the wall potential (Lieberman, 1994; Ehlers, 1979).

Glow discharge is triggered by two methods: thermionic filament or pulsed high voltage emission. Thermionic discharge relies on electron emission from a hot cathode to ionize the background gas. Plasma generation requires the suitable selection of a cathode heated by a floating power supply. Refractory

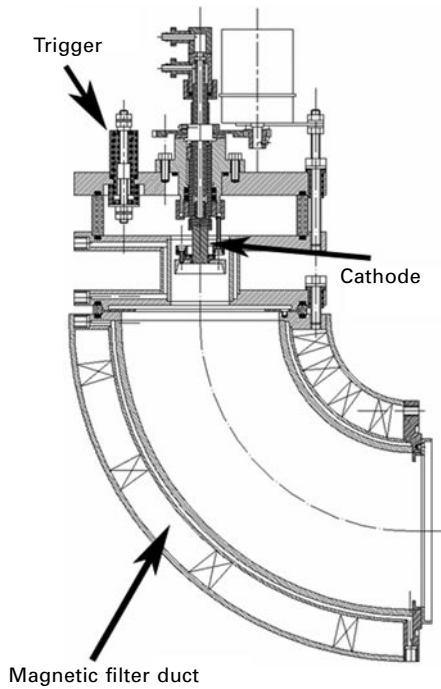


11.2 Schematic diagram of a capacitively-coupled plasma sources with equivalent electrical circuit.

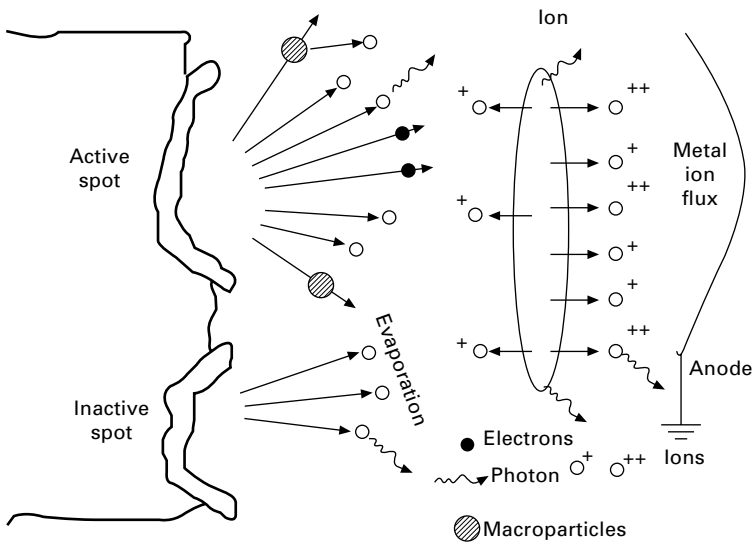
metals are usually used as the filament cathode as they are easy to fabricate and have sufficiently low evaporation rates. The electron currents range from 1 A to several kA, depending on the gas, plasma density, and plasma size. In addition, the applied voltage between the cathode and anode can be lower than the ionization energy and is usually in the range of 25–100 V, where the maximum of the ionization cross-section occurs for most gases (Lieberman, 1994). In pulsed high-voltage glow discharge, the pulsed voltages play dual roles, namely generation of the plasma, and acceleration of ions through the sheath to the substrate. Since it works for many electrode geometries and gases, the method is very versatile. The pulsed high voltage generates a sudden electric field between the substrate (cathode) and surrounding system (anode). The emitted free electrons from the cathode are accelerated and collide with gas molecules or the anode. Ions produced during the collisions continuously strike the cathode to generate secondary ions, which are accelerated back into the discharge volume (Lieberman, 1994).

11.2.2 Metal PIII

Metal plasma immersion ion implantation needs a cathode arc discharge system, as shown in Fig 11.3. A typical cathodic arc plasma source comprises two parts: a plasma production unit and a macro-particle filter. The characteristics of arc discharge are relatively high current (tens or hundreds of Amperes) and low voltage (10–80 V) between the cathode and anode. The vacuum is sustained by materials originating from the cathode. As shown in Fig 11.4, a small area on the cathode is heated by the arc and many particles together with a high density metal plasma are ejected. During the cathodic arc process, an ensemble of luminous cathode spots moves in a rapid and



11.3 Schematic diagram of a cathodic arc plasma source with a magnetic filter duct.

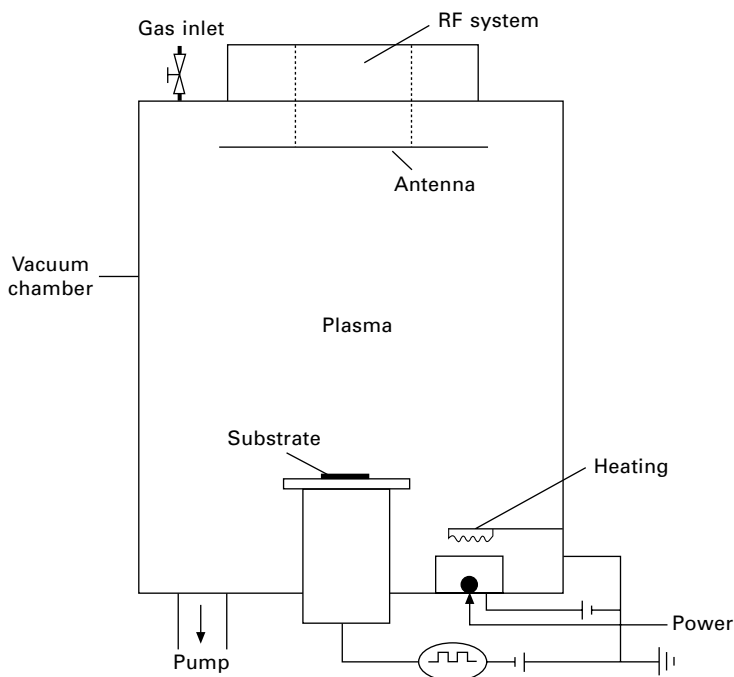


11.4 Particle emission from the arc spots (Lafferty, 1980).

chaotic manner across the surface. The plasma expands in all directions from the cathode spots towards the anode and vacuum chamber walls. The cathode spot is usually small, while producing an intense plasma with current densities of 10^6 – 10^{12} A $^{-2}$ (Lieberman, 1994). The spot velocity is determined by factors including the nature of the cathode, residual vacuum, and external magnetic field. The ejected macroparticle size ranges from 0.1 to 100 μm in diameter. The electron density in the cathodic plasma can reach 10^{20} cm $^{-3}$ and the expanding plasma produces a highly ionized jet with mean ion charges state greater than 1+ for many elements. A curved duct filter with a magnetic field is usually utilized to mitigate particle contamination from the arc. Another aim of the filter is to increase the plasma transportation efficiency through the duct, and an optimized 90° curved duct can achieve plasma transport efficiency of about 35% (Schulke, 1997). In metal PIII, the metal ions condense on the material's surface as a film in the time duration between the high voltage pulses. Ions accelerated by the high voltage bias pulses bombard the deposited metal atoms, giving rise to recoil implantation. This affects the elemental depth profiles which may deviate from the usual Gaussian-like shape (Schulke, 1997).

11.2.3 Hybrid PIII processes

Many researchers, such as those in City University of Hong Kong, have developed several hybrid processes such as PIII/nitriding (PIII&N) and PIII/deposition (PIII&D). In order to perform these hybrid processes, different types of hardware have been designed. The gaseous plasma is usually produced inductively or by capacitively coupled radio-frequency plasma sources as well as hot filament glow discharge plasma sources, and sustained by direct high-voltage glow discharge between the chamber wall and the target (Tian, 2001a). In the City University of Hong Kong instrument, four sets of filtered cathodic arcs are used to generate various metal ions free of macroparticles. The sputtering system can be operated either by RF or DC, even when high-voltage pulses are applied to the samples. There is also an evaporation system for solid elements such as calcium, phosphorus, and sodium that are difficult to handle using conventional cathodic arcs (Li, 2003). A schematic of the evaporation system is displayed in Fig 11.5. Evaporation of the powders is accomplished by filament heating and the solid entering the chamber is further ionized by the RF. The high-voltage switch is hard-tube-based and the pulsed voltage, pulsed frequency and pulsing phase relative to the vacuum arc phase can be flexibly adjusted to optimize various processes. In addition, a high frequency/low frequency modulator has been developed for plasma nitriding or sample biasing during physical vapor deposition (Tian, 2004). Both PIII&N (Tian, 2000a, 2000b) and PIII&D (Tian, 1999, 2001b) process have been successfully conducted using this facility (Bilek, 2000).



11.5 Schematic illustration of evaporation in the PIII and PIII&D processes.

PIII/nitriding (PIII&N)

In conventional nitriding processes, nitrogen must first absorb onto the sample surfaces and then diffuse into the substrate by thermal effects and the established concentration gradient. The surface conditions and materials' species play a critical role on the effective particle flux arriving at and penetrating the materials' surface. For example, it is quite difficult for nitrogen to penetrate the surface oxide barrier on aluminum alloys or stainless steels since N possesses quite small diffusion coefficients in the dense oxide layers. Consequently, a higher sample temperature is required but this may degrade certain properties. In the PIII/nitriding process, the mechanism of particles trapped on the top surface can be altered. The absorption and reaction mechanisms in conventional plasma nitriding still play an important role, but the direct penetration of high energy particles by implantation is responsible for subsequent diffusion. In this way, the processing temperature can be lowered without compromising the resulting surface properties (Bilek, 2000).

PIII/Deposition (PIII&D)

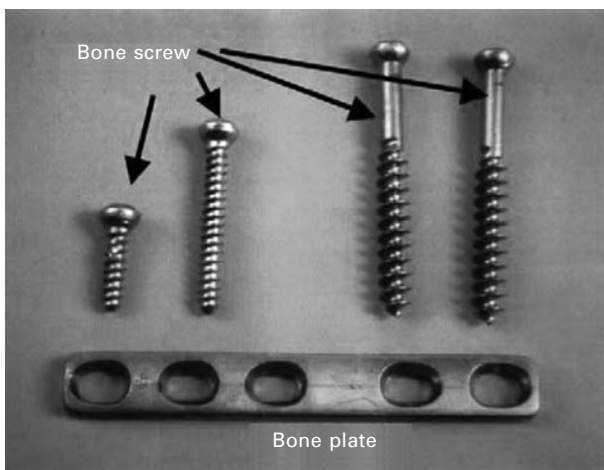
PIII&D, which is low-temperature process, is a variation of the conventional ion beam assisted deposition technique. The major difference lies in the

acceleration mechanism of impinging ions and the non-line-of-sight process. The ions can be generated by sputtering, evaporation, cathodic arc, etc. During PIII&D, typical multiple plasmas are used. It is common to have gas plasmas composed of one or more species, and for metal plasmas to be generated simultaneously in the same vacuum chamber. The implantation process can be performed before deposition to form a gradient layer, and simultaneous deposition and implantation can also be carried out. By adjusting the durations of the high voltage (implantation process) and low voltage (deposition process), flexible processes can be carried out to optimize the surface properties of the modified layer (Bilek, 2000).

11.3 PIII surface modification of titanium (Ti) alloys

Titanium and its alloys are widely used as structural materials in aerospace and aeronautic crafts due to their high strength-to-weight ratio and high temperature resistance (Jackson, 2006; Naka, 1996). Usually, the corrosion resistance of Ti alloys is good, due to the naturally-formed dense and corrosion resistant surface titanium oxide layer. Another important application of Ti-based alloys is for orthopaedic implants, such as bone screws, bone plates and artificial hip joints, due to their excellent biocompatibility, mechanical strength, and chemical stability (Niinomi, 2008). Figure 11.6 shows one set of bone fixation implants – bone screws, and a bone plate for fixation of a fractured bone (Liu, 2004a).

According to their applications, special surface treatments are usually required. In industrial applications, treatments to enhance the corrosion resistance and tribological properties are usually carried out. Titanium-



11.6 Bone plate and bone screws made of titanium (Liu *et al.*, 2004a).

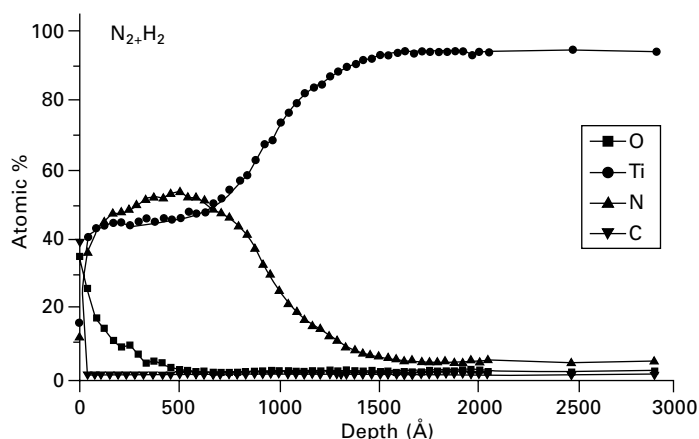
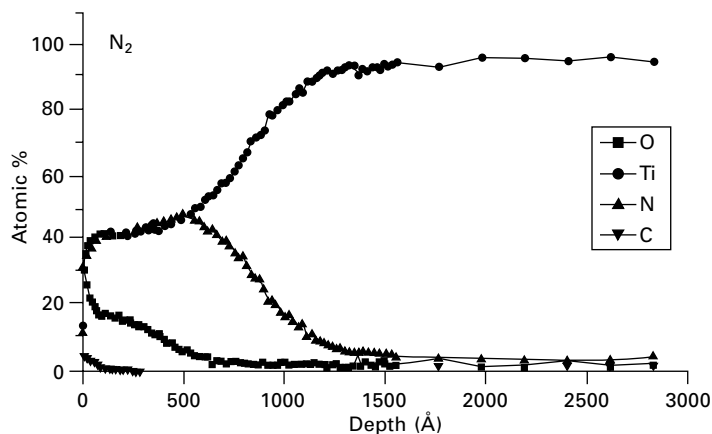
base implants are generally considered to be bio-inert in a physiological environment, as the naturally-formed titanium oxide can hardly induce growth of hydroxyapatite (HAP) from body fluids, leading to formation of fiber capsule around the implant (Long, 1998). Thus, a suitable surface treatment needs to be performed in order to improve the ability to induce precipitation HAP (named bioactivity or bone conductivity) and enhanced osteoblast adhesion (biocompatibility).

11.3.1 Influence of PIII process on corrosion and surface mechanical properties

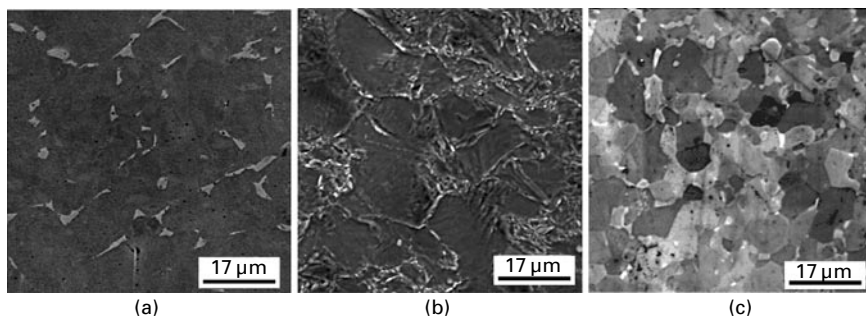
Nitriding is found to be very effective for enhancing the surface hardness and wear resistance of titanium alloys (Zhecheva, 2006; Sha, 2008; Pohreluk, 2007). Thus, nitrogen PIII can improve the tribological properties of titanium alloys. The formation of a hard and dense TiN layer is responsible for enhancement of surface hardness and wear resistance. Without substrate heating, the modified layer is usually several tens of nanometers thick, depending on the applied voltage. Heating the substrate will lead to diffusion of the implanted N, and N can penetrate more than one hundred nanometers (Mandl, 2007). As shown in Fig 11.7, pure nitrogen implantation usually causes recoil implantation of C-H contamination from the surface, but the utilization of a gas mixture of N_2/H_2 can exclude C implantation (Lacoste, 2002). Hence, N_2/H_2 mixtures with various volume ratios are usually adopted in practice. Implantation also induces changes in the surface morphology. As demonstrated in Fig. 11.8, the untreated sample typically exhibits a two phase structure, the matrix and β phase. After pure nitrogen implantation, the two phases are more evident and the bright structure (β phase) becomes rougher. This is natural in PIII treatment as PIII induces slight sputtering of the surface. Implantation using N_2/H_2 results in complete modification of the surface morphology suggesting more severe sputtering-induced damage.

The influence of nitrogen PIII on the surface mechanical properties of Ti-6Al-4V has been systematically investigated (Ueda, 2003). Figure 11.9 shows that the near surface possesses the highest hardness, which is several times higher than that of the substrate. In deeper sites, increased hardness ($\sim 70\%$) is observed, even at depths eight times that of the maximum penetration of nitrogen (30 nm). The increased dose results in higher hardness, but we believe that a treatment time longer than 2 h (corresponding to the highest dose in Fig. 11.9) poses little influence on the surface hardness. Although the modified layer is very thin (about 30 nm), a reduction of the coefficient of friction of about one third can be obtained compared with the untreated samples.

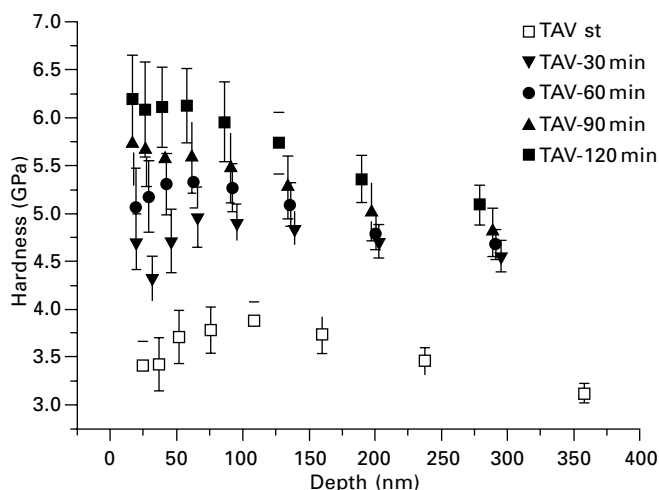
The influence of nitrogen PIII on the corrosion resistance of Ti-6Al-4V has also been studied (da Silva, 2007). Different kinds of nitrogen PIII processes,



11.7 Depth profiles of Ti, O, N and C measured by XPS in titanium after PIII using N_2 and $N_2 + H_2$ ($P_{N_2}:P_{H_2} = 5:4$), respectively (Lacoste *et al.*, 2002).



11.8 SEM images of the Ti-6Al-4V alloys: (a) untreated sample; (b) after PIII processing using N_2 ; (c) after PIII processing using N_2/H_2 mixture (da Silva *et al.*, 2007).



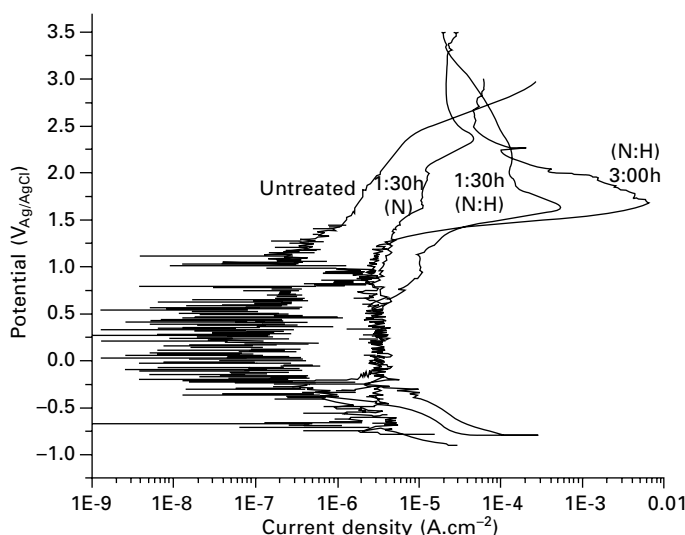
11.9 Surface hardness of Ti-6Al-4V subjected to nitrogen PIII at a bias voltage of 20 kV as a function of penetration depths. (Ueda *et al.*, 2003).

such as pure N_2 implantation and N_2/H_2 co-implantation (with different gas ratios) have been performed. Electrochemical tests reveal that all these PIII processes do not improve the corrosion resistance of the treated alloys. On the contrary, they all pose slightly deleterious effects. More negative corrosion potentials are observed on all the treated samples and the passive current densities are all about ten times higher than that of the untreated sample, as shown in Fig 11.10.

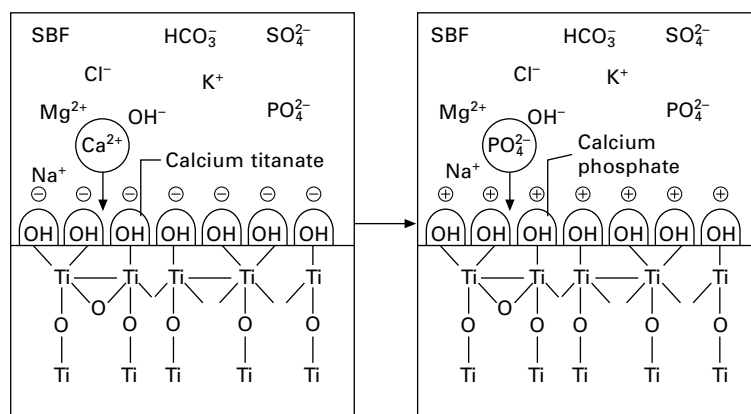
Oxygen and carbon PIII have also been performed on Ti-6Al-4V. The structure evolution after implantation has been investigated (Han, 1996). Carbon implantation can also improve the surface mechanical properties of the treated sample, whereas oxygen implantation seems to be more effective in enhancing the corrosion resistance of Ti alloys (Loinaz, 1998).

11.3.2 Modification of Ti alloy by PIII for biological applications

As aforementioned, Ti-based implants are typically bio-inert in a physiological environment. PIII has been extensively employed to engineer a functional surface on Ti-base implants. It is well accepted that Ti-OH groups play an important role in the bioactivity of Ti-based implants. The mechanism of the Ti-OH groups inducing precipitation of HAP is illustrated in Fig. 11.11. The surface with Ti-OH groups is negatively charged in a physiological environment, with a pH of around 7.4. The negatively charged surface attracts positively charged Ca^{2+} ions, forming positively charged calcium



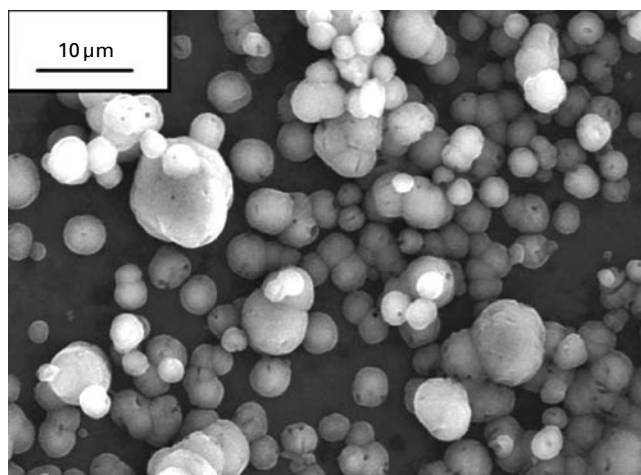
11.10 Potentiodynamic polarization curves of Ti-6Al-4V subjected to PIII at a bias voltage 11 V and substrate 400°C: N, pure N₂ PIII; N-H; PIII with N₂ and H₂ mixture gas (da Silva *et al.*, 2007).



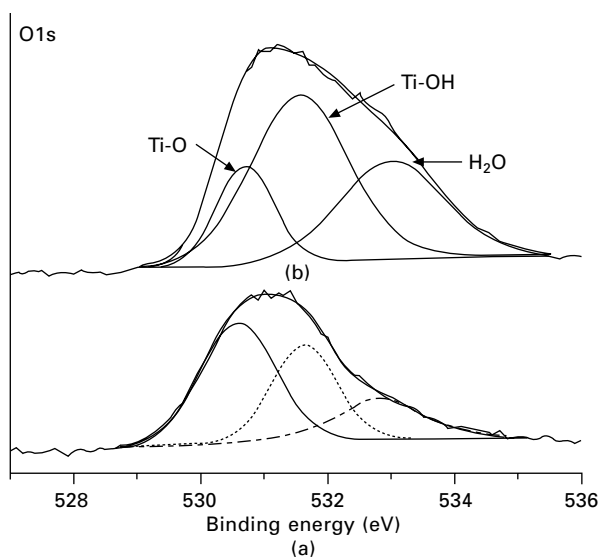
11.11 Illustration of HAP precipitation process on the surface with Ti-OH groups (Kokubo *et al.*, 2003).

titanate on the surface. With accumulation of positive charges on the surface, the surface becomes positively charged, consequently attracting negatively charged phosphate ions. The absorbed Ca²⁺ and phosphate ions combine to form apatite (Kokubo, 2003). The HAP then grows by consuming more Ca²⁺ and phosphate ions from the surrounding body fluids. Thus, fabrication of surface Ti-OH groups is an effective way to enhance the bioactivity of titanium-based implants. Hence, H₂ and H₂O PIII have been conducted into

titanium (Xie, 2005). Ball-like HAP clusters are observed on the surface of sample after $H_2 + H_2O$ PIII and soaking in synthetic body fluid (SBF) for only 14 days (see Fig. 11.12). The dramatically increased Ti-OH groups after $H_2 + H_2O$ implantation can be clearly discerned by XPS analysis, as shown in Fig. 11.13. The increased number of Ti-OH groups accounts for the improved bioactivity.



11.12 SEM views of H_2+H_2O PIII of pure titanium after soaking in SBF for 14 days (Xie *et al.*, 2005).



11.13 High resolution XPS O1s spectrum acquired from pure titanium before (a) and after (b) $H_2 + H_2O$ implantation (Xie, 2005).

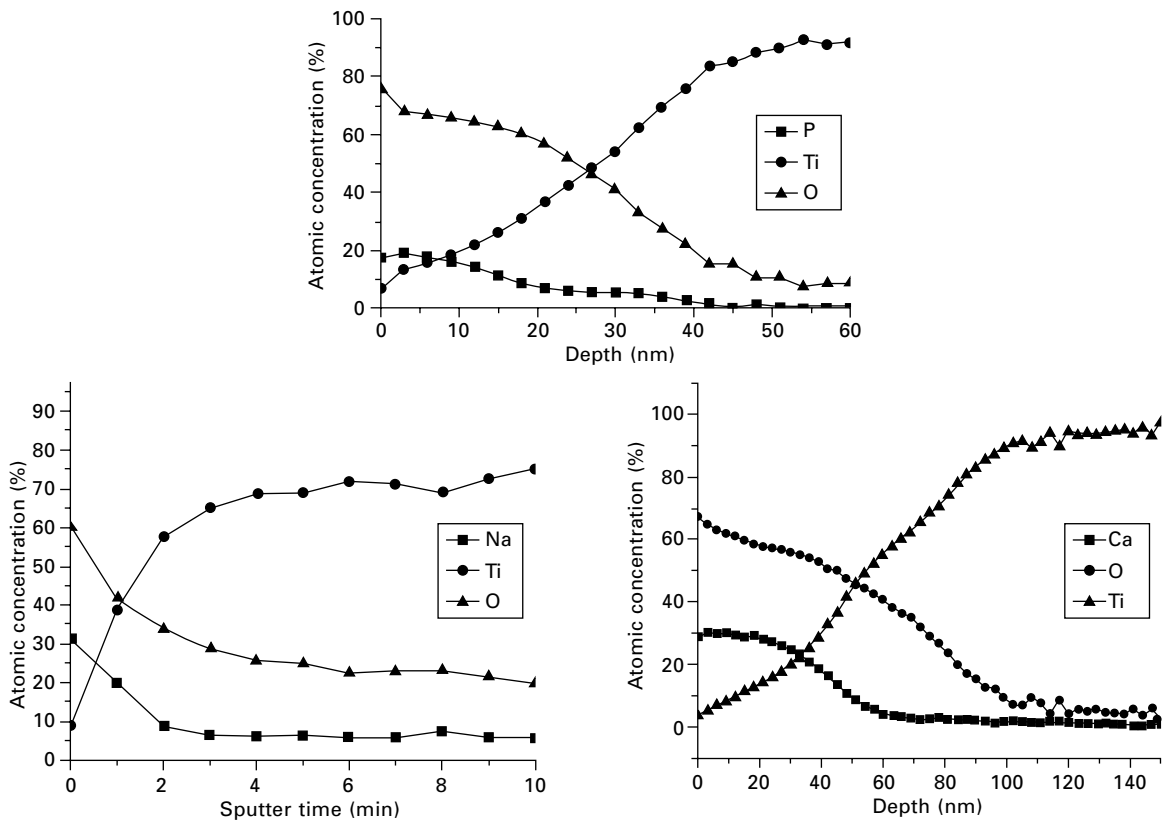
Ca is a biological active element in bone tissue growth. Much work has been carried out to investigate the effect of Ca PIII on the biological properties of titanium alloys. However, due to the low melting point and high activity of Ca, PIII of Ca via the traditional approach is very difficult. Ca, P and Na implantation has been successfully performed by Liu and co-workers (2004b) using the evaporation system stated above (see Fig. 11.5) as confirmed by the XPS results in Fig. 11.14. However, the XPS results also imply that deposition is inevitably present during implantation. Thus, this treatment should be described as PIII&D. Later, they utilized PIII&D to fabricate a thick modified layer with a thick deposition layer (about 0.5 μm in thickness) and implantation layer (about 0.6 μm), as shown in Fig. 11.15. The modified layer has a bi-layered structure with the top layer being calcium hydroxide and the inner layer being calcium titanate, as schematically shown in Fig. 11.16. In the vacuum chamber, the top layer after PIII&D is mainly composed of CaO. When exposed to air, CaO turns into calcium hydroxide and/or carbonates. The SEM views (Fig. 11.17) demonstrate that the original smooth surface becomes very rough, with many ball-like protuberances. After soaking in SBF for 14 days, needle-like HAP covers the entire surface of the treated sample (Fig 11.18).

The good bioactivity of the PIII&D titanium alloys are considered to be associated with the dissolution of the top calcium hydroxide layer. The increased Ca ion concentration in the vicinity and local pH both benefit nucleation of HAP. The biological response of the Ca implanted titanium alloys has also been studied by *in vivo* and *in vitro* experiments. The Ti surface implanted with Ca enhances the expression of certain bone-associated components and promotes MG-63 cell adhesion and spreading. *In vivo* experiments show that bone formation on the Ca implanted surface is superior to that of the untreated one (Liu, 2005). Using the same equipment, Na and P PIII has also been carried out. No obvious cytotoxicity effects are discovered (Liu, 2005; Maitz, 2005) whereas good bioactivity is observed from the Na implanted samples. In comparison, only a small improvement in bioactivity is observed from the P implanted samples (Liu, 2004b).

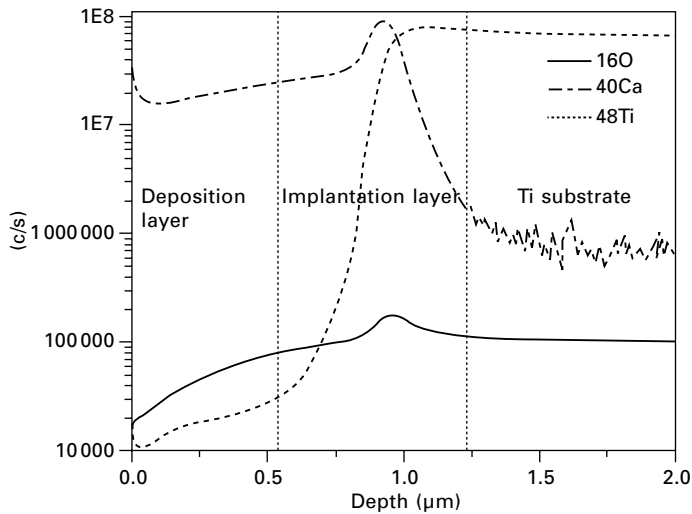
Modification of the biological properties of titanium using PIII and PIII&D is effective and promising. The advantage is that the modified layer bonds strongly to the substrate as there is no distinctive interface between the modified layer and substrate. However, more effective processes and better understanding of the corresponding mechanism are still required.

11.4 PIII surface modification of magnesium (Mg) alloys

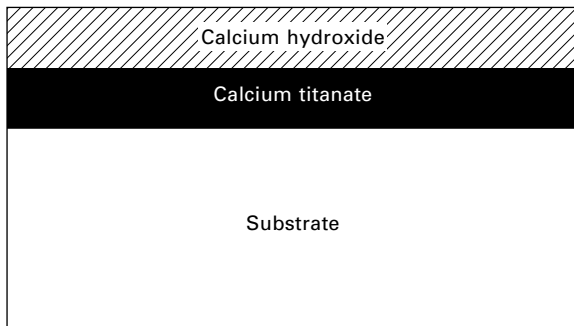
Magnesium and its alloys possess many unique properties, such as low density, high specific strength and good electromagnetic shielding effects. They are



11.14 XPS depth profile of elements of pure titanium subjected to P, Ca and Na PIII (Liu, 2004b).

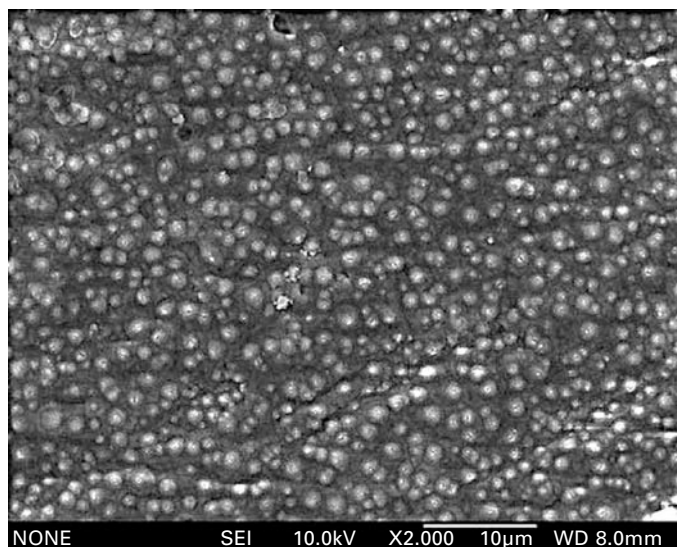


11.15 XPS depth profile of pure titanium after Ca PIII&D (Liu, 2005).

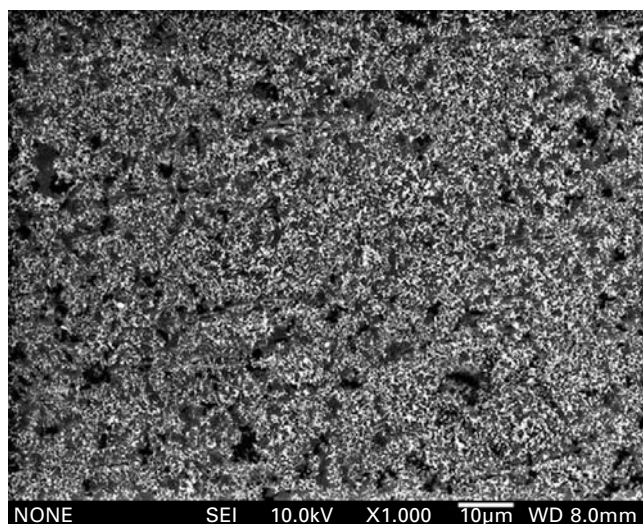


11.16 Schematic illustration of the structure of titanium subjected to Ca PIII&D.

therefore attractive for many applications in transportation, aerospace, and electronics (Hort, 2006; Kaufmann, 2001). As magnesium and its alloy can degrade in a physiological environment by corrosion, they also play an important role in biodegradable implants (Staiger, 2006). However, magnesium is chemically very active. The naturally-formed MgO (or Mg(OH)_2) layer is loose and cannot provide adequate protection to suppress further corrosion of the substrate. Therefore, magnesium alloys usually have poor corrosion resistance (see Chapter 1 for more details). In addition, the surface mechanical properties of magnesium alloys are usually unsatisfactory. In practical applications, suitable surface treatments are necessary. Surface modification of magnesium alloys falls mainly in two families, namely (i) coating the base materials by anodizing, plasma electrolytic oxidation (PEO),



11.17 SEM views of Ca PIII&D treated titanium (Liu, 2005).



11.18 SEM views of Ca-PIII&D treated titanium after soaking in SBF for 14 days (Liu, 2005).

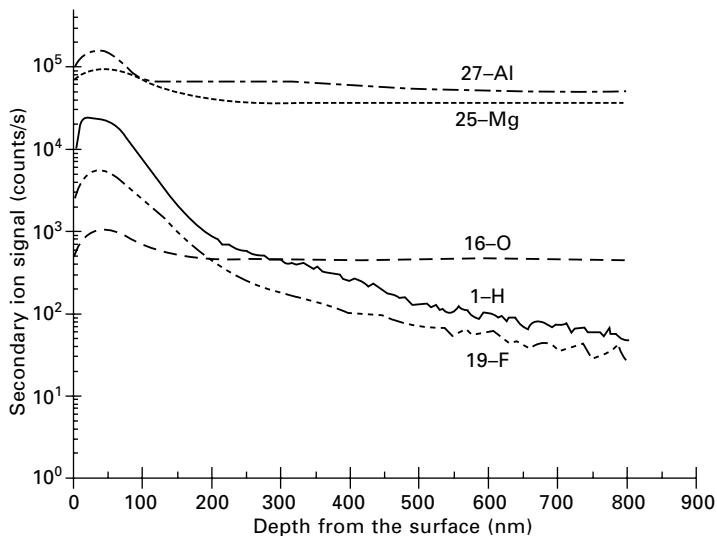
chemical conversion coating and various ceramic coating (Xin, 2008) and (ii) ion implantation (Zhang, 2007b). Fabrication of a coating may provide better corrosion protection, but the adhesion strength is a crucial issue. Usually, ion implantation generates a gradient layer which does not easily delaminate from the substrate. However, ion implantation can usually provide

only moderate effects on the corrosion resistance and surface mechanical properties. Thus, the choice of surface modification techniques should take into account various needs. As such, surface treatments of Mg alloys by PIII can be classified into two groups: gaseous PIII and metal PIII.

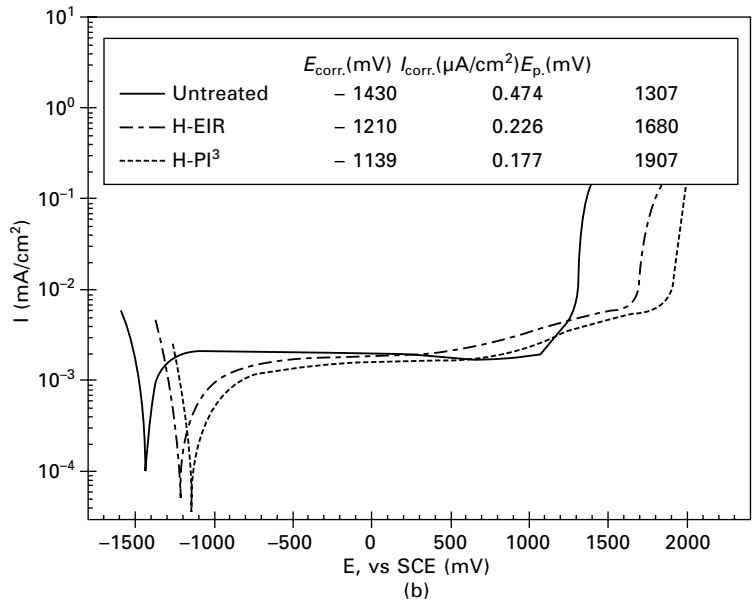
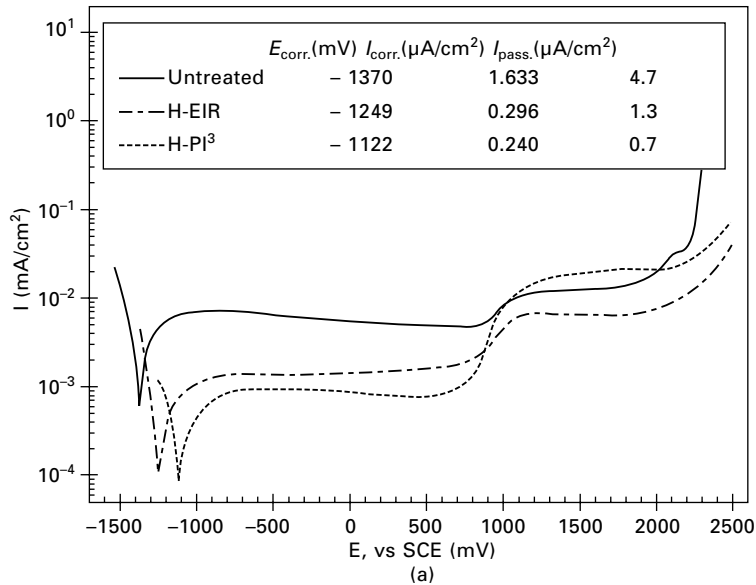
11.4.1 Gaseous PIII of magnesium alloys

Implantation of gaseous ions aims at fabricating a barrier layer on the surface to block attack from aggressive ions in the environment. Up to now, oxygen, hydrogen, and nitrogen have been implanted into magnesium alloys. MgH_2 formed by electrochemical ion reduction (EIR) can significantly improve the corrosion resistance of magnesium alloy (Bakkar, 2005). Researchers have tried to generate a denser MgH_2 barrier layer via hydrogen PIII (Bakkar, 2005). Hydrogen implantation conducted at a bias voltage 30 kV and substrate temperature of 200°C leads to a penetration depth of about 200 nm for H in AZ91 magnesium alloys, as shown in Fig 11.19.

The potentiodynamic polarization results in Fig. 11.20 show that the corrosion potential of the treated pure magnesium is positively enhanced by more than 200 mV. The improvement in the corrosion resistance is more obvious in the PIII AZ91 magnesium alloy, with an enhanced corrosion potential of nearly 300 mV. Another significant change is the dramatically enhanced pitting corrosion potentials. The electrochemical test also implies that both the hydrogen PIII pure magnesium and AZ91 magnesium alloys



11.19 SIMS analysis of H distribution in pure magnesium subjected hydrogen PIII at 30 kV and substrate temperature of 300°C (Bakkar, 2005).



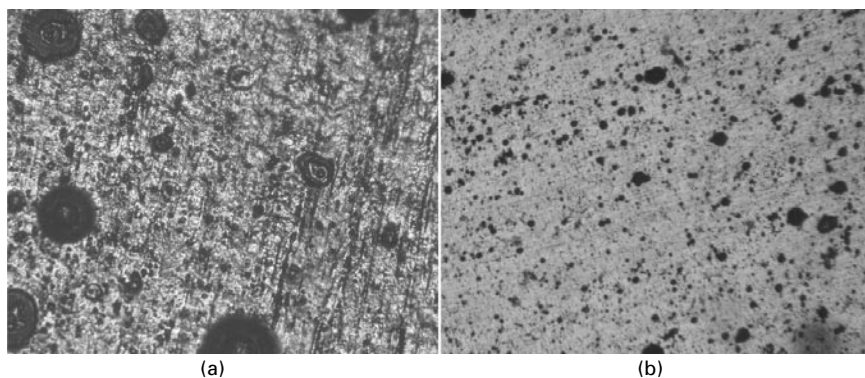
11.20 Potentiodynamic polarization curves of pure magnesium (a) and AZ91 magnesium alloy (b): hydrogen PIII at 30 kV; H-EIR, electrochemical ion reduction. (Bakkar, 2005).

exhibit better corrosion resistance than samples treated by the EIR treatment. However, in our experiments, it was also found that the implantation voltages play an important role in the modification effects. Below 30 kV,

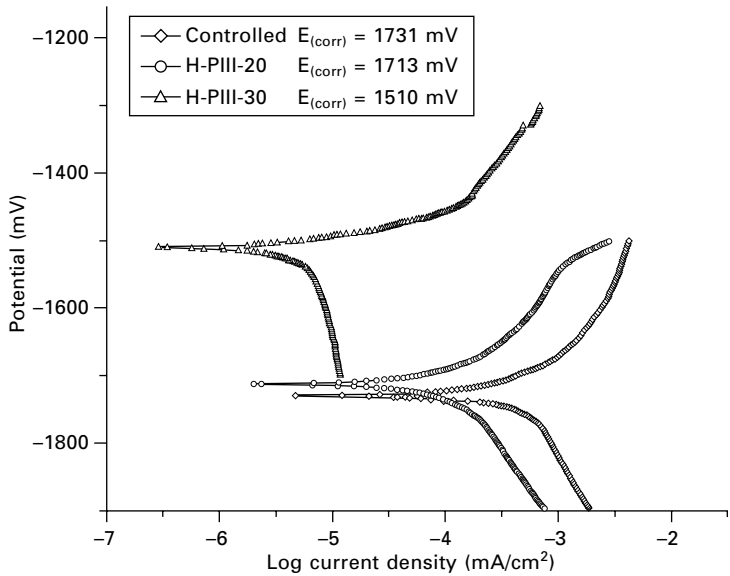
no improvement in the corrosion resistance could be obtained. This could be readily observed by *in situ* observation of the samples immersed in the test solution (simulated body fluids, SBF). As shown in Fig. 11.21, when exposed to the SBF, serious corrosion takes place immediately on the sample treated at 20 kV, but the magnesium alloy implanted at 30 kV is stable even after 1 day of immersion and only small corrosion sites can be seen. The potentiodynamic polarization test results shown in Fig. 11.22 are in good agreement with the results from *in situ* observation. The corrosion potential of the sample treated at 30 kV is enhanced by more than 200 mV, whereas no obvious enhancement in the corrosion potential can be seen from the sample after 20 kV PIII.

Tian *et al.* have investigated the effects of nitrogen implantation on the corrosion behavior of magnesium alloys (Tian, 2005). The electrochemical test results in Fig. 11.23 show enhanced corrosion potential after nitrogen PIII. However, both the implantation voltage and dose affect the corrosion resistance. The corrosion resistance is not very good for both very low (M-22) and very high doses (M-44). It is believed that N implantation can result in the formation of Mg_3N_2 (Fukumoto, 2001). However, Mg_3N_2 is sensitive to atmospheric modification and a high amount of Mg_3N_2 will pose negative effects on the corrosion resistance. Thus, the enhanced corrosion resistance is ascribed to the compactness of the loose natural oxide layer and ion irradiation effects. It is also conjectured that the excess ions agglomerating and moving to the interface during high dose implantation make the surface more active.

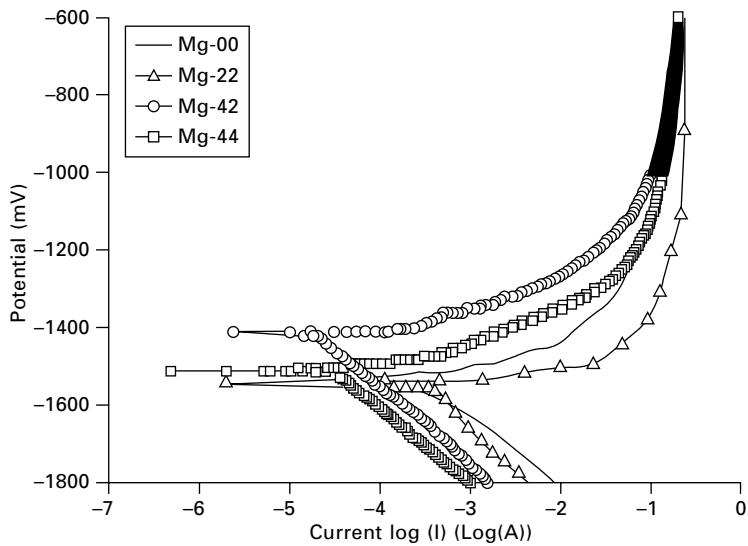
Researchers have also tried to fabricate dense oxide layers on magnesium by oxygen implantation and/or water PIII (Wan, 2007; Tian, 2006). As shown in Fig. 11.24, implantation of oxygen leads to enhancement in the



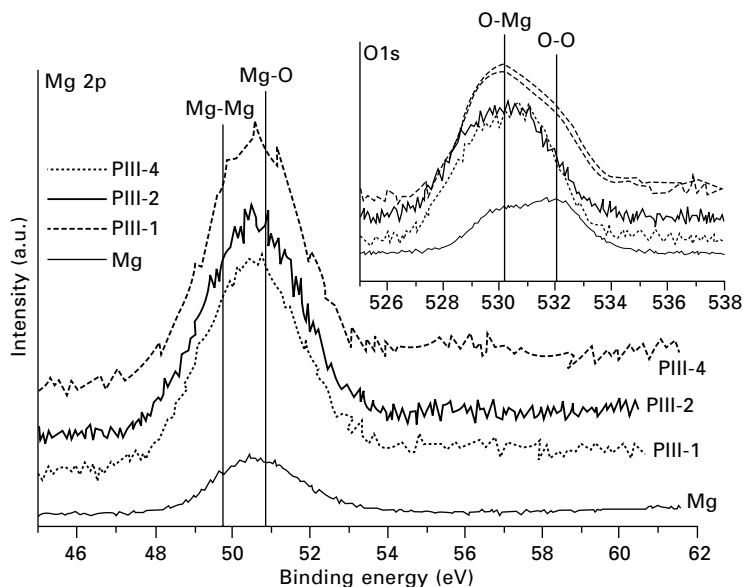
11.21 *In situ* corrosion morphology observation of AZ91 magnesium alloys subjected hydrogen PIII: (a) implantation at 20 kV after exposure in SBF for 5 min; (b) implantation at 30 kV after exposure in SBF for 1 day.



11.22 Potentiodynamic polarization curves of hydrogen PIII of AZ91 magnesium alloy: H-PIII-20, hydrogen PIII treatment at voltage 20 kV; H-PIII-30, hydrogen PIII treatment at voltage 30 kV.



11.23 Potentiodynamic polarization curves of AZ91 magnesium alloy after nitrogen PIII: Mg-00, untreated alloy; Mg-22, nitrogen PIII at 20 kV voltage for 4 h; Mg-42, nitrogen PIII at 40 kV for 2 h; Mg-44, nitrogen PIII at 40 kV for 4 h. (Tian, 2005).



11.24 Mg 2p and O 1s core level XPS spectra of untreated and oxygen PIII processed Mg: PIII-1, oxygen PIII at voltage 20 kV for 0.5 h; PIII-2, oxygen PIII at voltage 20 kV for 1 h; PIII-4, oxygen PIII at voltage 20 kV for 4 h. (Fukumoto, 2001).

binding energy of Mg-O and the binding energy increases with increased implantation dose. Ion bombardment also induces a smoother surface. In fact, the higher the implantation dose, the smoother is the surface. The oxygen PIII magnesium alloys exhibit interesting changes of corrosion performance in different test solutions. Low dose implantation results in more negative corrosion potentials in a phosphate buffer solution (PBS). However, the higher implantation dose also degrades the corrosion potential, while a five orders of magnitude reduction in the corrosion current density is present. The chloride ion concentrations also affect the effects of oxygen PIII. In the solution containing a high concentration of chloride ions, dramatic degradation in the corrosion resistance takes place. This behavior is probably associated with the attack by chloride ions onto the Mg-O bonds. The chloride ions can transform the magnesium oxide ions into soluble magnesium chloride as follows (Song, 2003):



Dissolution of magnesium oxide leads to more active regions on the surface and promotes further dissolution of the substrate. In a high concentration

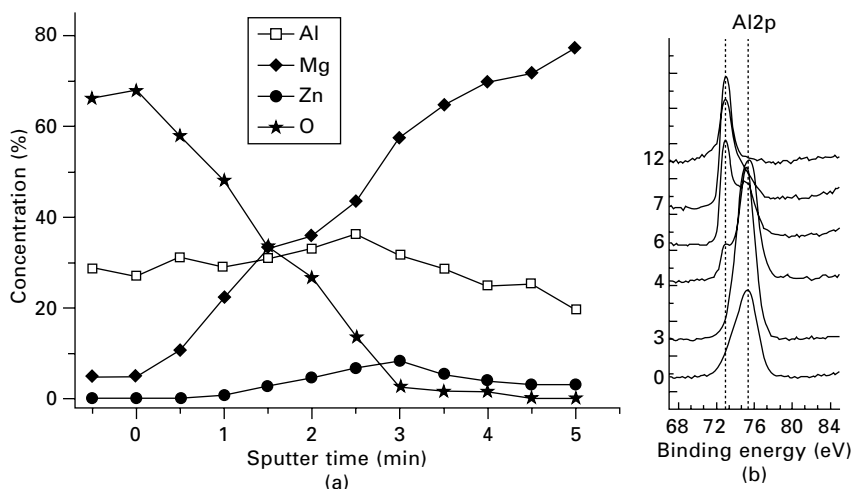
of chloride ions, attack by aggressive chloride ions mitigates the protection efficiency of magnesium oxide.

Gaseous PIII can only enhance the corrosion resistance to a certain extent. Among the gases, hydrogen implantation appears to be more effective. It can induce the formation of corrosion-resistant MgH_2 . Nitrogen implantation and oxygen implantation result in the formation of non-corrosion-resistant Mg_3N_2 and MgO . The limited enhancement in the corrosion resistance is thought to arise from irradiation effects and surface compactness. The mechanical property changes after gas ion implantation are seldom covered in current publications

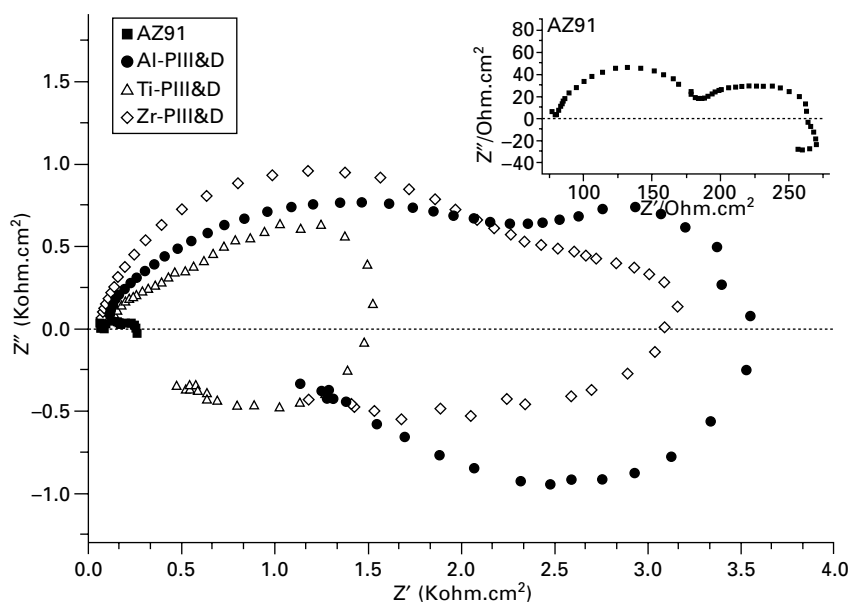
11.4.2 Metal PIII of magnesium alloys

It is well known that metal alloying elements affect both the mechanical properties and corrosion resistance of magnesium alloys. Many metal elements have therefore been implanted into magnesium alloys to achieve surface alloying. In conventional alloying processes, the contents of incorporated alloying elements depend on the solid solubility of elements in the substrate. However, in PIII, the amounts of alloying elements are not limited by solid solubility, leading to supersaturation of the alloying elements in the near surface. This process induces dramatic changes in the surface properties compared to conventional alloying processes. Metal PIII of Al, Ti, Zr, Ag and Ta have been studied.

Aluminum is an important alloying element in magnesium alloys. The incorporation of Al not only enhances the mechanical properties, but poses great influence on the corrosion resistance. It is generally accepted that a higher content of Al will lead to better corrosion resistance. However, the sensitivity of stress corrosion increases with higher Al contents. Variations in the surface properties after Al implantation have been reported (Liu, 2007a; Lei, 2007). The Al content in the surface increases to about 30% after Al PIII, as shown in Fig. 11.25. The penetration depth of Al exceeds 100 nm. A high resolution Al 2p XPS spectrum (Fig. 11.25b) reveals that at depths below about 40 nm, Al is mainly in the form of Al_2O_3 and at depths between 40 and 60 nm, aluminum oxide and metallic Al co-exist. At depths over 60 nm, only metallic Al is present. Generally, PIII is not conducted at ultra-high vacuum, and residual oxygen is implanted into the substrate at the same time. Formation of the aluminum oxide should be related to the incorporation of Al and implanted O. The corrosion resistance of Al-implanted AZ91 magnesium alloys has been evaluated by electrochemical impedance spectroscopy (EIS). The total impedance value of the Al-implanted sample, is about ten times higher than that of the untreated sample as shown in Fig. 11.26. The dramatically improved corrosion resistance is considered to result from the formation of a large amount of Al_2O_3 . Al implantation can also



11.25 XPS depth profile and Al fine scanning spectra obtained from AZ91 magnesium alloys subjected Al PIII at bias voltage 10 kV for 4 h: sputtering rate ~ 20 nm/min referenced to SiO_2 (Liu, 2007b).

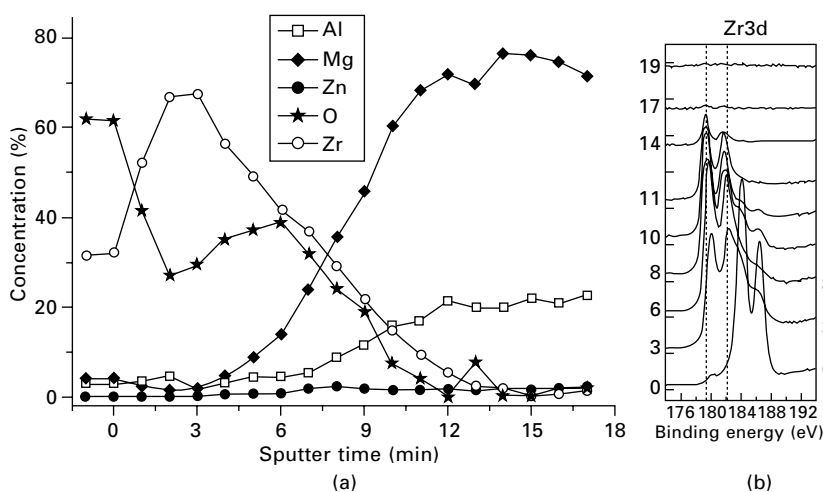


11.26 Electrochemical impedance spectra (EIS) of AZ91 magnesium alloy subjected Al, Ti and Zr PIII in SBF: Al-PIII&D, Al PIII at 10 kV for 4 h; Ti-PIII&D, Ti PIII at 10 kV for 4 h; Zr-PIII&D, Zr PIII at 10 kV for 4 h (Liu, 2007b).

enhance the wear resistance of magnesium alloy (Lei, 2007). Conventional ion beam implantation of Al via MEVVA (dose 2×10^{16} ions/cm²) can reduce the wear rate by 30–40% compared to the untreated alloy. However, no such investigation upon Al PIII has been attempted, to our knowledge.

Zr is also an important alloying element in magnesium alloys. Addition of Zr not only enhances the strength of magnesium alloys but also yields higher corrosion resistance. Liu *et al.* (2007a) have investigated the effects of Zr PIII on the corrosion resistance of AZ91 magnesium alloys. Similarly to Al PIII, Zr PIII produces a thick modified layer about 100 nm thick, as shown in Fig. 11.27. High resolution spectra also reveal the formation of ZrO₂ at the near surface. Enhanced corrosion resistance is observed in the EIS measurement, as shown in Fig. 11.26. As Ti is a biologically friendly element, Liu has also tried to conduct Ti PIII on AZ31 magnesium alloy, to suppress the fast degradation rates in a physiological environment (Liu, 2007b). An electrochemical test in SBF also disclosed improved corrosion resistance to some extent, but it was not as effective as with Al PIII. In the depth profiles of a PIII-treated sample, it is noted that Al PIII and Zr PIII of AZ91 magnesium alloy both lead to much smaller contents of Mg in the modifier layers. Reduction in the active magnesium is also responsible for the improved corrosion resistance.

It can be concluded that metal implantation into magnesium alloys is effective to improve both the corrosion resistance and surface mechanical properties. Improvement in the corrosion resistance is often related to the formation of a corrosion resistant metal oxide and the dramatically reduced Mg content in the top surface layer.

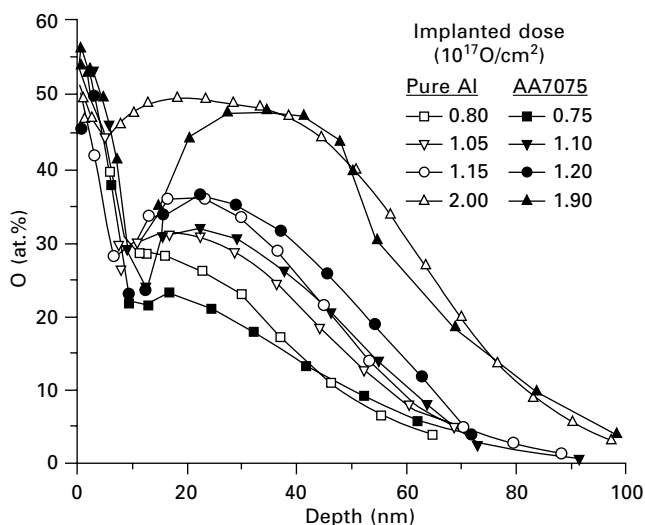


11.27 XPS depth profile and high resolution spectra of Zr 3d spectra of AZ91 magnesium alloy subject Zr PIII at a bias voltage 10 kV for 4 h: Sputtering rate 5.6 nm/min referenced to SiO₂ (Liu, 2007b).

11.5 PIII surface modification of aluminum (Al) alloys

Al alloys have high strength-to-weight ratio and good formability, and have many applications in the aviation, space, as well as in automobile industries (Maddox, 2003; Wang, 1995). The corrosion resistance of Al-based alloys is generally considered to be good due to the native aluminum oxide surface layer. However, many of their applications are limited by the poor surface mechanical properties, such as low hardness and low wear resistance (see Chapter 1). Therefore, surface modification is conducted to enhance the surface mechanical properties. The most popular surface treatments are nitriding and PEO. Studies on PIII treatment of Al alloys are less common.

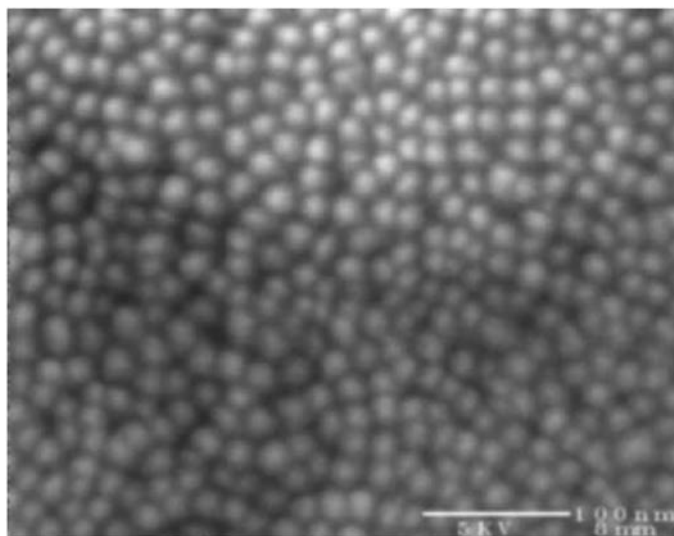
Al_2O_3 has good tribological properties such as high hardness and wear resistance and a low friction coefficient. However, the naturally formed alumina layer on Al alloys is only several nanometers in thickness. Oxygen PIII has been carried out to fabricate a thicker aluminum oxide layer (Bolduc, 2003). The tribological properties of oxygen PIII-treated pure aluminum and alloyed aluminum (AA7075) are optimized by controlling the implantation dose. As shown in Fig. 11.28, the penetration depths of O at the bias voltage are around 90 nm, independent of implantation dose. The higher implantation dose results in increased O content across the modifier layer. It is noted that the depth profiles of O in the pure aluminum and AA7075 alloys are also similar for the same implantation dose. Evolution of the implantation dose may be observed up to near the saturation dose of $2.0 \times 10^{17} \text{ O/cm}^2$



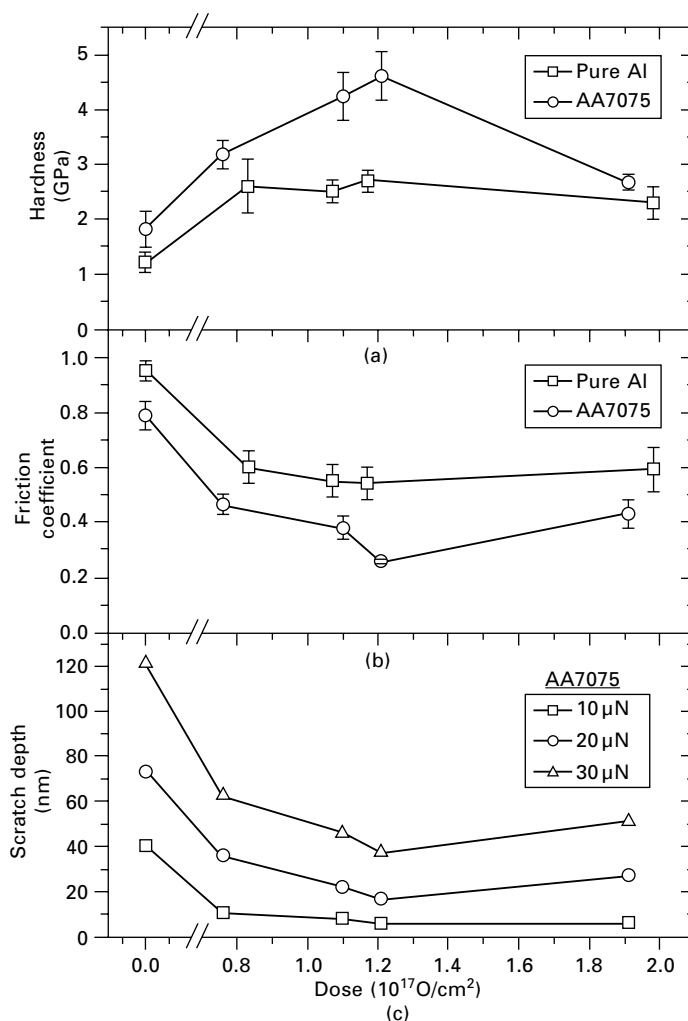
11.28 XPS depth profile of O pure Al and AA7075 subjected to oxygen PIII at low temperature with various doses (Bolduc, 2003).

(triangles), which almost corresponds to stoichiometric Al_2O_3 . SEM views of pure Al after oxygen PIII at the saturation dose are displayed in Fig. 11.29. Many nano-scale Al_2O_3 balls, about 20 nm in diameter, cover the whole surface. Oxygen PIII results in great changes in the surface mechanical properties, depending on the implantation dose. Changes in the surface mechanical properties of the two substrates as a function of implantation doses are demonstrated in Fig. 11.30. The highest hardness (about twice that of the untreated one) of treated AA7075 alloy occurs at a dose of 1.2×10^{17} O/cm^2 , corresponding to 70–80% oxide. When the implantation dose increases to the saturation dose, the hardness dramatically drops, but it is still higher than that of the untreated. For pure Al, the hardness is independent of the implantation dose and is about twice that of the untreated one. The friction coefficients of both the pure Al and AA7075 alloy are about half of that of the untreated sample, and both are independent of implantation doses. The scratch depths observed from the oxygen PIII AA7075 alloy are reduced greatly at all loads, 30 μN , 20 μN , 10 μN .

Diamond-like carbon films (DLC) possess many unique properties, such as ultra-high hardness and low friction coefficient, and are desirable as coating materials (Hainsworth, 2007; Robertson, 2002). PIII&D is an attractive process to prepare adhesive DLC coatings on various substrates in order to impart their unique properties (Ensinger, 2006). Pre-implantation can generate a gradient layer that can release the stress resulting from the serious mismatch of mechanical properties between the DLC and substrate. High-voltage

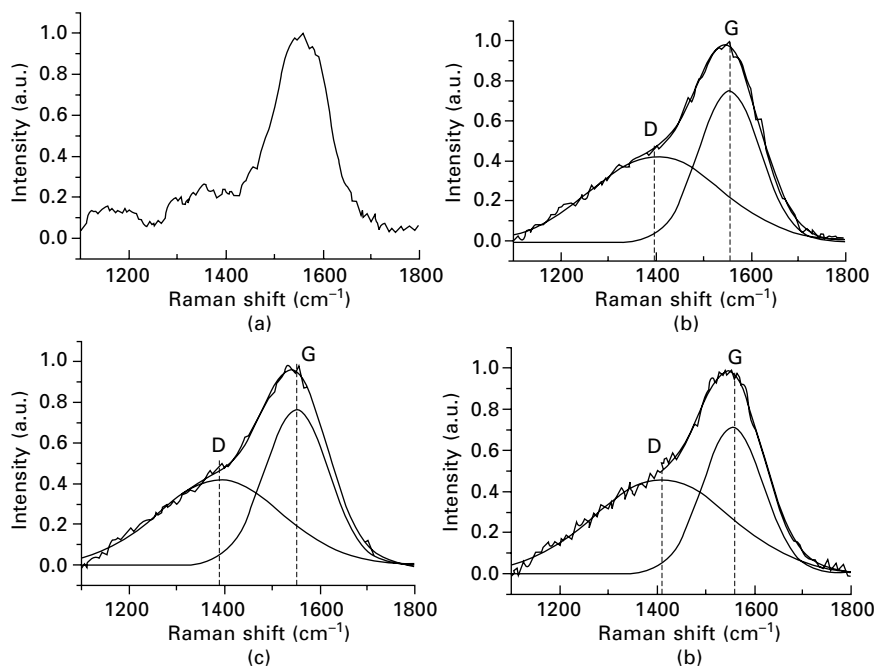


11.29 SEM view of pure Al after oxygen implantation at a saturation dose 2×10^{17} O/cm^2 (Bolduc, 2003).



11.30 Surface mechanical properties of pure Al and A7075 alloy subjected to implantation at a bias voltage 30 kV with various doses: Implantation is denoted as implantation dose (Bolduc, 2003).

implantation between deposition cycles also benefits the growth of a compact and adhesive DLC coating. DLC coating has been successfully fabricated on pure aluminum via PIII&D (Xu, 2006) and the structural changes with processing parameters have been systematically investigated. The Raman spectra as a function of implantation voltage are shown in Fig. 11.31. The Raman spectrum of DLC is different from that of diamond C at 1332 cm^{-1} and that of single crystalline graphitic C at 1580 cm^{-1} (Liao, 2004a). The spectra can be deconvoluted into two bands identified as G and D, centered



11.31 Raman spectra of the carbon films prepared for 3 h on Al as a function of implantation voltage: (a) 5 kV; (b) 10 kV; (c) 30 kV; (d) 50 kV (Liao, 2004b).

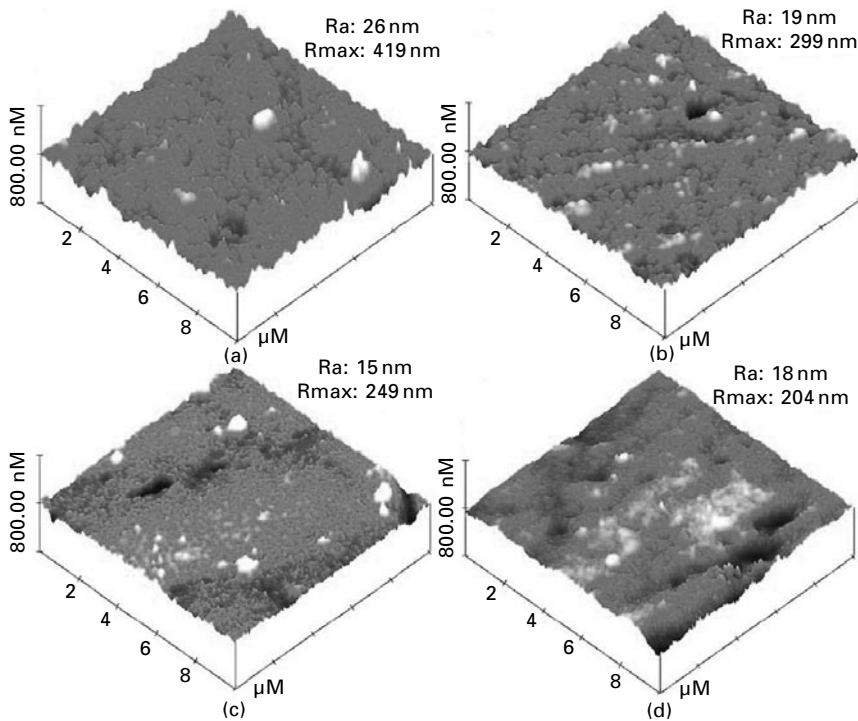
at about 1545 and 1362 cm^{-1} . The ratio of the G to D intensities (denoted as the integral area under the D and G bands) I_D/I_G is roughly proportional to the ratio of sp^2/sp^3 bonds. The ratio of sp^2/sp^3 (I_D/I_G) is one of the most important factors governing the quality of the DLC films. Generally, the lower the ratio, the closer the properties of the DLC films are to those of diamond. The spectrum of the sample produced at a bias voltage of 5 kV shows a broad and symmetrical band centered at 1560 cm^{-1} , which differs from that of DLC films, and it corresponds to polymer-like carbon. The spectra at 10, 30 and 50 kV are all typical DLC films. It is obvious that in the range of 5–10 kV, there is an important voltage threshold value for the formation of the DLC film. The three DLC films are also different with each other according to the deconvoluted spectra. As the voltage increases from 10 to 50 kV, I_D/I_G shifts from 1.06 to 0.93 and then to 1.55. These changes correspond to the change of the ratio of sp^2/sp^3 resulting from the different ion bombardment energy. Below 30 kV, increased ion bombardment induces disorder in the C structure leading to increment of the sp^3 bonds. However, when the ion energy is too high, the ions may damage the sp^3 bonds. Therefore, there is an optimal energy favoring sp^3 formation.

The morphologies and roughness of the DLC fabricated at different

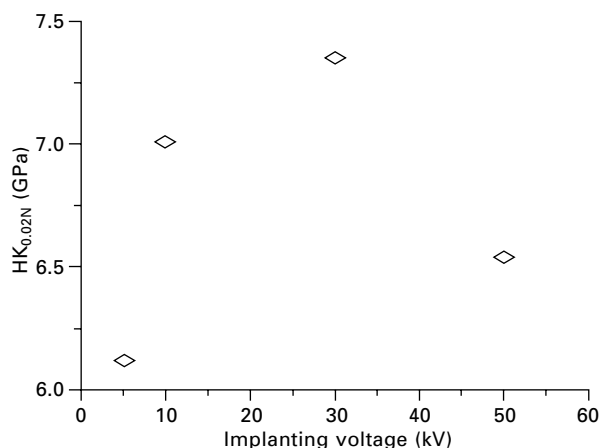
voltages also differ from each other (see Fig. 11.32). As the voltage increases, the morphologies become smoother and more compact. The changes in the morphology and roughness are related to the different ion bombardment effects at different energies. The hardness values of the fabricated DLC films are demonstrated in Fig. 11.33. These changes in the hardness is consistent with the change in I_D/I_G at different implantation voltages. The higher content of sp^3 results in higher hardness.

PIII has also been used as a pre-treatment process to generate a gradient layer for subsequent deposition of the coating (Knight, 1989; Liao, 2004b). C PIII and N PIII have been used to fabricate a gradient layer for subsequent deposition of DLC and TiN, respectively. This PIII pre-treatment process is found effective for enhancing the load-bearing capacity and bonding strength of the deposited coating.

Studies on PIII surface modification of Al have not been extensive. This PIII process is more often used as a pre-treatment process or is combined with other techniques in deposition and nitriding. The development of effective hybrid treatments is promising for future studies and applications.



11.32 AFM morphologies and roughness of carbon films fabricated on Al substrate as a function of implantation voltage: (a) 5 kV; (b) 10 kV; (c) 30 kV; (d) 50 kV (Liao, 2004b).



11.33 Surface hardness of carbon films on Al as a function of implantation voltage (Liao, 2004b).

11.6 Future trends

PIII is an important surface modification technique for the surface treatment of light alloys. The main advantage is its non-line-of-sight nature as compared to beamline ion beam implantation, allowing treatment of samples with complex geometries. In addition, the modified layers possess good bonding strength with the substrate, as there is no distinct interface between the modified layer and substrate. Ion penetration is usually very shallow, typically ranging from tens of nm to more than 100 nm, depending on the nature of the substrate, implantation voltage, and substrate temperature. Processing parameters such as the implantation dose, implantation voltage, frequency, pulsing duration, and substrate temperature all affect the treatment.

For Ti alloys, PIII can enhance the corrosion resistance and surface mechanical properties. However, the modified layer is usually too thin to satisfy the stringent requirements imposed by industry. PIII of biomedical Ti alloys to improve the biological performance, such as bioactivity and biocompatibility, is effective and promising. As the interactions between tissues and implants proceed at the interface, the functions of the generated functional layers are not limited by the thickness of the modified layers. Magnesium alloys are too active chemically, and the thin modified layer usually cannot provide satisfactory protection to the substrate. Therefore, in practical applications, PIII is not a good choice. In surface modification of Al alloys, hybrid treatments combining PIII and other techniques, such as deposition and nitriding, are promising applications. The choice of proper PIII techniques should consider the alloys and optimization of processing parameters such as the implantation dose, voltage, frequency, and pulsing duration, in order to achieve the best effects.

Development of PIII as an effective surface modification technique for light alloys in the future may fall in two categories, namely fabrication of a functional modified layer and development of hybrid PIII processes. The high energy of the implanted species benefits generation of various functional layers with unique properties, as well as good adhesion with the substrate. On the other hand, the development of PIII-based hybrid processes can generate much thicker modified layers with dramatically enhanced surface properties. Development of more effective PIII-based hybrid processes will lead to wider applications in surface modification of light alloys.

11.7 Sources of further information and advice

- P. K. Chu, 'Improvement of Surface and Biological Properties of Biomaterials Using Plasma-based Technology', in *Trends in Biomaterials Research* (ISBN 1-1-60021-361-8), P. J. Pannone (Ed.), Nova Science Publishers, Inc., New York, Chapter 2, pp. 81–108 (2007).
- L. R. Shen and P. K. Chu, 'Improvement of Corrosion Resistance by Plasma Surface Modification', in *Trends in Corrosion Research*, Vol. 3 (ISSN: 0972-4826), Marcel Dekker, India, pp. 41–57 (2004).
- P. K. Chu and X. B. Tian, 'Plasma-based Surface Modification', in *Surface Modification and Mechanisms: Friction, Stress, and Reaction Engineering* (ISBN 0-8247-4872-7), G. E. Totten and H. Liang (Eds.), Marcel Dekker, New York, Chapter 15, pp. 543–601 (2004).
- J. Matossian, G. Collins, P. K. Chu, C. Munson and J. Mantese, 'Design of a PIII&D Processing Chamber', in *Handbook of Plasma Immersion Ion Implantation and Deposition* (ISBN 0-471-24698-0), A. Anders (Ed.), John Wiley & Sons, New York, Chapter 6, pp. 343–379 (2000).
- P. K. Chu, S. Qin, C. Chan, N. W. Chung and L. A. Larson, Plasma immersion ion implantation – a fledgling technique for semiconductor processing. *Mater. Sci. Eng. R-Rep* 1996; 17: 207–280.
- M. A. Lieberman, A. G. Lichtenberg, *Principle of Plasma Discharges and Materials Processing*. Wiley, New York (1994).

11.8 References

- Bakkar A and Neubert V (2005), 'Improving corrosion resistance of magnesium-based alloys by surface modification with hydrogen by electrochemical ion reduction (EIR) and by plasma immersion ion implantation (PIII)', *Corrosion Sci.* 47, 1211–1225.
- Bilek MMM, Evans P, McKenzie DR, McCulloch DG, Zreiqat H and Howlett CR (2000), 'Metal ion implantation using a filtered cathodic vacuum arc', *J. Appl. Phys.* 87, 4198–4204
- Bolduc M, Terreault B, Reguer A, Shaffer E and St-Jacques RG (2003), 'Selective modification of the tribological properties of aluminum through temperature and dose control in oxygen plasma source ion implantation', *J. Mater. Res.* 18, 2779–2792

- Chu PK, Qin S, Chan C, Chung NW and Larson LA (1996), 'Plasma immersion ion implantation – a fledgling technique for semiconductor processing', *Mater. Sci. Eng. R* 17, 207–280
- Conrad JR, Radtke JL, Dodd RA, Worzata FJ and Tran NC (1987), 'Plasma source ion-implantation technique for surface modification of metals' *J. Appl. Phys.* 62, 4591–4596
- da Silva LLG, Ueda M, Silva MM and Codaro EN (2007), 'Corrosion behavior of Ti-6Al-4V alloy treated by plasma immersion ion implantation process' *Surf. Coat. Technol.* 201, 8136–8139
- Ehlers KW and Leung KN (1979), 'Some characteristics of tungsten filaments operated as cathodes in a gas-discharge', *Rev. Sci. Instrum.* 50, 356–361
- Ensinger W (2006), 'Formation of diamond-like carbon films by plasma-based ion implantation and their characterization', *New Diam. Front. Carbon Technol.* 16, 1–32
- Fukumoto S, Yamamoto A, Terasawa M, Mitamura T and Tsubakino H (2001), 'Microstructures and corrosion resistance of magnesium implanted with nitrogen ions', *Mater. Trans.* 42, 1232–1236
- Hainsworth SV and Uhure NJ (2007), 'Diamond like carbon coatings for tribology: Production techniques, characterisation methods and applications', *Int. Mater. Rev.* 52, 153–174
- Han SH, Kim HD, Lee Y, Lee J and Kim SG (1996), 'Plasma source ion implantation of nitrogen, carbon and oxygen into Ti-6Al-4V alloy', *Surf. Coat. Technol.* 82, 270–276
- Hort N, Huang YD and Kainer KU (2006), 'Intermetallics in magnesium alloys', *Adv. Eng. Mater.* 8, 235–240
- Jackson M and Dring K (2006), 'Materials perspective – A review of advances in processing and metallurgy of titanium alloys', *Mater. Sci. Technol.* 22, 881–887
- Kaufmann H and Uggowitzer PJ (2001), 'Fundamentals of the new rheocasting process for magnesium alloys', *Adv. Eng. Mater.* 3, 963–967
- Knight DS and White WB (1989), 'Characterization of diamond films by Raman-spectroscopy', *J. Mater. Res.* 4, 385–393
- Kokubo T, Kim HM and Kawashita M (2003), 'Novel bioactive materials with different mechanical properties', *Biomaterials* 24, 2161–2175
- Kostov KG, Ueda M, Lepiensky A, Soares PC, Gomes GF, Silva MM and Reuther H (2004), 'Surface modification of metal alloys by plasma immersion ion implantation and subsequent plasma nitriding', *Surf. Coat. Technol.* 186, 204–208
- Lacoste A, Bechu S, Arnal Y, Pelletier J, Vallee C, Gouttebaron R and Stoquert JP (2002), 'Nitrogen profiles in materials implanted via plasma-based ion implantation', *Surf. Coat. Technol.* 156, 125–130
- Lafferty JM, ed. (1980), *Vacuum Arcs – Theory and Application*. Wiley, New York
- Lei MK, Li P, Yang HG and Zhu XM (2007), 'Wear and corrosion resistance of Al ion implanted AZ31 magnesium alloy', *Surf. Coat. Technol.* 201, 5182–5185
- Li LH, Poon RWY, Kwok SCH, Chu RK, Wu YQ and Zhang YH (2003), 'Hybrid evaporation: Glow discharge source for plasma immersion ion implantation', *Rev. Sci. Instrum.* 74, 4301–4304
- Liao JX, Xia LF, Sun MR, Liu WM, Xa T and Xue QJ (2004a), 'The structure and tribological properties of gradient layers prepared by plasma-based ion implantation on 2024 Al alloy', *J. Phys. D – Appl. Phys.* 37, 392–399
- Liao J, Liu WM, Xu T and Xue QJ (2004b), 'Characteristics of carbon films prepared by plasma-based ion implantation', *Carbon* 42, 387–393

- Lieberman MA and Lichtenberg AG (1994), *Principle of Plasma Discharges and Materials Processing*, New York, Wiley
- Liu CL, Xin YC, Tian XB and Chu PK (2007a), 'Corrosion behavior of AZ91 magnesium alloy treated by plasma immersion ion implantation and deposition in artificial physiological fluids', *Thin Solid Films* 516, 422–427
- Liu CG, Xin YC, Tian XB, Zhao J and Chu PK (2007b), 'Corrosion resistance of titanium ion implanted AZ91 magnesium alloy', *J. Vac. Sci. Technol. A* 25, 334–339
- Liu XY, Chu PK and Ding CX (2004a), 'Surface modification of titanium, titanium alloys, and related materials for biomedical applications', *Mater. Sci. Eng. R* 47, 49–121
- Liu XY, Poon RWY, Kwok SCH, Chu PK and Ding CX (2004b), 'Plasma surface modification of titanium for hard tissue replacement', *Surf. Coat. Technol.* 186, 227–233
- Liu XY, Poon RWY, Kwok SCH, Chu PK and Ding CX (2005), 'Structure and properties of Ca-plasma-implanted titanium', *Surf. Coat. Technol.* 191, 43–48
- Loinaz A, Rinner M, Alonso F, Onate JI and Ensinger W (1998), 'Effects of plasma immersion ion implantation of oxygen on mechanical properties and microstructure of Ti6Al4V', *Surf. Coat. Technol.* 104, 262–267
- Long M and Rack HJ (1998), 'Titanium alloys in total joint replacement – a materials science perspective', *Biomaterials* 19, 1621–1639
- Maddox SJ (2003), 'Review of fatigue assessment procedures for welded aluminium structures', *Int. J. Fatigue* 25, 1359–1378
- Maitz MF, Poon RWY, Liu XY, Pham MT and Chu PK (2005), 'Bioactivity of titanium following sodium plasma immersion ion implantation and deposition', *Biomaterials* 26, 5465–5473
- Mandl S (2007), 'PIII treatment of Ti alloys and NiTi for medical applications', *Surf. Coat. Technol.* 201, 6833–6838
- Miyake S, Setsuhara Y, Sakawa Y and Shoji T (2000), 'Development of high-density RF plasma and application to PVD' *Surf. Coat. Technol.* 131, 171–176
- Naka S (1996), 'Advanced titanium-based alloys', *Curr. Opin. Solid State Mat. Sci.* 1, 333–339
- Niinomi M (2008), 'Biologically and mechanically biocompatible titanium alloys', *Mater. Trans.* 49, 2170–2178
- Pohrelyuk IM, Fedirko VM and Kravchyshyn TM (2007) 'Influence of the parameters of nitriding on the subsurface hardening of TV6 titanium alloy', *Mater. Sci.* 43, 807–813
- Poon RWY, Yeung KWK, Liu XY, Chu PK, Chung CY, Lu WW, Cheung KMC and Chan D (2005), 'Carbon plasma immersion ion implantation of nickel–titanium shape memory alloys', *Biomaterials* 26, 2265–2272
- Powles RC, McKenzie DR, Meure SJ, Swain MV and James NL (2007), 'Nanoindentation response of PEEK modified by mesh-assisted plasma immersion ion implantation', *Surf. Coat. Technol.* 201, 7961–7969
- Robertson J (2002), 'Diamond-like amorphous carbon', *Mater. Sci. Eng. R* 37, 129–281
- Schulke T, Anders A and Siemorth P (1997), 'Macroparticle filtering of high-current vacuum arc plasmas', *IEEE Trans. Plasma Sci.* 25, 660–664
- Sha W, Ali AMFP and Wu XM (2008), 'Gas nitriding of titanium alloy Timetal 205', *Surf. Coat. Technol.* 202, 5832–5837
- Song GL and Andrej Atrons (2003), 'Understanding magnesium corrosion – A framework for improved alloy performance', *Adv Eng Mater.* 5, 837–858

- Staiger MP, Pietak AM, Huadmai J and Dias G (2006), 'Magnesium and its alloys as orthopedic biomaterials: A review', *Biomaterials* 27, 1728–1734
- Tendys J, Donnelly IJ, Kenny MJ and Pollock JTA (1988), 'Plasma immersion ion-implantation using plasmas generated by radio-frequency techniques', *Appl. Phys. Lett.* 53, 2143–2145
- Tian XB and Chu PK (2001a), 'Target temperature simulation during fast-pulsing plasma immersion ion implantation', *J. Phys. D-Appl. Phys.* 34, 354–359
- Tian XB, Chu PK and Yang SQ (2004), 'Hybrid process based on the plasma immersion ion implantation: A brief review', *Surf. Coat. Technol.* 186, 190–195
- Tian XB, Wei CB, Yang SQ, Fu RKY and Chu PK (2006), 'Water plasma implantation/oxidation of magnesium alloys for corrosion resistance'. *Nucl. Instrum. Methods Phys. Res. Sect. B* 242, 300–302
- Tian XB, Zeng ZM, Zhang T, Tang BY and Chu PK (2000a), 'Medium-temperature plasma immersion-ion implantation of austenitic stainless steel', *Thin Solid Films* 366, 150–154.
- Tian XB, Zeng ZM, Tang BY, Kyok TK and Chu PK (2000b), 'Fast pulsing plasma immersion ion implantation for tribological applications', *Surf. Coat. Technol.* 128, 226–230
- Tian XB, Zhang T, Zeng ZM, Tang BY and Chu PK (1999), 'Dynamic mixing deposition/implantation in a plasma immersion configuration', *J. Vac. Sci. Technol. A.* 17, 3255–3259
- Tian XB, Wang LP, Zhan QY and Chu PK (2001b), 'Dynamic nitrogen and titanium plasma ion implantation/deposition at different bias voltages', *Thin Solid Films* 390, 139–144.
- Tian XB, Wei CB, Yang SQ, Fu RKY and Chu PK (2005), 'Corrosion resistance improvement of magnesium alloy using nitrogen plasma ion implantation', *Surf. Coat. Technol.* 198, 454–458
- Ueda M, Silva MM, Otani C, Reuther H, Yatsuzuka M, Lepienski CM and Berni LA (2003), 'Improvement of tribological properties of Ti6Al4V by nitrogen plasma immersion ion implantation', *Surf. Coat. Technol.* 169, 408–410
- Wan GJ, Maltz MF, Sun H, Li PP and Huang N (2007), 'Corrosion properties of oxygen plasma immersion ion implantation treated magnesium', *Surf. Coat. Technol.* 201, 8267–8272.
- Wang L, Makhlof M and Apelian D (1995), 'Aluminium die casting alloys: Alloy composition, microstructure, and properties–performance relationships', *Int. Mater. Rev.* 40, 221–238
- Xie YT, Liu XY, Huang AP, Ding CX and Chu PK (2005), 'Improvement of surface bioactivity on titanium by water and hydrogen plasma immersion ion implantation', *Biomaterials* 26, 6129–6135
- Xin YC, Liu CL, Zhang WJ, Jiang J, Guoyi TY, Tian XB and Chu PK (2008), 'Electrochemical behavior $\text{Al}_2\text{O}_3/\text{Al}$ coated surgical AZ91 magnesium alloy in simulated body fluids', *J. Electrochem. Soc.* 155, C178–C182
- Xu M, Li LH, Cai X, Liu YM, Chen QL and Chu PK (2006), 'Improvement of adhesion strength of amorphous carbon films on tungsten ion implanted 321 stainless steel substrate', *Diam. Relat. Mat.* 15, 952–957
- Zhang W, Chu PK, Ji JH, Zhang YH, Liu XY, Fu RKY, Ha PCT and Yan Q (2006), 'Plasma surface modification of poly vinyl chloride for improvement of antibacterial properties', *Biomaterials* 27, 44–51
- Zhang W, Zhang YH, Ji JH, Yan Q, Huang AP and Chu PK (2007a), 'Antimicrobial

polyethylene with controlled copper release', *J. Biomed. Mater. Res. Part A* 83A, 838–844

Zhang XP, Zhao ZP, Wu FM, Wang YL and Wu J (2007b), 'Corrosion and wear resistance of AZ91D magnesium alloy with and without microarc oxidation coating in Hank's solution', *J. Mater. Sci.* 42, 8523–8528

Zhecheva A, Malinov S and Sha W (2006), 'Titanium alloys after surface gas nitriding', *Surf. Coat. Technol.* 201, 2467–2474

Abstract: The laser surface engineering of titanium alloys has been developed over the past thirty years to produce a modified layer up to 1mm in depth, thicker than alternative techniques. Continuous wave CO₂ lasers have been the main lasers used for both surface cladding and alloying. Much of the early work was based on laser nitriding forming titanium nitrides throughout the molten pool. Subsequent alloying developments have included the incorporation of carbides, nitrides, oxides and silicides; and also intermetallics and rare earths, added as powders. Laser processing can now tailor surfaces with superior tribological and erosion resistant properties, compared with the untreated titanium alloys.

Key words: laser melting, cladding, alloying, microstructure, tribological properties.

12.1 Introduction

12.1.1 Why use titanium alloys?

Titanium alloys have been developed widely as commercial alloys for over 60 years, fulfilling the requirement for materials with high strength-to-weight ratios at elevated temperatures, initially used in the aerospace and defence industries. Over 80% of titanium alloys are used in these industries, mostly in the wrought form, but many other applications are restricted due to their poor tribological and oxidation properties, and high relative cost, which is about five times that of steels and aluminium alloys.

Titanium and its alloys have excellent corrosion resistance in rainwater and sea water environments, through the formation of protective oxide films. These films have been recognized and utilized by the chemical industry and also have led to applications in dentistry and by the medical profession in prostheses for implanting in the human body. Titanium has a high melting point, 1678°C, which indicates that the alloys will show good creep resistance over a significant range of temperatures.

12.1.2 The need for surface engineering

While titanium alloys also possess good fatigue resistance, they have a high coefficient of friction (μ) in the region of 0.6, both against each other, against other alloys, and against non-metallic materials such as polymers, which means that they suffer from low resistance to wear. The poor tribological

properties are normally associated with the transfer of titanium to the mating surfaces, resulting in severe adhesive wear. In some cases, the situation can be alleviated through the application of lubricants, for example when titanium alloys are in contact with polymers. The improvement in wear resistance due to lubricants, in general, decreases with temperature. For this reason, surface modifications of titanium alloys have been used to increase the near-surface strength, reducing the coefficient of friction and lowering the tendency for material transfer and adhesive wear (Heyman, 1992). In addition to aerospace applications, the attractive high temperature properties of titanium alloys have been extended to land-based turbines. This has been particularly the case in Japan (Yamada, 1996). The density advantage of titanium alloys over such steels as Cr-Mo-V and 12%Cr has led to their use in the low-pressure end of steam turbines. Under operating conditions, liquid impingement erosion is a well-recognized damage mechanism associated with moving blades (Robinson and Reed, 1995). The loss of material that occurs from the leading edges of the blades is a result of cumulative damage from the impact of water droplets formed by the condensation of steam in the later stages of the steam turbine. The impact of each droplet generates, very briefly, a high local force. The pressure forces are generally normal to the direction of impact, whereas forces due to splashing or jetting, as the droplet disperses, are tangential to the impacted surface. These two sets of forces produce characteristic pitting or tunnelling damage to the surface (Hu *et al.*, 1997). Therefore, protection of the blade surfaces is essential if they are to function effectively and within acceptable commercial economic limits. The use of laser surface engineering to develop this protection, by creating surface coatings on titanium alloys, has some advantages over alternative coating techniques (Zhecheva *et al.*, 2005). These include a precise control over the width and depth of surface modification, and the ability, through computer-controlled work tables, to process complex shapes and target specific areas of a component. Laser surface processing methods have been reviewed by Tian *et al.* (2005) who included a brief, but useful description of biomedical applications, not covered in the present chapter (which concentrates on more extensive consideration of what are, in effect, functionally gradient layers for structural engineering applications).

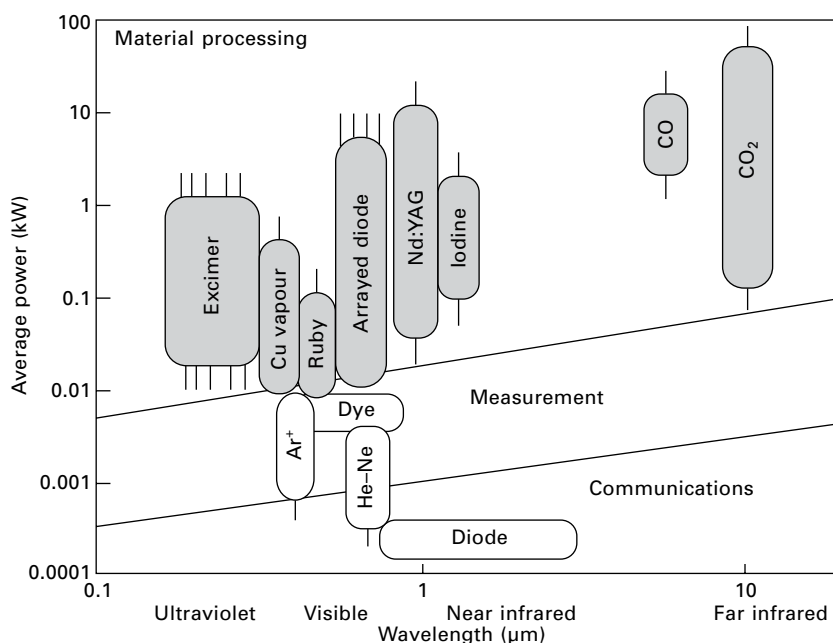
12.2 Lasers used in surface engineering

With the need to improve the surface properties of titanium alloys, such as the tribological, high-temperature and corrosion aspects, the normal approach has been to modify the surface to one with a higher hardness and/or a lower coefficient of friction than the substrate, while retaining the attractive properties of the bulk material of the alloy. Lasers are one of many tools that have been used to modify the surface of alloys. They involve light

amplification by stimulated emission of radiation, which gives rise to the acronym *laser*. The different types of laser are grouped according to the active medium (gas, liquid or solid), wavelength, power, energy and mode of operation (continuous or pulsed). These are shown in Fig. 12.1, by Ion (2005), characterized by plotting the average power versus the wavelength, and vary from excimer, Nd:YAG, diode, through to CO₂ lasers, the last being the main tool used in most of the work reported in the literature on surface alloying. Ion (2005) attributes the popularity of CO₂ lasers to their 'efficient use of gases, which reduces running costs, that the pulsed or continuous wave emission is produced in a high quality beam at superkilowatt power levels, and that far-infrared light is transmitted readily in air, being absorbed by a wide range of engineering materials'. However, he also expects there to be a growth in the use of multikilowatt diode-pumped solid state (DPSS) lasers, which offer compactness, high power efficiency and high beam quality. Information on the physics associated with lasers and their construction is to be found in Duley (1983) and Ion (2005).

12.3 Laser surface modification methods

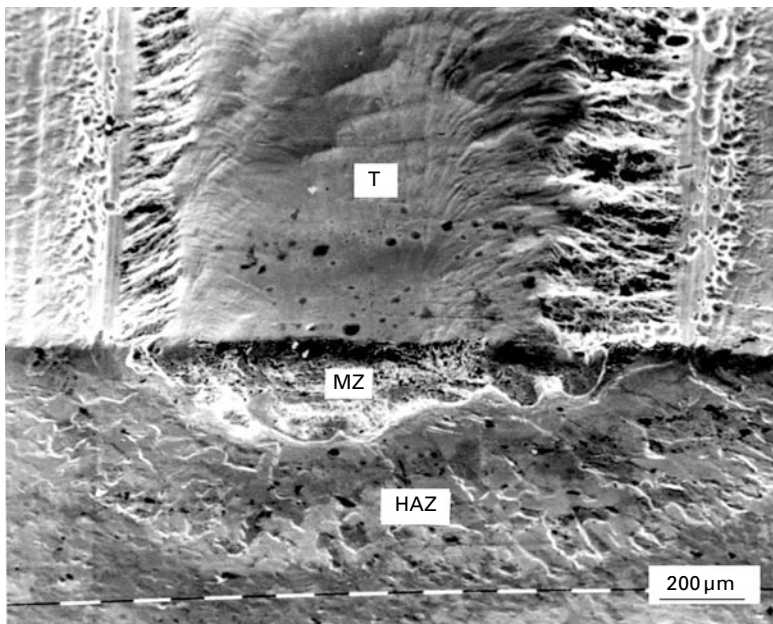
The simplest application of laser processing, laser heating, involves the rapid heating of the surface layers to a temperature well below the melting



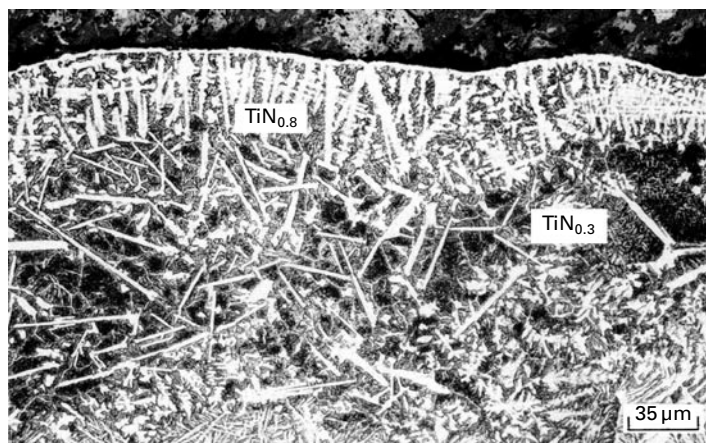
12.1 A selection of commercial lasers characterized by wavelength and average power shown on a background of applications (Ion, 2005).

point, followed by rapid cooling. While this technique is widely applied to steels, where it results in transformation hardening due to the development of martensite, in laser-processed titanium alloys, the martensitic phase transformation has no significant effect on the hardness. However, the technique has been reported to increase the fatigue life of Ti-6Al-4V alloy due to both a reduced fraction of α -Ti and to a reduction in the grain size (Konstantino and Altus, 1999).

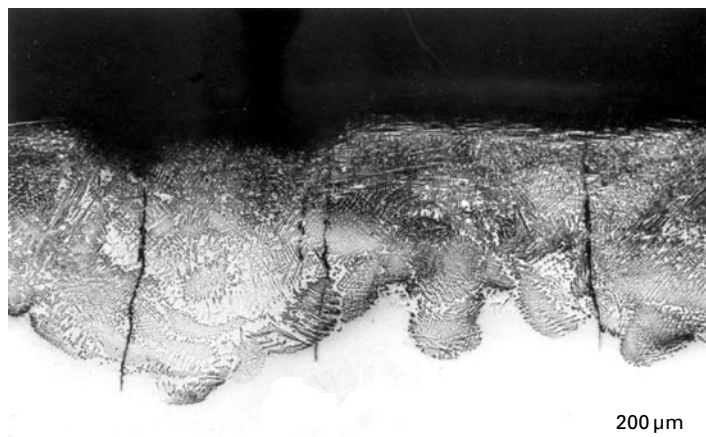
Laser processing, using around three times the beam energy used in laser heating, can develop a deeper melt pool than other surface modification techniques (Fig. 12.2) (Gates, 1986; Deng and Braun, 1994; Zhecheva *et al.*, 2005), and a rapidly solidified melt pool, with a >1000 HV surface zone, followed by a zone of a hardness gradually decreasing to that of the titanium substrate, 325–350 HV. This modified microstructure has been described as a functional gradient layer, Fig. 12.3. Many applications result in the removal of the surface during service. Therefore, the thicker the modified layer, the longer the in-service life of the component. However, defects may be introduced during the surface modification process. These include cracks, Fig. 12.4, and porosity in the surface layer, and in the case of the incorporation of particles, undissolved particles and heterogeneous particle distribution, which may result in an early deterioration of the surface properties.



12.2 Macrograph showing the top (T), melt zone (MZ) and heat affected zone (HAZ) following laser melting (Mridha and Baker, 1991).



12.3 Micrograph showing functionally gradient layer followed by laser nitriding of titanium.



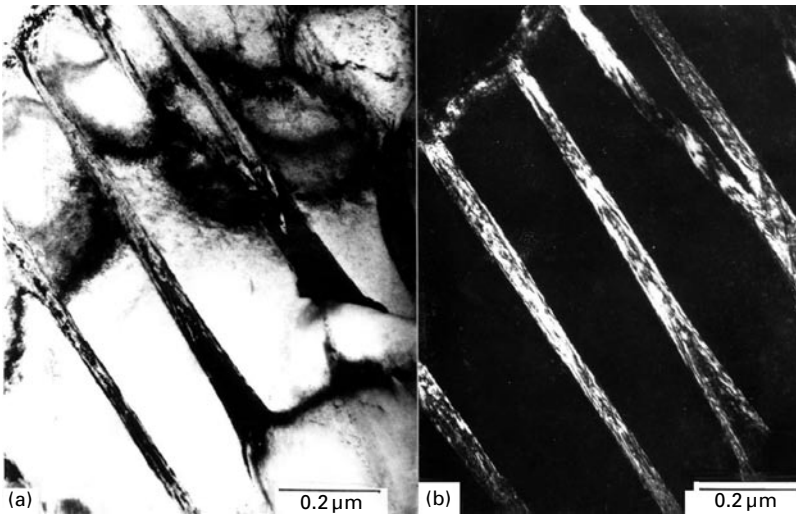
12.4 Laser induced cracks through the entire depth of the melt pool arrested at the HAZ (Mridha and Baker, 1991).

Several laser surface modification methods have been developed and include:

- (i) surface alloying using an element which is well distributed throughout the Ti matrix, such as Al in low concentrations, to provide solid solution hardening, resulting in improved surface properties. Secondly, alloying with a solute element which will form a compound with a higher hardness than the titanium alloy. This situation occurs following alloying with higher concentrations of Al, forming TiAl, and with Si, which forms Ti_5Si_3 , either as needles, or together with α Ti as a eutectic, Figures 12.5 and 12.6 (Hu *et al.*, 1998),



12.5 SEM micrograph showing Ti_5Si_3 particles A and B, spherical TiC in C and E, and a eutectic of Ti_5Si_3 and α' -Ti, at D (Hu *et al.*, 1998).



12.6 TEM micrographs of eutectic of Ti_5Si_3 and α' -Ti (a) bright field (b) dark field, with Ti_5Si_3 in light contrast (Hu *et al.*, 1998).

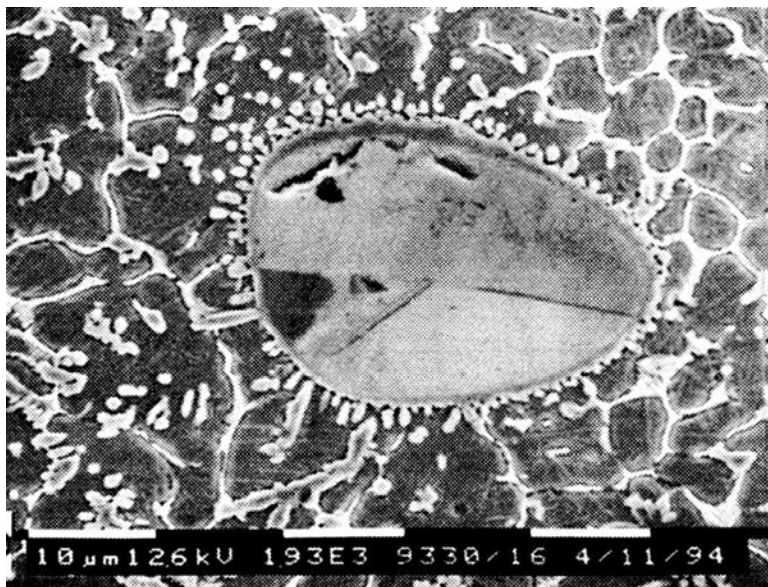
- (ii) the use of compounds that will completely dissolve, providing solute atoms which react with titanium to form hard particles, such as borides, carbides, nitrides, oxides or silicides. An example is SiC particles, 3–7 μm in size, which dissociate to give elemental Si and C. These atoms

- then react with Ti, forming Ti_5Si_3 and TiC precipitates respectively, both significantly harder than Ti and its alloys, Table 12.1. Another example is 10 μm BN powder dissolved in Ti-6Al-4V alloy, to give compounds of Ti_2N , TiB and Ti_3B_4 , producing a surface hardness between 1500–1700 HV, due to presence of the hard TiB and TiN phases (Selvan *et al.*, 1999),
- (iii) the incorporation of hard compounds, such as SiC, which will dissolve partially, leaving sufficient of the original particles well distributed throughout the Ti-matrix, together with solute elements which will react with α -Ti to form a fine dispersed phase. SiC particles, in the range 30–100 μm have been found to partially dissolve, giving the same phases described in (ii), Fig. 12.7 (Mridha *et al.*, 1996),
 - (iv) intermetallic coatings of Ti-Al (Garcia *et al.*, 2002), developed on Ti alloys by laser processing as a means of improving high temperature properties, while $\text{Ti}_2\text{Ni}_3\text{Si}$ -toughened by a ductile NiTi (Dong and Wang, 2008) has potential for improved corrosion and wear resistance,
 - (v) a series of amorphous alloys (Inoue, 2000), based on rare-earth (R-E) oxides, with a high glass-forming ability (GFA). A Zr based amorphous alloy with the widest supercooled liquid region has an extremely high glass-forming ability and was applied by Wang *et al.* (2004) to coat CPTi using Zr based alloy powders, and
 - (vi) laser nitriding to form a hard TiN surface layer $\sim 5 \mu\text{m}$, followed by dendrites, needles and quasi-spherical particles at lower depths in the melt pool, Fig. 12.3. This technique has received widespread attention for many years, initially through the use of continuous wave (CW) CO_2 lasers (Katayama *et al.*, 1983, 1984), but also using Nd-YAG pulsed lasers (Ettaqi *et al.*, 1998, Santos *et al.*, 2006). Bianco *et al.* (1995) investigated laser processing with CO_2 gas to form TiC precipitates, while the effect of TiC_xN_y by laser processing with a combination

Table 12.1 Data of compounds incorporated into titanium alloys

Material	Melting temperature (°C)	Vickers hardness (VHN)	Density (g/cm ³)
Ti	1650–1670	60	4.54
TiC	3067	2800–3200	4.92
SiC	2760	2600	3.22
TiN	2930	~ 2500	5.43
WC	2870	2400	15.77
VC	2830	2800	5.81
ZrC	3500	2600	6.73
ZrN	2980	1510K	7.35
ZrB	2990	2200	6.09
TiSi ₂	1540	870	4.39

Note: K is Knoop hardness



12.7 SEM micrograph of partially dissolved SiC particle acting as a nucleant for TiC (Mridha *et al.*, 1996).

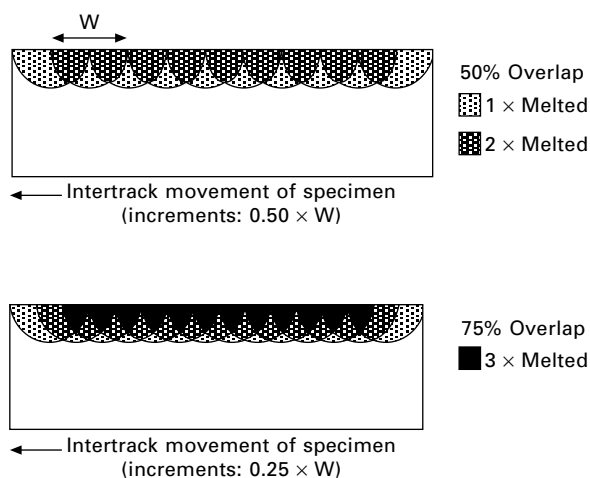
of carbon and nitrogen was addressed by Covelli (1996), and using gas mixtures of CO and N by Grenier (1997). However, the reader should be aware that a review of 'laser nitriding of metals' by Schaaf (2002) does not consider titanium alloys. Examples of these different approaches are discussed below.

12.4 Laser processing conditions for surface engineering

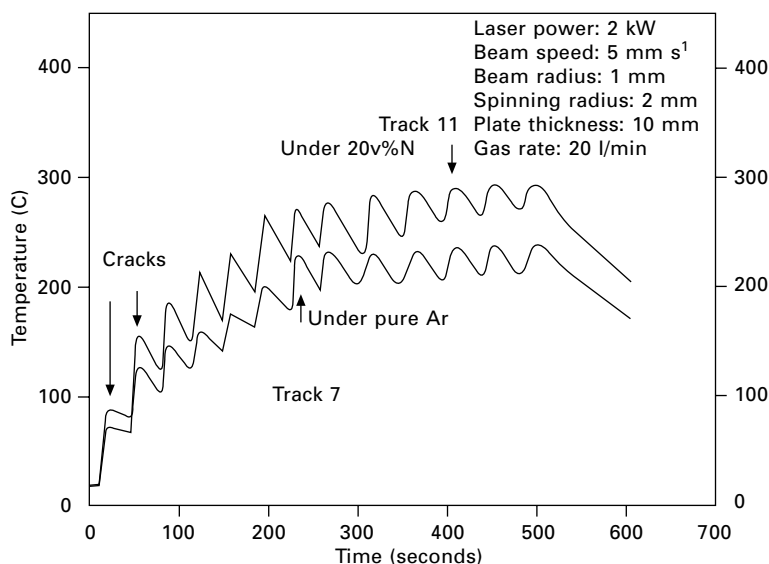
The main laser parameters that can be controlled during processing include the laser power, q , the beam radius, r_b , the specimen or work-piece velocity, v , and the beam mode, which may be stationary, spinning, top hat, or Gaussian (Ion, 2005); in addition, in the case of alloying, the composition and concentration of the alloy, and if the processing involves a gas such as nitrogen, the concentration and the flow rate (Mridha and Baker, 1998). Other important factors are the dimensions, particularly the thickness of the work-piece (Hu *et al.*, 1997) and its absorptivity of the laser energy. Many of the studies on laser surface modification describe work which involved either a small hemispherical melted volume (Abboud and West, 1994) or a single laser track with a width of a few millimetres (Mridha and Baker, 1996). In practice, there is frequently a requirement to produce surface modification over a much greater area. This necessitates overlapping of

many laser melted tracks. The best results for laser processing Ti-6Al-4V alloy plate using a stationary beam were obtained with medium scanning velocities of $15\text{--}50\text{ mms}^{-1}$ and with a minimum overlap of 50%, otherwise it was found that a part of each track would be molten only once, Fig. 12.8 (Morton *et al.*, 1992). Work by Baker and Selamat (2008) used a spinning beam to produce a broad laser track, lower scanning velocities, usually in the range $3\text{--}10\text{ mms}^{-1}$, and in agreement with Morton *et al.* (1992) and Robinson and Reed (1995), they also found that an overlap of 50% provided the best surface finish. However, in earlier work (Xin *et al.*, 1996), also using a spinning beam, where the economics were not a prime concern, it was found that a 35% overlap gave a satisfactory surface. A consequence of overlapping of laser tracks is a build-up of heat in the work-piece, resulting in preheating, which increases the temperature of subsequent tracks. This effect has received little attention in the literature but has been the subject of two papers, (Hu and Baker, 1997, 1999). The melting of 13 tracks on a 10 mm thick plate of Ti-6Al-4V under an atmosphere of Ar, showed that a constant preheat temperature of 235°C was reached by Track 7. With a 20% nitrogen atmosphere, under the same processing conditions, a temperature plateau of 290°C was reached by Track 11, Fig. 12.9. Higher temperatures were reached with 5 mm thick plate. Therefore it is not surprising that variations in the melt depth, in the microstructure and therefore in the properties such as hardness, occur, from the first to the last melted tracks, although these changes are rarely reported in the literature.

The laser energy density, E , is related to the laser power, q , the scanning velocity, v , which is normally the traverse speed of the work-piece, and the radius, r_b , of the laser probe by



12.8 Figure showing the effect of percentage overlapping on the remelting of solidified alloy (after Robinson *et al.*, 1995).



12.9 Effect of multi-track alloying on the preheat temperature in Ar environment and in 40% nitrogen 60% argon environment, (Hu and Baker, 1999).

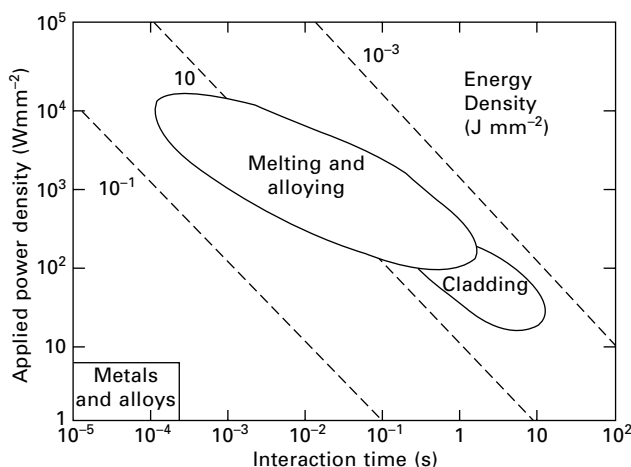
$$E = (q/r_b v) \quad [12.1]$$

expressed in MJm⁻², and for CO₂ lasers is normally in the range 50–600 MJm⁻².

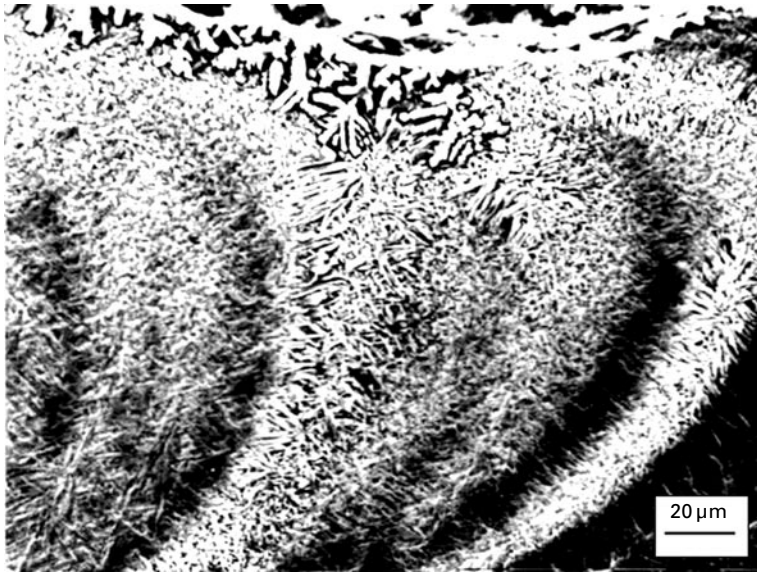
The variation in the input energy density, that is the energy density absorbed by the alloy surface, controls the depth of the melt pool and therefore the volume of the molten alloy. The laser processing is characterized by high heating and cooling rates, in the range 10⁴ to 10¹⁰ Ks⁻¹, thermal gradients between 10⁵ and 10⁸ K/m, and solidification velocities up to 30 ms⁻¹ (Draper and Poate, 1985). These laser surface alloying parameters have the effect of extending the solid solubility limit and may result in metastable non-equilibrium phases, leading to novel microstructures due to the rapid solidification conditions. The most important characteristic of the modified layer is the depth of penetration, which is related to the maximum temperature reached during processing. As described by Steen *et al.* (1994), several attempts have been made to predict the melt depth. These include those 'based on experimental studies which analysed statistically a large number of measurements to develop a master correlation. At the other extreme, those based on the laws of physics which provide 'exact' predictions, but the dominant physics is often lost in the wealth of information generated and the nature of the simulations limit their engineering application'. However, Shercliff and Ashby (1991) 'provide a balance between these two extremes

and their work results in plots of dimensionless parameters which capture the significant trends of a large number of experimental data, including their own measurements'. Ion *et al.* (1992) and Ion (2005, p. 525) have summarized some of the available approaches and collated the main relationships required to develop model process diagrams, while Hu and Baker (1996) considered the case of a spinning beam. A modified laser processing diagram, showing the conditions for laser melting and laser cladding, is given in Fig. 12.10.

While the melt depth, surface temperature, and heating and cooling rates are of primary importance to the mechanical properties developed on solidification, the surface roughness can have important consequences for erosion resistance. Anthony and Cline (1977) explored the development of surface ripples during laser processing. They considered that 'during laser surface melting and alloying, a temperature gradient extends radially away from the centre of the laser beam. Under the beam, the temperature of the liquid is at its highest level and the surface tension of the liquid is at its lowest value. As the temperature of the liquid decreases away from the centre of the laser beam, the surface tension of the liquid increases. This increase of the surface tension of the liquid away from the centre of the beam, pulls the liquid away from the centre of the beam, thereby depressing the surface of the liquid under the beam and heightening the liquid surface elsewhere'. This effect is known as Marangoni flow and is the dominant convective mechanism in the melt pool. It can have a controlling effect on the microstructure [Fig. 12.11]. Chan *et al.* (1984), in modelling heat flow, predicted that the melt pool rotates approximately five times before solidification. This effect manifests itself on occasions in the heterogeneous distribution of dendrites, [Fig. 12.12]. As the beam passes to other areas of the surface, this distortion



12.10 Laser processing diagram showing the conditions for laser melting and laser cladding (after Ion, 2005).



12.11 SEM micrograph showing the capillary convective flow patterns in the melt pool (Marangoni flow) highlighted by precipitation of needle particles along the flow lines (Mridha and Baker, 1994).



12.12 Heterogeneous distribution of dendrites following laser nitriding (Mridha and Baker, 1996).

of the liquid surface is frozen in, creating a roughened rippled surface, Fig. 12.13. The roughness of the surface has been shown to be a major factor in erosion of titanium alloys, considered in Section 12.7.4.

12.5 Laser surface melting and cladding

12.5.1 Laser surface melting

The process whereby the alloy surface is laser melted and then resolidified without any attempt to modify the surface layer chemical composition is normally referred to as laser glazing or melting. The sequence of surface changes following the instant that the laser beam contacts the alloy surface is summarized below. Firstly, the near-surface region rapidly reaches the melting point and a liquid/solid interface starts to move through the alloy.



12.13 Surface topography showing rippling following laser melting of CPTi (Mridha and Baker, unpublished).

Diffusion of elements commences in the liquid phase. The laser pulse is nearly terminated while the surface has remained below the vaporization temperature. At this stage the maximum melt depth has been attained, interdiffusion continues, and the re-solidified interface velocity is momentarily zero and then rapidly increases. The interface moves back to the surface from the region of maximum melt depth. Interdiffusion continues in the liquid, but the re-solidified metal behind the liquid/solid interface cools so rapidly that solid state diffusion may be negligible. Finally, re-solidification is complete and a surface alloy has been created. Due to the relatively small melted zone of 50 to 1000 microns, very high quench rates are achieved, in the range of 10^3 to 10^6 Ks⁻¹, resulting in non-equilibrium martensitic microstructures (Draper and Ewing, 1984; Draper and Poate, 1985). The re-solidified alloy has a titanium oxide film on the surface, which confers good wear resistance. Langlade *et al.* (1998) used a YAG-Nd laser to study oxides on T40Ti and Ti-6Al-4V alloys. Stratified layers, giving different coloured films, were related to oxide thicknesses and oxide compositions. TiO + Ti₂O₃ followed TiO, and finally Ti₂O₃ + anatase TiO₂ + rutile TiO₂. It was noted that titanium oxides may exhibit a solid lubricant effect, while the oxygen dissolved in the titanium matrix had a hardening effect.

One of the characteristics of the laser surface melting technique is the rapid solidification, which can produce hardening through the introduction of crystalline defects, such as vacancies and dislocations. Often residual stresses are developed, which result in a distortion of the work-piece, but this can be overcome by the application of a low-powered surface heating procedure following the laser melting process.

12.5.2 Cladding

Ion (2005) defined cladding as 'a surface melting process in which the laser beam is used to fuse an alloy addition onto a substrate'. The alloy may be introduced into the beam-material interaction zone either during or prior to processing, usually as powder, wire or foil. The object is to melt a thin layer of substrate together with as much alloy addition as possible, which must be able to homogenize before it solidifies. Therefore, very little of the substrate is melted and ideally, vaporization is avoided, as the molten clad solidifies rapidly; a clad with a nominal composition of the alloy is produced, which has a strong metallurgical bond with the substrate and increased hardness. The process may be used for large area coverage by overlapping tracks, but it is the ability to protect smaller localized areas that, according to Vilar (1999), makes the technique unique. Most of the substrates that can be subjected to laser melting techniques are suitable for producing clad surfaces and, in the case of powder additions, cladding and alloying processes often overlap. As seen in the schematic diagram Fig. 12.10, laser cladding, uses

a lower power density, around 10^2 Wmm^{-2} compared with $10^3\text{--}10^4 \text{ Wmm}^{-2}$ for laser surface melting. This lower power density not only reduces the relative extent of distortion, but also ensures a closer control of the dilution of the clad, leading to a more exact coating composition.

Cladding was considered by Ion (2005) and Bao *et al.* (2006), and reviewed by Vilar (1999) and Wu and Li (2006). The pioneering work was undertaken by Ayers (1981), who injected into Ti, powders of TiC (Ayers *et al.*, 1981, 1984) or WC (Ayers *et al.*, 1981, 1984) and recently Chen *et al.* (2008), and later Abboud and West (1989) with SiC. Abboud and West (1989, 1990, 1991, 1991a, 1944, 1944a) also laser-surface clad CPTi with Al powder to produce titanium aluminide coatings. This was followed by a study of the wear and oxidation properties of titanium aluminides on CPTi (Hirose *et al.*, 1993). Recently, interest in cladding with Al on titanium alloys has been revived by Guo *et al.* (2007, 2008, 2008a) and Pu *et al.* (2008). Guo *et al.* (2008) studied the effect of preplaced aluminium powders between 14.7 and 29.7 at% on the phase composition and tribological properties of CPTi. Cracking was found in all the laser-modified specimens. Cai *et al.* (2007) used a mixture of titanium and B_4C precursor powders to form a mixture of carbide and boride precipitates, which raised the hardness of the Ti-6Al-4V substrate from ~ 350 to ~ 600 HV through the formation of TiC, TiB and TiB_2 . Unusually, the precursor powders were placed in grooves machined to depths of 0.2 to 1.0 mm. Work by Wang and Liu (2002) is an example of a study to develop a wear-resistant $\text{Ti}_5\text{Si}_3/\text{NiTi}_2$ intermetallic composite coating fabricated on a near alpha titanium alloy, BT9. In the laser clad intermetallic composite, Ti_5Si_3 primary particles were uniformly distributed in the NiTi_2 matrix and metallurgically bonded to the titanium substrate. It was free from porosity and microcracks, with a hardness of ~ 1000 HV at the surface retained to a depth of $800 \mu\text{m}$. Recently, cladding of Ti-6Al-4V by cobalt has been studied by Majumdar *et al.* (2009), who developed several titanium cobalt compounds that were associated with improved corrosion resistance.

Laser cladding is also one of the surface amorphization technologies associated with the rapid heating and cooling rates that inhibit long-range diffusion and avoid crystallization (Morris, 1988). However, the amorphous alloys found before the 1990s required cooling rates above 10^5 Ks^{-1} for amorphization, and the resulting amorphous layer thickness was limited to less than 50 nm (Wang *et al.*, 2004). Since 1988, Inoue and co-workers have discovered a series of amorphous alloys with high glass forming ability (GFA) and much lower critical cooling rates in the Mg-, Zr-, Fe-, Pd-, Ti- and Ni-based alloy systems (Inoue, 2000). The alloy $\text{Zr}_{65}\text{Al}_{7.5}\text{Ni}_{10}\text{Cu}_{17.5}$ which has the widest supercooled liquid region, also has the high GFA at an extremely low critical cooling rate of 1.5 K/s (Inoue *et al.*, 1993). The discovery of these GFAs has opened up significantly greater prospects for laser cladding of amorphous coatings with a thicknesses $>1 \text{ mm}$, able to cover

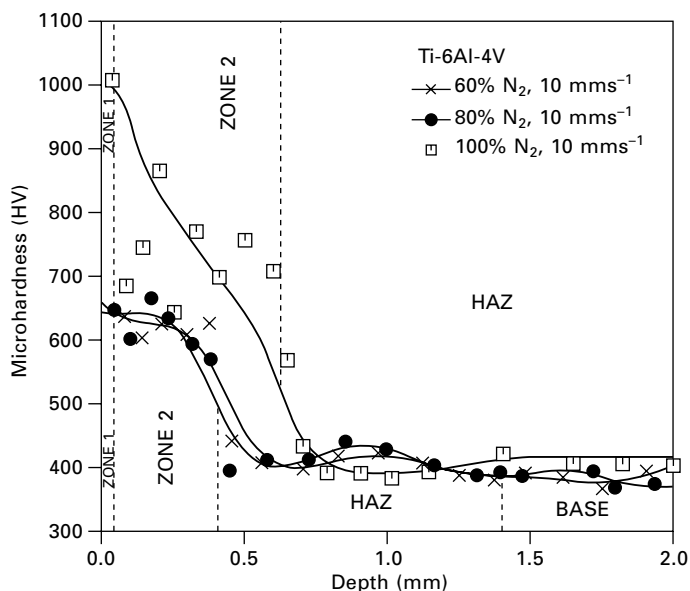
a large area. Various alloys have been laser-clad on a variety of substrates. Wang *et al.* (2004) have studied Zr-based alloy powders laser-clad on a pure Ti substrate in an attempt to form an amorphous coating. No cracks or voids were observed within the coating. There were clear tendencies of composition separation in different phases. The extensive growth of titanium in the form of columnar crystallites into the coating, provided a good metallurgical bond between the coatings and substrate. This clad coating showed a higher but varying microhardness 650–1000 HV. As mentioned in Section 12.3, titanium-based intermetallics, such as γ -TiAl, are of interest for structural applications at elevated temperatures (Ye, 1999). Whereas γ -TiAl possesses a low density ($3.7\text{--}4.6\text{ g cm}^{-3}$), high specific strength and excellent high temperature resistance, the sliding wear resistance at elevated temperatures needs improvement. Coatings of TiN on γ -TiAl by multiarc implantation of a $3\text{ }\mu\text{m}$ film of Ti_2AlC using plasma carburizing, were found to have inadequate oxidation resistance with increasing temperature. Also, the ductility at room temperature is a major obstacle to the use of Ti_3Al , TiAl and TiAl_3 (Hirose *et al.*, 1993). However, Chen and Wang (2003) found that laser surface alloying Ti-48Al-2Cr-2Nb (γ -TiAl) with carbon, resulted in a thick composite coating of TiC, which exhibited $>700\text{ HV}$ and a 5x improvement in sliding wear resistance at 600°C over untreated γ -TiAl. Liu and Wang (2006, 2007) investigated the effect of laser cladding the same alloy with a mixture powders of Ni-20wt-%Cr alloy and Cr_3C_2 in the ratios of 20:80, 50:50 and 80:20, as a means of further improving the high-temperature wear resistance. The main clad phases were γ Ni solid solution matrix, Cr_7C_3 and TiC. The cladding processed with the 50:50 alloy showed a two times improvement in room-temperature sliding-wear resistance. An extension to this work (Liu and Yu, 2007a) involved the incorporation of between 1 and 10wt-% of a rare-earth metal oxide, La_2O_3 , to the 50:50 ratio Ni-20wt-%Cr alloy: Cr_3C_2 alloy. An addition of 4 wt-% La_2O_3 refined the carbide microstructure and produced the highest values of microhardness, combined with the lowest wear rate, during room-temperature sliding wear experiments. Possible improvements to the high-temperature wear resistance of γ TiAl alloy were investigated by developing laser-clad $\gamma/\text{W}_2\text{C}/\text{TiC}$ composite coatings through the use of different concentrations of Ni-Cr-W-C precursor mixed powders, and testing the response of the coatings to dry sliding wear at 600°C and isothermal oxidation at 1000°C . Improved wear resistance was obtained, but oxidation resistance was reduced (Liu and Yu, 2007b).

12.6 Laser surface alloying

Laser surface alloying was first reviewed by Draper and Poate (1985) and later by Ion (2005). Here, the gaseous, solid and gaseous plus solid methods are considered.

12.6.1 Laser nitriding

Laser surface engineering requires the protection of the molten surface by an inert gas, such as argon or helium, to prevent oxidation during processing. In the case of titanium alloys, the replacement of the inert gas by nitrogen is a technique which has been developed over the past 30 years for modifying the near-surface region without altering the bulk characteristics of titanium alloys (for example, Katayama *et al.*, 1983; Walker *et al.*, 1985; Bell *et al.*, 1986; Mridha and Baker, 1991; 1994; Jianglong, 1993; Kloosterman and De Hosson, 1995; Xin *et al.*, 1996; Nwobu *et al.*, 1999; Kasper *et al.*, 2007; Abboud *et al.*, 2008). Laser nitriding with a 100% nitrogen atmosphere was used in most of the early work, and produced a thin 5–10 μm surface layer of titanium nitride. The hardness recorded closest to the surface was $\sim 1000\text{--}2000$ HV, and in addition, the TiN layer provided improved corrosion resistance, a lower coefficient of friction and wear resistance. However, cracking was often observed, Fig. 12.4 (Katayama *et al.*, 1985; Morton *et al.*, 1992; Hu *et al.*, 1997b; Nwobu *et al.*, 1999). Morton *et al.* (1992) found that when laser nitriding CPTi and Ti-6Al-4V alloy produced a surface with a hardness >600 HV, cracking was likely to occur, but could be avoided by preheating prior to nitriding, which reduced the cooling rate and controlled the level of the residual stresses developed on solidification. An alternative method of alleviating this problem is the use of dilute nitrogen atmospheres, usually in the form of an argon–nitrogen mixture, together with lower nitrogen flow rates (Mordike, 1985; Bell *et al.*, 1986; Morton *et al.*, 1992; Mridha and Baker, 1994; Xin and Baker, 1996; Grenier *et al.*, 1997; Xin *et al.*, 1998; Selamat *et al.*, 2001). Dilute nitrogen atmospheres were found to significantly reduce or eliminate cracking, but at the expense of a decrease in surface hardness, Fig. 12.14, and a smaller melt depth. In the work of Selamat *et al.* (2001), no cracking was observed following processing with a dilute nitrogen atmosphere of 20%N- 80% Ar, while laser nitriding using a 50%N50%Ar atmosphere coincided with a reduction in hardness to ~ 800 HV (Xue *et al.*, 1997). As described by Mridha and Baker (1994) and Kloosterman and De Hosson (1995), a thin surface TiN layer <10 μm , will initially solidify, out of which titanium nitride dendrites will grow due to constitutional undercooling. The dendrites grow by rejecting titanium into the melt. At the same time there will be a solidification front at the bottom of the melt pool and, somewhere in between, these fronts will meet. If the cooling rate is sufficiently fast, and the nitrogen concentration in the titanium is below 6.2at%, a martensitic transformation (α' -Ti) is possible. In general, the nitrided surface develops better properties than those produced by glazing in an inert gas atmosphere (Baker *et al.*, 1994). Below the surface, the hardness normally decreases rapidly, due to the TiN layer being replaced by TiN dendrites in an α' Ti-N solid solution matrix (Katayama, 1983; Walker



12.14 Microhardness–depth profile of specimens laser processed with varying nitrogen percentages (Xin and Baker, 1996).

et al., 1985; Bell *et al.*, 1986; Mridha and Baker, 1991; Kloosterman and De Hosson, 1995), Fig. 12.3. Closer to the melt zone–HAZ boundary, only the δ Ti–N solid solution is present, and this is reflected in the level of the hardness.

Microstructural characterization has been related to the processing, hardness and roughness data. Previous studies by the present author and co-workers used TEM/SAED, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to characterize titanium nitride phases in a Ti–6Al–4V alloy produced by laser nitriding (Xin *et al.*, 1998, 2000; Selamat *et al.*, 2001). Single phase δ TiN has a NaCl type fcc structure and is more accurately expressed as TiN_x , as it can have a wide range of homogeneity from ~ 30 to 55 at% nitrogen. In the transition elements, the cubic nitrides can exist in a wide range of non-stoichiometry, and TiN_x can be obtained with $0.5 \leq x \leq 1.1$ (Selamat *et al.*, 2003). The values of x have been shown to depend on the percentage N in the nitriding atmosphere. With 100%N, x has been estimated to be close to 1, with 80%N, $x = 0.8$, while when 20%N is employed, x decreases to 0.75 (Selamat, 2001). The XPS spectra obtained from different depths in the melt zone indicated that the quantity of TiN_x precipitates decreased with increasing depth from the surface. Only a small quantity was present at 100 μm , while none was detected below 300 μm from the surface.

TiN coatings are used mostly for their low coefficient of friction in order to reduce adhesive wear, while TiC coatings increase both the surface hardness

and the resistance to ploughing wear (Moskowitz *et al.*, 1986). Bianco *et al.* (1995) have shown the potential use of CO₂ as an alloying gas, and noted that the abrasive wear resistance of Ti-6Al-4V, laser alloyed in a gaseous atmosphere of CO₂, is improved, relative to TiN layers produced by laser nitriding. They considered that under the laser beam, CO₂ dissociates to CO and O₂, which then reacts with Ti to give a hard TiC surface containing TiO.

It is also known that the wear resistance of titanium is enhanced by TiC coatings produced by laser alloying using preplaced graphite powders, originally added to improve the absorptivity (Flower *et al.*, 1985; Walker *et al.*, 1985; Covalli *et al.*, 1996). Unlike nitriding, which results in a layer of TiN, alloying with graphite did not produce a surface layer of TiC. The use of a gas instead of preplaced graphite allows a more precise control of the relative concentration of the carbon content of the molten layer. Also, laser gas alloying can be undertaken more easily on complex shapes without the feeding difficulties associated with powders or wires.

Deng and Braun (1994) have observed that the wear behaviour of TiC_xN_y is superior with carbon-rich coatings to TiN or TiC, which led Grenier *et al.* (1997) to study the effect of mixtures of carbon monoxide and nitrogen gases on the microstructure and wear resistance of laser processed CPTi using a Nd:YAG pulsed laser. These authors concluded that the abrasive wear resistance of coatings alloyed with a mixture of gases was superior to that of coatings alloyed with either nitrogen or carbon monoxide alone. However, their coatings did contain cracks.

12.6.2 Laser powder alloying

The early work using powders as a source of alloying (Ayers *et al.*, 1981, 1984; Abboud and West, 1989) was based on injection of powders of around 150 µm in size, which may be described more accurately as cladding rather than surface alloying. Later, this average particle size was reduced to within the range 60–100 µm (Cooper and Slebodnick, 1989; Kloosterman *et al.*, 1998; Kool *et al.*, 1999; Pei *et al.*, 2002). An alternative method is the preplacement of particles on the surface of the substrate alloy in the form of a slurry, where in general, the particles have a smaller average size, ~45–60 µm (Hu *et al.*, 1997; Pang *et al.*, 2005). Both these techniques result in the partial dissolution of the powders, Fig. 12.7, which can provide a strong bond with the matrix, and confer significant wear resistance to the substrate (Ayers and Bolster, 1984; Hu *et al.*, 1997; Ettaqi *et al.*, 1998; Pang *et al.*, 2005). However, for some applications that require improved surface strength through dispersion hardening, and/or improved corrosion properties, a complete dissolution of the particles during laser processing is beneficial. This is possible using laser powers of ~3kW, when the particle size is less than

10 μm . With SiC particles, both of these techniques provided an opportunity for the precipitation, in a fine state, of new phases such as Ti_5Si_3 and TiC , Fig. 12.15 (Mridha *et al.*, 1993; Baker *et al.*, 1994; Hu *et al.*, 1997; Mridha and Baker, 1997, 2007; Selamat *et al.*, 2003; Poletti, 2008). It is generally found that the hardness of the powder alloyed surface is lower than that of the nitrided specimens. Some of the other elements and compounds, including NiCr1BSiC (Sun *et al.*, 2002a), that have been incorporated into titanium alloys are collated in Table 12.2. The laser alloying invariably resulted in



12.15 SEM micrograph of laser processed SiC preplaced powder on CPTi, showing small needles (10–15 μm) below larger needles (30–35 μm) following a concentrated dendritic structure (D). Platelet particles (P) in the needle structures and variation of the hardness indentations (H) are also visible (Mridha and Baker, 2007).

Table 12.2 Elements and compounds incorporated into titanium alloys by laser processing

Material	Addition	Laser	Reference
CPTi	Al	CO ₂	Abboud and West (1990)
CPTi	Al	CO ₂	Abboud and West (1991)
CPTi	Al + N	CO ₂	Garcia <i>et al.</i> (2002)
CPTi	Al, Si, Al + Si	CO ₂	Majumdar <i>et al.</i> (1999, 2000)
Ti-6Al-4V	B ₄ C	CO ₂	Mehlmann <i>et al.</i> (1990)
CPTi	BN, B ₄ C, TiB ₂		
Ti-6Al-4V	MoB, MoB ₂	CO ₂	Badini <i>et al.</i> (1992)
Ti-4Al-2Sn-4Mo	W ₂ B ₅		
Ti-6Al-4V	BN	CO ₂	Selvan <i>et al.</i> (1999)
γ-TiAl	C	CO ₂	Chen and Wang (2003)
CPTi	graphite	Nd:YAG	Courant <i>et al.</i> (2005)
Ti-6Al-4V	Co	CO ₂	Majumdar <i>et al.</i> (2009)
Ti-6Al-4V	Cr ₂ C ₃ + Ti	YAG	Zang <i>et al.</i> (2001)
Ti-6Al-4V	Cr ₂ O ₃ + Ti	Nd:YAG	Man <i>et al.</i> (2001)
Ti-6Al-4V	Mo + WC	Nd:YAG	Pang <i>et al.</i> (2005)
CPTi	Ni + SiC, SiC	CO ₂	Selvan <i>et al.</i> (1999a)
Ti-6Al-4V	Ni + SiC	CO ₂	Selvan and Subramanian (2003)
Ti-6Al-4V	Si + Ti	Nd:YAG	Alhammad <i>et al.</i> (2008)
CPTi, Ti-6Al-4V	SiC (150 μm)	CO ₂	Abboud and West (1989)
CPTi	SiC (6 μm)	CO ₂	Mridha <i>et al.</i> (1993)
CPTi,	SiC (3 μm)	CO ₂	Mridha and Baker (2007)
Ti-6Al-4V	SiC + N	CO ₂	Hu <i>et al.</i> (1998)
Ti-6Al-4V	SiC	Nd:YAG	Pei <i>et al.</i> (2002)
CPTi	TiC	CO ₂	Abboud and West (1992)
Ti-6Al-4V	TiC	CO ₂	Sun <i>et al.</i> (2001)
Ti-6Al-4V	TiN, ZrC, ZrN	CO ₂	Hu <i>et al.</i> (1997)
CPTi	TiN	Nd:YAG	Ettaqi <i>et al.</i> (1998)
Ti-6Al-4V	TiN	CO ₂	Yilbas and Shuja (2000)
Ti-6Al-4V	TiN	CO ₂	Yilbas <i>et al.</i> (2001)
Ti-6Al-4V	WC	CO ₂	Chen <i>et al.</i> (2008)
Ti-6Al-4V	Ti + B	Nd:YAG	Banerjee (2004)
Ti-6Al-4V	AlNi + VC + Cr ₂ O ₃	Nd:YAG	Duraiselvan <i>et al.</i> (2007)
Ti-6Al-4V	BN + NiCrCoAlY	CO ₂	Molian and Hualun (1989)
Ti-6Al-4V	NiCrBSi	CO ₂	Sun <i>et al.</i> (2000)
Ti-6Al-4V	NiCrBSi + TiC	CO ₂	Sun <i>et al.</i> (2001)
Ti-6Al-4V	NiCrBSiC	CO ₂	Sun <i>et al.</i> (2002)
Ti-6Al-4V	NiCoCrAlY	CO ₂	Meng <i>et al.</i> (2005)
Ti-Al-Mo-Zr-Si	TiSiNi	CO ₂	Wang and Liu (2002)
CPTi	Zr ₆₅ Al _{7.5} Ni ₁₀ Cu _{17.5}	CO ₂	Wang <i>et al.</i> (2004)
Ti-6Al-4V	graphite + Si	CO ₂	Tian <i>et al.</i> (2006)
CPTi, Ti-6Al-4V + Y ₂ O ₅ + Ti	graphite + B + Ce ₂ O ₃	CO ₂	Tian <i>et al.</i> (2006a)

a harder melt zone than the substrate, and many papers reported significant improvements in other properties such as wear resistance and erosion. In the case of injected powders, the protective gas used to avoid oxidation has

been employed as a carrier, and some studies have found that positioning the powder stream out of the laser beam minimizes the reaction layer between the particles and the titanium matrix (Kloosterman *et al.*, 1998).

12.6.3 Laser surface nitriding plus powder alloying

The combination of powders with gaseous atmospheres has also been studied; in particular, mixtures of nitrogen with SiC (Hu *et al.*, 1997, 1998; Mridha and Baker, 1996, 1997; Selamat *et al.*, 2003), TiN (Ettaqi *et al.*, 1998), ZrC (Ettaqi *et al.*, 1998) and ZrN (Hu *et al.*, 1997). Dilute nitrogen atmospheres combined with powder alloying have been found to produce crack-free surfaces having additional hardness relative to the titanium parent alloy and the powder alloying alone (Baker *et al.*, 1994; Mridha and Baker, 1996, 1997, 2007; Hu *et al.*, 1998; Selamat *et al.*, 2006; Garcia *et al.*, 2002; Baker and Selamat, 2008; Guo *et al.*, 2008a).

12.7 Effect of laser surface modification on properties

12.7.1 Hardness and residual stress

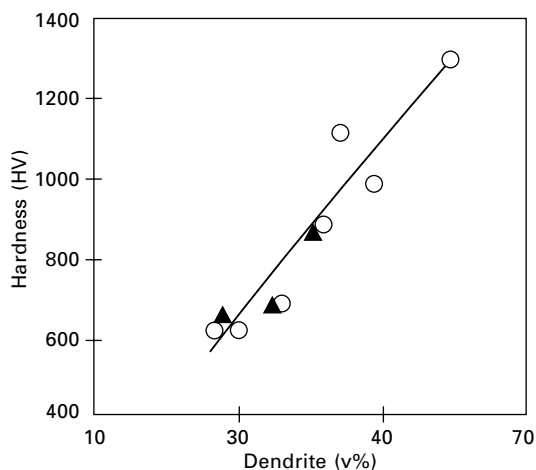
The hardness of laser modified titanium surfaces has a significant influence on the wear properties. The aim is to precipitate hard ceramic particles, sometimes as dendrites, as quasi-spherical particles, needles or in a eutectic with α -Ti, together with a solid solution-strengthened Ti matrix. In the case of laser nitriding, the formation of a hard surface TiN layer is followed by a dendrite microstructure (Bell *et al.*, 1986; Morton *et al.*, 1992; Hu *et al.*, 1996). The hardness, HV, is controlled by the volume fraction dendritic phase, V%, Fig. 12.16, by the equation:

$$HV = 23 V\% \quad [12.2]$$

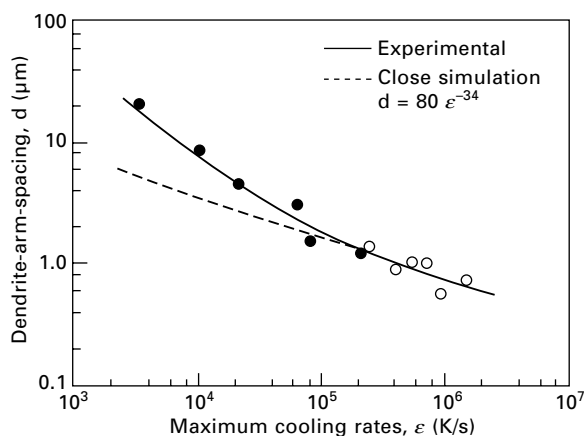
which is related to the details of the secondary arm spacing. This in turn is controlled by the rate of cooling. Peng *et al.* (1983) used the Cline and Anthony (1977) model to calculate the maximum cooling rate, ϵ , in Ks^{-1} following laser melting through a correlation with dendrite arm spacings, d , in μm , measured from photomicrographs. The best functional correlation was:

$$d = 80 \epsilon^{-0.34} \quad [12.3]$$

Figure 12.7 shows that this holds for values of ϵ between 8×10^4 and $1.5 \times 10^6 \text{ Ks}^{-1}$, as described by the model. The open circles show the experimental points that agree with the calculated curve, while solid circles show the cooling rates where the simulation broke down.

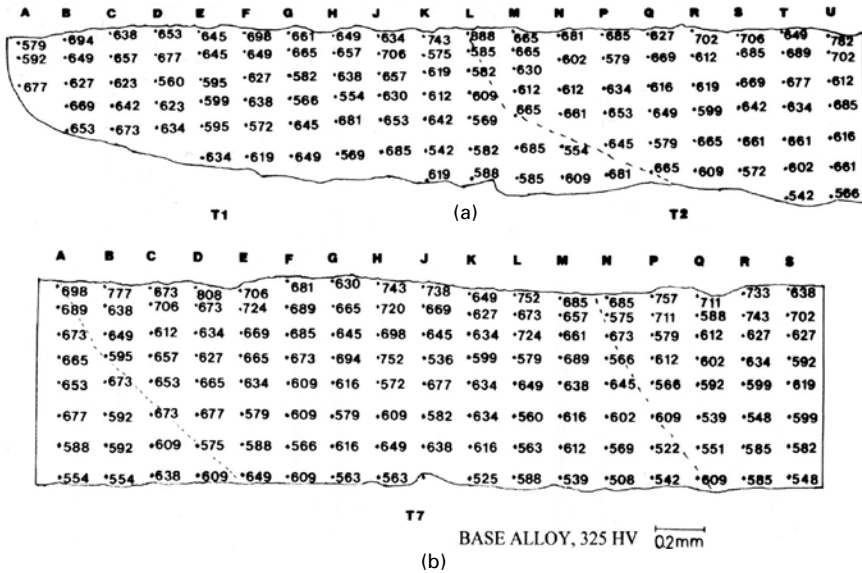


12.16 Hardness versus dendrite volume fraction in laser nitrided Ti-6Al-4V, showing a near linear correlation. The open circles denote individual specific dendrite volume fractions and the corresponding microhardness data, while the closed triangles relate the average microhardness data of three nitrogen levels investigated to the corresponding average dendrite volume fractions, and show a good agreement with the straight line (Hu *et al.*, 1996).



12.17 Correlation between the observed dendrite arm spacing and the calculated maximum cooling rate (Peng *et al.*, 1983).

Whereas most research reports the hardness as a single series of microhardness measurements taken close to the surface down to the substrate, Baker and Selamat (2008) produced hardness maps, Fig. 12.18, which, by allowing a comparison of hardness over several laser tracks, provides a much more accurate picture of hardness variation throughout processing.



12.18 Microhardness map of Ti-6Al-4V alloy after laser nitriding with 20%N-80%Ar (a) tracks T1 and T2 (b) track T7 (Baker and Selamat, 2008).

Laser nitriding Ti with 100% N produced surface hardness values in the range 1600–2000 HV (Katayama *et al.*, 1983; Bell *et al.*, 1986; Mridha and Baker, 1994a; Ettaqi *et al.*, 1998), which decreased with increasing work-piece velocity, %N in the atmosphere, Fig. 12.14 (Hu *et al.*, 1996; Xin *et al.*, 1996; Hu and Baker, 1999; Nwobu *et al.*, 1999; Kasper *et al.*, 2007; Raaif *et al.*, 2008) and flow rate (Mridha and Baker, 1998). The variation of hardness of TiN_x as a function of N/Ti ratio was shown by Sproul *et al.* (1989) for sputtered coatings, to have a narrow range between 3140 and 3400 Kgmm^{-2} , the latter figure also given by Perry *et al.* (1999). On the other hand, Munteau and Vaz (2006) examining sputtered TiN_x films found that the hardness remained constant, with a value about 2000 Kgmm^{-2} within the range 45–55 at% N. This variation has been explained by Perry *et al.* (1999) as due to an indentation size effect, the higher figure associated with the hardness nearer to the surface. To date, it has not been possible to find hardness data related to the stoichiometry of bulk TiN_x , over a wide x range.

Laser alloying Ti with powders also increased the surface hardness. For example, Tian *et al.* (2005) obtained hardnesses of 1500–1600 HV after laser processing TiN/B/Si/Ni powders, while slightly higher hardnesses, 1600–1700 HV0.1, were found in work on C/TiB/Ti powders (2006b). By comparison, the hardness of individual Zr-based amorphous alloys were

much lower, and varied from ~650 to 1000HK, still higher than the single amorphous alloy at 450–500HK (Wang *et al.*, 2004).

Another effect that has received little attention is the residual stress that develops as a result of laser surface modification processing. Ubhi *et al.* (1988) showed, by X-ray diffraction, that the residual stress across a single track in a laser glazed Ti-6Al-4V plate was +170MPa (+ve is a tensile stress) compared to +100MPa in the parent as rolled plate, and these values were reduced on annealing. Mridha *et al.* (1993) determined the residual stress of laser-processed CPTi alloyed with 6 μm SiC particles. They showed that the tensile stresses determined parallel to the track direction, decreased with depth from +259MPa at the surface to +124MPa at a depth of about 200 μm . The compressive stresses determined perpendicular to the track direction also decreased from –244MPa at the top to –170MPa at 100 μm subsurface. A detailed study of the surface residual stresses developed in both single-track and multi-track laser nitrided Ti-6Al-4V specimens was undertaken by Robinson *et al.*, (1996). The tracks, unlike in the work of Mridha *et al.* (1993), were allowed to cool to below 50°C between each successive pass to avoid preheating effects. In the single track specimen, the residual stress state prior to laser treatment was compressive (–562MPa), due to the severity of the grit blasting, and was considered to be the maximum value of elastic stress. A progressive increase in the level of the tensile residual stress occurred as successive adjacent melt tracks were formed, reaching a maximum tensile stress of ~+560MPa, corresponding approximately to the compressive stress in the grit-blasted surface prior to laser melting. Cracking was not observed when the alloy was melted in Ar. However, the introduction of nitrogen led, on occasion, to longitudinal cracks parallel to the laser track in the multi-track case, but perpendicular to the melt track in the single-track experiments. The work emphasizes the importance of conducting multi-track studies, but avoiding inter-pass cooling, and using conditions that are more appropriate to engineering applications than single-track work.

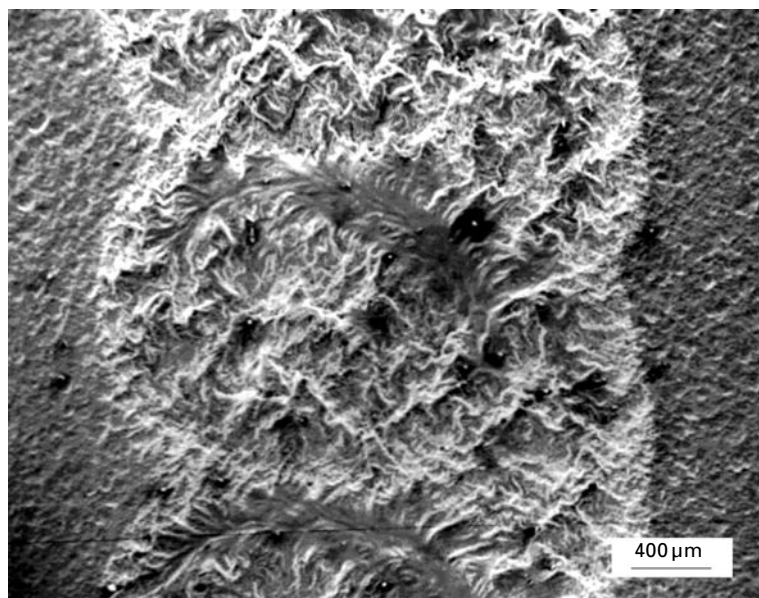
12.7.2 Surface roughness

The roughness of the laser modified surface layer has received less attention in the literature. This may be because many applications require the machining of a surface before service, which may remove up to 40 μm of the modified surface and entails additional costs. However, very smooth surfaces following laser processing have been reported.

The origin of laser-induced surface roughness is due to the development of morphologies such as ridges, Fig. 12.13, large scale periodic structures, cones, or columns. The surface micro-structuring of titanium in the presence of nitrogen following processing using a Nd-YAG laser was investigated in detail by György *et al.* (2003, 2004). They showed that initially, a rippled

structure developed, which under further irradiation gave way to micro-columns, uniformly distributed on the whole irradiated surface. Nitrogen pressure had a significant influence on the surface morphology. However, 'in argon, smooth flat islands appear, surrounded by a wave-like micro-relief, which evolves with increase in the number of laser pulses towards a smooth surface with polyhedral structures' (György *et al.*, 2004). The characterization of the surface finish of laser molten layers following CW CO₂ laser processing was considered in terms of roughness and waviness (Morton *et al.*, 1992). Roughness, according to Morton *et al.* (1992), is due to the amount of surface rippling, which in turn is dependent on the viscosity of the melt (Anthony and Cline, 1977). In agreement, Xue *et al.* (1997) noted that the surface roughness in laser nitrided surfaces is related to the laser process parameters, the nitrogen concentration and the track overlap ratio. To this list, in the case of powder alloying, it is necessary to include the concentration and size of the powder and details of the carrier gas flow. Whilst rippling as a result of laser nitriding is widely reported, it has also been observed after laser boronizing Ti 6Al-4V with a preplaced layer of BN (Selvan *et al.*, 1999). Waviness is a function of the convectional flow of the melt surface and again is influenced by the percent overlap (Morton *et al.*, 1992). The use of a spinning rather than a stationary beam had an influence on the surface morphology, which developed cellular-like structures with oval-shaped shiny bands across the tracks, Fig. 12.19 (Mridha and Baker, 1994a). After laser nitriding titanium, Bell *et al.* (1986) found the surface roughness, $R_a < 10 \mu\text{m}$; that is, smoother than the as-ground condition or following shot peening (Xue *et al.*, 1997), which can show an R_a value of up to $15 \mu\text{m}$ (Drechsler *et al.*, 1999). These data compare with an as-machined roughness of Ti-6Al-4V that can vary widely from $1.4 \mu\text{m}$ (Ribeiro *et al.*, 2003; Nalla *et al.*, 2003) to $5 \mu\text{m}$, depending on the tools and machining parameters (Che-Haron, 2001).

Laser nitriding using 100% N₂ produces the smoothest surface for both CPTi and Ti-6Al-4V alloys, with R_a values of $2.7 \mu\text{m}$ and $4.6 \mu\text{m}$ respectively, but this was greater than by laser processing in 100% argon or under a vacuum (Hu and Baker, 1999). Baker and Selamat (2008) compared (in Table 12.3) the surface roughness of laser processed Ti-6Al-4V following nitriding in 20% N₂:80% Ar (Specimen A), SiC powder melting (Specimen B) and combined nitriding 40% N₂ plus SiC powder addition (Specimen C). It is interesting to note that the R_a value varied with Track number. For Specimen A, R_a decreased with increasing track number, while with Specimens B and C, the roughness increased as the track number increased. The data in Table 12.3 show that laser processing Ti-6Al-4V following preplacing of SiC powder produced a very smooth surface, as R_a values increased from $0.94 \mu\text{m}$ to $1.8 \mu\text{m}$ from Track 1 to Track 6 but were still significantly smaller than any other R_a values collated in this work. However, combining nitriding



12.19 Surface morphology after laser processing using a spinning beam, showing the origin of roughness bands across the track. (Mridha and Baker, 1994a).

Table 12.3 Surface roughness measurements according to the sequence of laser track number for specimens A, B and C (Baker and Selamat, 2008)

Specimens	Track number	R_a μm
A – Nitrided (20%N)	1	5.10
	6	3.10
	12	2.70
B – SiC preplaced	1	0.94
	3	0.70
	6	1.80
C – Combination of nitrided (40%N) and SiC preplacement	1	4.40
	6	7.50
	12	7.20

with powder placement resulted in a marked deterioration in the surface smoothness, with the R_a values again increasing with track number, from 4.4 μm for Track 1 to >7 μm for Tracks 6 and 12. These were the highest values recorded in the work, but still fall within the limits given by Bell *et al.* (1986).

12.7.3 Wear

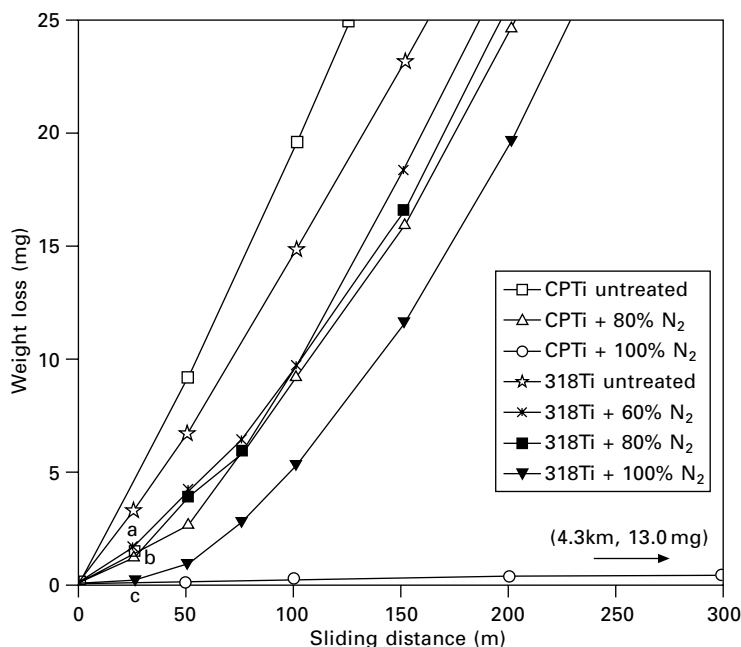
Titanium alloys have poor fretting fatigue resistance and poor tribological properties. Kustas and Misrta (1994), discussing the work of Miyoshi and Buckley (1984), note that 'theoretical calculations have shown that metals with low theoretical tensile and shear strengths exhibit higher coefficients of friction (μ) than higher strength materials'. Within the class of alloys with hcp structures, titanium has relatively low values for these properties. Consequently, it is expected that it will have high frictional values, which is the case for titanium sliding against titanium in air, where $\mu = 0.6$ (Miyoshi and Buckley, 1982). Lower strength materials also show greater material transfer to non-metallic counter-faces than higher strength materials. The great affinity of titanium for oxygen leads to the formation of oxide, which is transferred and adheres to non-metallic materials, such as polymers, resulting in severe adhesive wear (Buckley, 1981). Surface modifications are therefore required to increase near-surface strength, thereby reducing μ and lowering the tendency for transfer of material and adhesive wear (Kustas and Misrta, 1994).

Following either laser nitriding or laser powder alloying, there are reductions in μ and improvements in wear resistance. At higher loads, there are several reports of three-body wear, due to hard ceramic particles, which were originally part of the modified layer, augmenting the wear debris.

Yerramarri and Bahadur (1991) were among the first to study both sliding wear and abrasive wear of titanium alloys following laser surface modification. They assessed the wear following (i) surface melting in an argon atmosphere, (ii) nitriding and (iii) nickel alloying, where an electroplated nickel layer 25–50 μm was surface melted in an argon atmosphere. Sliding wear tests were undertaken using a block-on-ring configuration in dry conditions, with the titanium alloy sliding against a tool steel. The steady-state wear rate decreased from $40 \times 10^{-4} \text{ mm}^3 \text{ m}^{-1}$ to $0.8 \times 10^{-4} \text{ mm}^3 \text{ m}^{-1}$ after Ni alloying, to $0.5 \times 10^{-4} \text{ mm}^3 \text{ m}^{-1}$ after surface melting, while the lowest wear rate was $0.3 \times 10^{-4} \text{ mm}^3 \text{ m}^{-1}$, following laser nitriding. The as-received value of μ was reduced from 0.62 to ~ 0.43 for all the laser-treated specimens. Ploughing, with some adhesive wear, was observed after testing the as-received alloy. The abrasive wear test involved dry sand and a rubber wheel, and the wear rate of the as-received titanium alloy was about $0.16 \text{ mm}^3 \text{ m}^{-1}$, which was reduced by a factor of 1.5 for the laser nickel alloying and 3.0 for laser nitriding. A higher abrasive wear resistance for Ti-6Al-4V coincided with greater surface hardness and N% (Xin and Baker, 1996; Hu *et al.*, 1997a). The thicker the TiN layer, the greater the abrasive wear resistance even when fine cracks were found in the layer. Three slopes, associated with different microstructures, were seen in the weight-loss versus sliding-distance graphs, Fig. 12.20. The wear rate for 100%N CPTi was 0.001 mg m^{-1} while that of

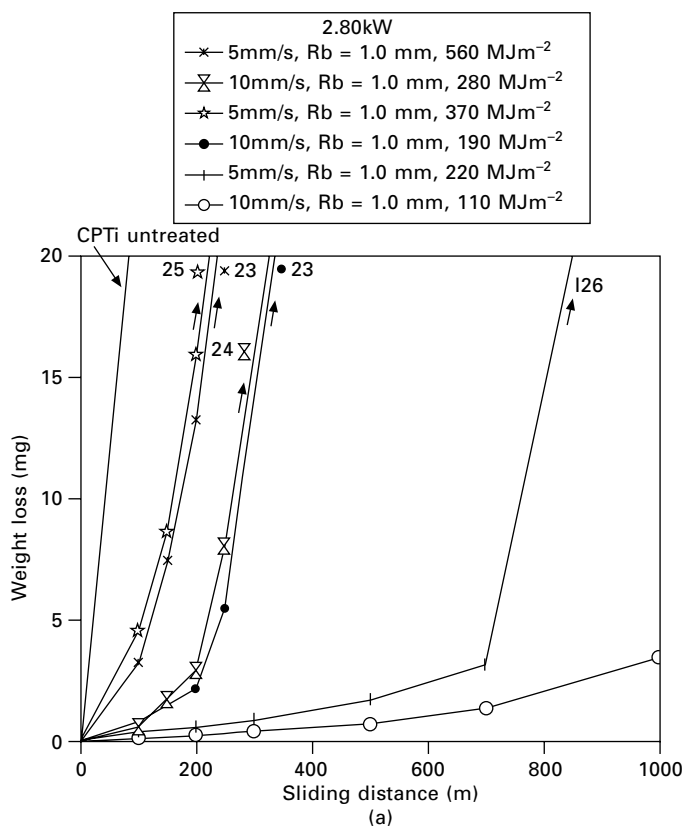
the untreated CPTi was 0.18 mg m^{-1} . Recently, Raaif *et al.* (2008) determined the sliding wear of laser nitrided Cp Ti for 40, 60 and 80%N atmospheres. They showed that μ decreased both with increasing load and %N. Baker *et al.* (1994) and Mridha and Baker (1997, 2007) looked in detail at the abrasive wear resistance of laser incorporated small SiC powders. Figure 12.21 shows that both processing conditions and powder volume fraction affect the weight loss. The best results are comparable with those of 100%N, Fig. 12.20. Also, combining laser nitriding with powder alloying using $6 \mu\text{m}$ SiCn gave excellent wear resistance to Ti-6Al-4V (Fig. 12.22).

The wear resistance developed by laser processing using intermetallic powders has been the subject of several investigations. Research by Majumdar *et al.* (2000), found that laser alloying of Ti-6Al-4V with Al, Si or Al+Si powders showed improved wear resistance in the order Ti(Si), Ti(Al+Si), Ti(Al) and CPTi. The rate of wear was a minimum in Ti(Si) and the improvements were considered to be due to $\text{Ti}_5\text{Si}_3 + \delta$ Ti eutectic following incorporation of the Si addition. In CPTi, an increase in μ was associated with severe adhesive wear and localized deformation, which was responsible for the formation and propagation of microcracks, while a gradual decrease or constant value of μ indicated that the wear was mainly

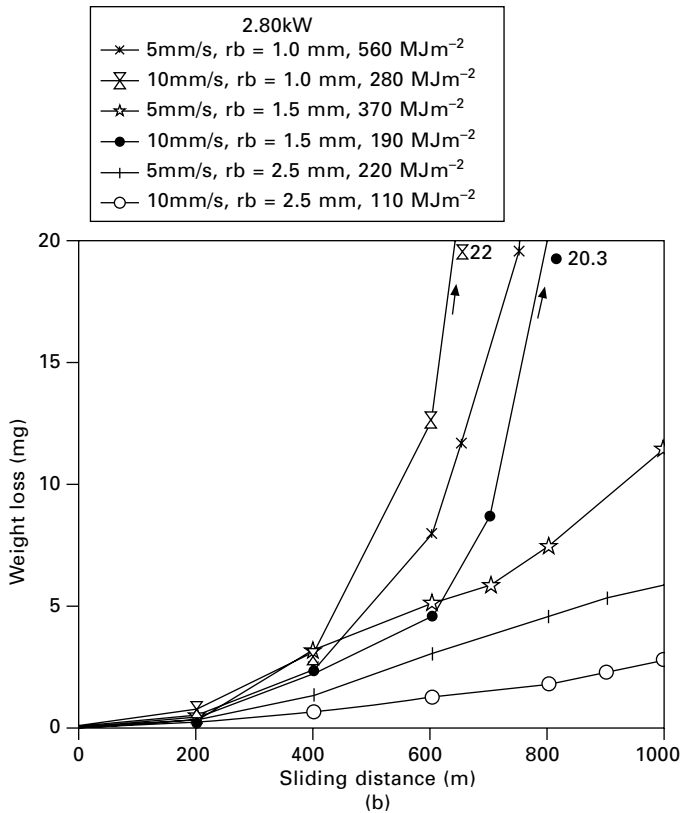


12.20 Weight loss versus sliding distance for specimens ground on 600 grit SiC paper for CPTi and Ti-6Al-4V alloys following laser nitriding (Xin and Baker, 1996).

abrasive in nature. Tian and co-workers laser synthesized a series of MMC coatings on titanium alloys, TiN/B/Si/Ni (2005b), TiB/TiB₂/Ti/TiNi (2005a), TiC/Ti₅Si₃/Ti (2006), and C/TiB/Ti (2006b). The TiN/B/Si/Ni (2005b) work showed the coating had a μ of ~ 0.4 , lower than that of the untreated alloy. Slightly higher hardness 1600–1700 HV_{0.1} values were found in the work on C/TiB/Ti powders (2006b), which developed coarse, needle TiB and dendritic TiC particles, conferring excellent dry sliding wear resistance. Dry sliding wear at RT of Ti-Al clad coatings on CPTi was studied by Guo *et al.* (2007). The best results were obtained from the clad 18 at%Al specimen, which was composed of α -Ti and α_2 -Ti₃Al. The hardness in all the clad specimens showed variations, but peaked at ~ 700 HV, which then gradually decreased to the substrate. This approach was extended to a study of TiN/Ti₃Al on CPTi by nitriding a coating of Al and Ti powders (Guo *et al.*, 2008a), and 40 vol%TiN, TiC or SiC powders, all mixed with Al powders



12.21 Weight loss versus sliding distance for specimens ground on 600 grit SiC paper of CPTi + (a) 5vol%SiC (b) 10vol% SiC (Baker *et al.*, 1994).

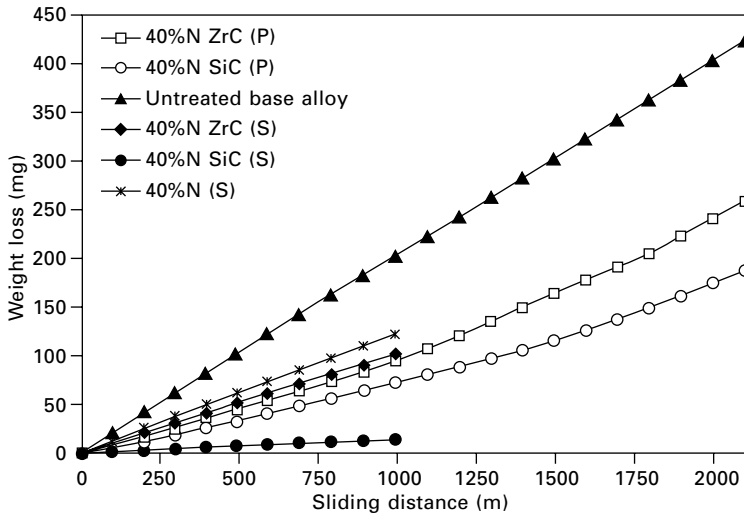


12.21 Continued

on CPTi, to give Ti₃Al (Pu *et al.*, 2008). The latter found that TiN/Ti₃Al and TiC/Ti₃Al coatings displayed the best wear resistance at a load of 5N, due to the presence of granular TiN/Ti₃Al/TiAl/Ti₂AlN₂/Ti₃AlN₂ phases, giving a surface hardness of 1124 HV.

In an attempt to form a hard amorphous coating, Zr-based alloy powders laser-clad on a pure Ti substrate were investigated by Wang *et al.* (2004). The un-lubricated coating showed a lower μ , 0.17–0.25, than that of the amorphous alloy, ~0.52, while the predominant wear mechanisms were abrasion and peeling. A series of papers (Wang *et al.*, 2000; Wang and Liu, 2002; Wang and Wang, 2004; Dong and Wang, 2008) have highlighted the combination of excellent tribological and corrosion properties of a multiphase structure consisting of a brittle Laves phase Ti₂Ni₃Si, toughened by a ductile NiTi phase. The properties were attributed to the chemical stability of the phases and their strong inter-atomic bonds.

A selection of relative wear loss values for CPTi and Ti-6Al-4V laser surface engineered surfaces is collated in Table 12.4.



12.22 Abrasive wear resistance of pulse (P) and continuous (S) CO₂ laser nitrided and powder alloyed Ti-6Al-4V (Hu *et al.*, 1999).

Table 12.4 Selection of relative wear loss values for CPTi and Ti-6Al-4V laser surface engineered surfaces

Alloy	Coating	Test	R	Reference
Ti-6Al-4V	Ti _p + Cr ₂ O _{3 p}	pin on disc - abrasive	4	Zang <i>et al.</i> (2001)
Ti-6Al-4V	100%N	" "	7.5	Xin and Baker (1996)
Ti-6Al-4V	100%N	dry sand/ rubber wheel abrasive	3	Yerramareddy and Bahadur (1992)
CPTi	100%N	pin on disc - abrasive	100	Xin and Baker (1996)
CPTi	33%N67%CO	dry sand/ rubber wheel abrasive	17	Grenier <i>et al.</i> (1997)
CPTi	10%SiC _p (3–6 μm)	pin on disc - abrasive	100	Baker <i>et al.</i> (1994)
CPTi	Ti ₃ Al _p	recip. ball on disc	1.86	Pu <i>et al.</i> (2008)
CPTi	Ti ₃ Al _p + 40%TiC _p (2–12 μm)	"	105	"
CPTi	Ti ₃ Al _p + 40%TiN _p (4–14 μm)	"	140	"
CPTi	Ti ₃ Al _p + 40%SiC _p (75–150 μm)	"	4.8	"

$$R = \text{Relative wear loss} = \frac{\text{wear loss of untreated alloy}}{\text{wear loss of laser surface coated alloy}}$$

(Because the testing conditions vary, R values can provide only an indication of the level of improvement in the wear)

12.7.4 Erosion of titanium alloys

Erosion is an accelerated form of attack, usually associated with high water or solid particle velocities and with local turbulence that removes the oxide film from the surface of metals, thus exposing bare metal to the corrodent. As a result of its ability to repair its protective oxide film quickly, titanium has an extremely high resistance to this form of attack. The erosion resistance of titanium alloys has been studied mainly from two aspects; firstly, resistance to solid particle erosion and secondly, resistance to water droplet impingement. Erosion of ductile metals is often the result of several simultaneous material removal mechanisms. Massoud and Coquerelle (1988) undertook erosion studies on Ti-6Al-4V alloy by impinging SiC particles onto the alloy surface at different angles. They found that the maximum rate of erosion coincided with an angle between 20 and 30°, which is well established for ductile metals, compared with 90° for brittle materials. Within this impingement angle range, impact craters were elongated in the direction of the particle motion and the predominant modes of erosion seem to be ploughing and cutting. At higher impingement angles, the main modes of erosion were deformation and extrusion of metal, to form a raised region around the crater. Many SiC particle fragments were embedded in the surface. Adherence of the target material to the eroding particle surface has been identified as an important material removal mechanism. Here, large Ti chips were adhered to SiC particles. No melting was observed in this work. The same features were recorded by Yerramarri and Bahadur (1991), again studying Ti-6Al-4V alloy impacted by SiC particles. Material removal was attributed to cutting, ploughing or pile-up leading to flake formation and separation, and lip fragmentation.

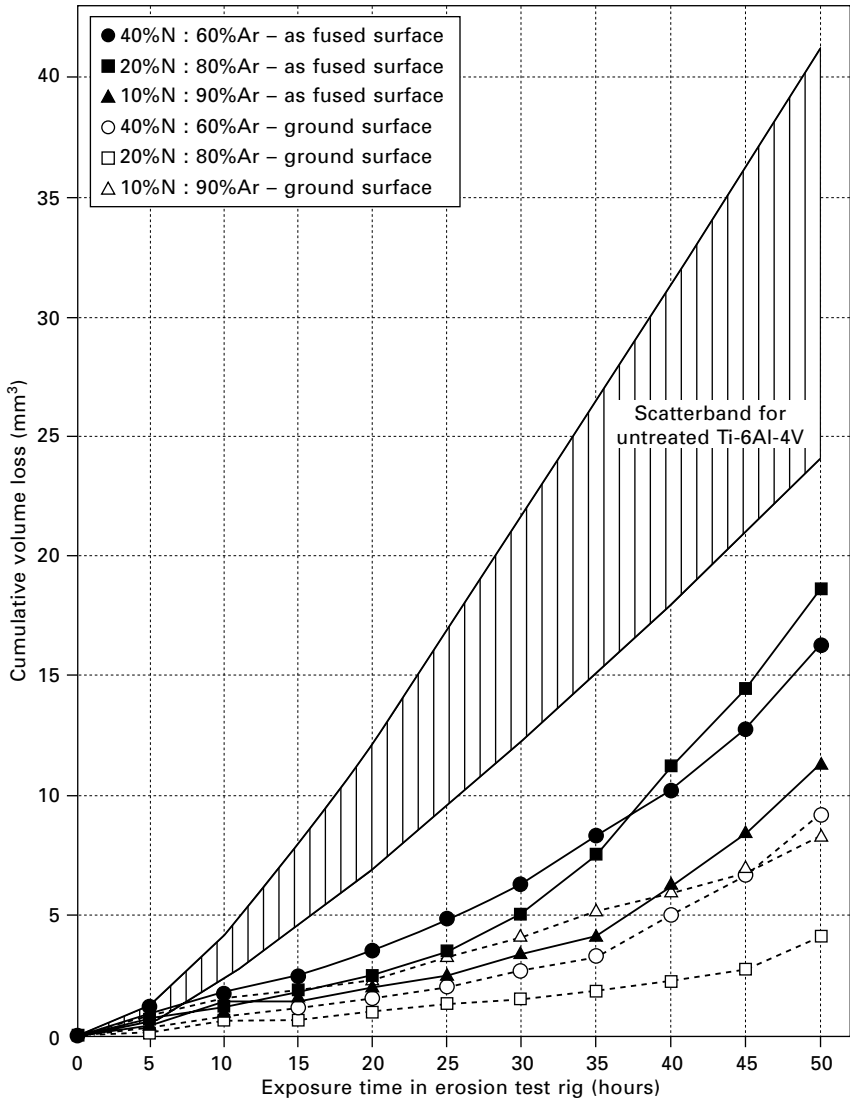
Erosion resistance of hard coatings

Singhal (1978) showed that TiB–TiN coatings were erosion resistant. Massoud and Coquerelle (1988) observed that the thickness of these nitrided coatings appeared to be crucial to the erosion resistance of laser nitrided titanium alloys. They found that laser nitrided surfaces had better erosion resistance than titanium nitride surfaces prepared by PVD, where spalling damage removed the TiN coating from the substrate after only a few impacts. However, hard dense coatings of TiB–TiN, 20 to 30 µm in thickness, with surface hardness of ~1400 HV, were rapidly damaged because of cracking due to the brittle nature of the layer, but thicker layers (80 µm) showed a slower erosion rate. Yerramarri and Bahadur (1991), again studying the effectiveness of laser surface modification on Ti-6Al-4V alloy, found that in their tests involving high velocity impacts by coarse SiC particles of 120 grit (100 µm), erosion of the surface produced deep craters which extended beyond the laser treated region for all the treatments. They concluded that laser treatments were ineffective in preventing severe erosion by coarse particles.

The ultrasonically-induced cavitation erosion in a 3.5% NaCl solution of laser nitrided CPTi and Ti-6Al-4V in a pure nitrogen atmosphere was considered by Man *et al.* (2003). They produced crack-free surfaces with a hardness of ~ 2000 HV, followed by a microstructure with a hardness of 800 HV retained to a depth of ~ 400 μm . The cavitation resistance was improved by twelve times following laser nitriding, and this was attributed to the increased surface hardness, which Neville and McDougall (2001) reported to be related to the erosion–corrosion resistance for Ti alloys.

Water droplet erosion

Laser nitriding using a CW CO₂ laser has been the most researched method of improving erosion resistance of Ti-6Al-4V alloy. Contrary to abrasion and sliding wear, hardness alone is not considered to be a major factor in effecting erosion resistance, as residual stress plays a major role in erosion resistance of TiN layers (Sue and Troue, 1988). Gerdes *et al.* (1995) showed that laser nitriding improved water droplet erosion resistance. More recently, Kasper *et al.* (2007) investigated the influence of percentage nitrogen on the erosion resistance of Ti-6Al-4V following water droplet testing. Again, they found an improvement once the nitrogen level was $>5\%$, but little difference in the cumulative volume loss for nitrogen levels between 9 and 25%. When the nitrogen content was $\leq 5\%$, the matrix was mainly martensitic α -Ti, and erosion proceeded along the boundaries of the martensitic needles, whereas with nitrogen $>5\%$, the microstructure consisted of small α -Ti grains with β -Ti between them, which eroded more rapidly. They attributed the best erosion resistance to the presence of a more homogeneous, crack-free microstructure. Two sets of researchers, Robinson and Reed (1995) with Robinson *et al.* (1995), and Hu *et al.* (1997b), used the same test rig to evaluate the water droplet erosion resistance of laser nitrided Ti-6Al-4V alloy. The conditions during testing were designed to approximate the actual operating conditions in the LP stage of a steam turbine, with a spray droplet size of ~ 100 μm . The impact velocity of ~ 500 ms^{-1} is well into the regime of impact velocities under which the wear mechanism is dominated by erosion alone (Coulon, 1986). Robinson and Reed (1995) compared three environments, Ar, 10%N + 90%Ar and 20%N + 80%Ar. They observed cracks after laser nitriding, but a significant reduction in the weight loss of the specimens laser nitrided in the 20% N. Hu *et al.* (1997a), using a spinning beam, extended the work to include nitriding under 60%Ar + 40%N. They also compared the effect of grinding 100–180 μm from the laser nitrided surfaces to give a smoother surface before testing. This would remove any TiN layer and expose the TiN + α -Ti microstructure to the erosion jets. Fig. 12.23 shows that grinding had a beneficial effect on the erosion resistance, thought to be due to reducing the level of the residual stress.



12.23 A comparison of water droplet erosion results from nitrided Ti-6Al-4V surfaces with and without grinding (Hu *et al.*, 1997a).

The solid particle and cavitation erosion of titanium aluminide intermetallic alloys was investigated by Howard and Ball (1995). They concluded that the γ -TiAl alloys they examined were more resistant to cavitation erosion than the super α_2 -TiAl alloy, while the particle erosion due to the impact of angular 120 grit ($\sim 100 \mu\text{m}$ dia.) SiC, of both types of TiAl alloys, was similar to that of 304 stainless steel.

12.7.5 Oxidation resistance

Hirose *et al.* (1993) were among the first to explore the oxidation resistance of laser alloyed titanium aluminides on CPTi. Testing at 1000°C, they found that the layer comprising TiAl_3 + TiAl had the best oxidation resistance. In other work, a laser synthesized TiN/B/Si/Ni coating on titanium alloys was shown by Tian *et al.* (2005) to be ~four times more resistant than the untreated alloy to oxidation after 70 h at 750°C. Liu and Wang (2006, 2007) found that the high temperature oxidation resistance, measured after 50 h at 1000°C, of 50:50 mixed powders of Ni-20wt-%Cr alloy and Cr_3C_2 was 2.5x superior to the untreated TiAl alloy. This was shown to be associated with the compact oxide scale consisting of $\text{TiO}_2/\alpha\text{-Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$, which protected the $\gamma/\text{Cr}_7\text{C}_3/\text{TiC}$ composite coating from excessive oxidation attack. Al-rich TiAl_3 layers have superior oxidation resistance at ~800°C to that of Ti alloys (Garcia *et al.*, 2002) as does TiC formed on $\gamma\text{-TiAl}$ alloyed with carbon (Chen and Wang, 2003).

12.8 Summary

Laser surface modifications to produce clad and surface-alloyed coatings on titanium alloys have been extensively studied. Laser nitriding has been widely investigated, but when high concentrations of nitrogen are used, cracking is invariably found, often penetrating from the surface to the substrate. Preheating, or the use of dilute nitrogen atmospheres, avoids cracking but at the expense of lower surface hardness and poorer wear properties. However, significant reductions in water droplet erosion have been recorded compared with that of the untreated titanium. Powders, incorporated via the gas-flow injection technique, or as a preplaced slurry, have been used to precipitate borides, carbides, nitrides and silicides, singly or in combination, sometimes with nitriding, as a means of producing a thick, hard, crack-free coating having good wear and high temperature oxidation resistance. It is concluded that different applications require different properties in the laser modified surfaces. Whereas high hardness is important for dry sliding wear resistance, strong bonding between the new phases developed during laser processing are important for abrasive wear resistance. On the other hand, improved hardness, but with a smooth surface with $R_a < 5 \mu\text{m}$, together with a low residual stress, provide the best combination for erosion resistant surfaces.

12.9 Acknowledgements

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12.10 Sources of further information and advice

Materials Property Handbook: Titanium Alloys, 1994, 1169–1176, ASM International, Materials Park, OH.

Laser Processing of Engineering Materials, J.C. Ion, 2005, 296, Elsevier, Amsterdam.

The Development of Turbine Materials, ed. G.W. Meetham, R.M. Duncan, P.A. Blenkinsop and R.E. Goosey, Applied Science Publishers, London, 1981, 63–87.

Wu X (2007), 'A review of laser fabrication of metallic engineering components and of materials', *Mater Sci Technol*, 23, 631–640 doi: 10.1179/174328407X179593

12.11 References

Abboud J H and West D R F (1989), 'Ceramic–metal composites produced by laser treatment', *Mat Sci Technol*, 5, 725–728.

Abboud J H and West D R F (1990), 'Laser surface alloying of titanium with aluminium', *J Mater Sci Lett*, 9, 308–310.

Abboud J H and West D R F (1991), 'Processing aspects of laser surface alloying of titanium with aluminium', *Mater Sci Technol*, 7, 353–356.

Abboud J H and West D R F (1991a), 'Martensite formation in Ti–Al layers produced by laser surface alloying', *Mat Sci Technol*, 7, 827–834.

Abboud J H and West D R F (1992), 'In situ production of Ti–TiC composites by laser melting', *J Mater Sci Lett*, 11, 1675–1677.

Abboud J H and West D R F (1994), 'Titanium aluminide composites produced by laser melting', *Mater Sci Technol*, 10, 60–68.

Abboud J H, Rawlings R and West D R F (1994), 'Functionally gradient layers of Ti–Al based alloys produced by laser alloying and cladding', *Mater Sci Technol*, 10, 414–419.

Abboud J H, West D R F and Rawlings R (1994a), 'Microstructure and properties of laser produced Ti–Al functionally gradient clad', *Mater Sci Technol*, 10, 848–953.

Abboud J H, Fidel A F and Benyounis K Y (2008), 'Surface nitriding of Ti–6Al–4V alloy with a high power CO₂ laser', *Optics and Laser Technol*, 40, 405–414. doi: 10.1016/j.optlastec.2007.07.005

Alhammad M, Esmacili S and Toyserkani E (2008), 'Surface modification of Ti–6Al–4V using laser-assisted deposition of a Ti–Si compound', *Surf Coat Technol*, 203, 1–8. doi: 10.1016/j.surfcoat.2008.06.160

Anthony T R and Cline H E (1977), 'Surface rippling induced by surface-tension gradients during laser surface melting and alloying', *J Appl Phys*, 48, 3888–3894.

Ayers J D (1981), 'Particulate composite surfaces by laser processing', in Mukherjee K and Majumdar J (eds) *Lasers in Metallurgy*, Met. Soc. AIME, Warrendale, Penn., 115–120.

Ayers J D, Schaffer R T and Robey W P (1981), 'A laser processing technique for improving the wear resistance of metals', *J Metal*, 33, 19–23.

Ayers J D and Bolster R N (1984), 'Abrasive wear with fine diamond particles of carbide containing aluminium and titanium surfaces', *Wear*, 93, 193–205.

- Badini C, Bianco M, Talentino S, Guo X B and Gianoglio C (1992), *Appl Surf Sci*, 54, 374–380.
- Baker T N, Xin H, Hu C and Mridha S (1994), 'Design of surface *in-situ* metal–ceramic composite formation via laser treatment', *Mat Sci Technol*, 10, 536–544.
- Baker T N and Selamat M S (2008), 'Surface engineering of Ti-6Al-4V by nitriding and powder alloying using CW CO₂ laser', *Mater Sci Technol*, 24, 189–200. doi: 10.1179/174328407X226563
- Banerjee R, Genç A, Collins P C and Fraser H (2004), 'Comparison of microstructural evolution in laser-deposited and arc-melted *in-situ* Ti-TiB composites', *Met Mat Trans*, 35A, 2143–2152.
- Bao R L, Yu H J, Chen C Z, Qi B and Zang L J (2006), 'Development of laser cladding wear-resistant coating on titanium alloys', *Surf Rev Lett*, 13, 645–654.
- Bell T, Bergmann H W, Lanagan J, Morton P H and Staines A M (1986), 'Surface engineering of titanium with nitrogen', *Surf Eng*, 2, 133–143.
- Bianco M, Tosto S, Pierdominici F and Casaccia C R E (1995), 'CO₂ Gaseous Alloying of Ti6Al4V by Means of a Pulsed Laser', in Sudarshan T S and Jeandin M (eds) *Surface Modification Technologies VIII*, Inst. Metals, 320–326.
- Buckley D H (1981), '*Surface Effects in Adhesion, Friction, Wear and Lubrication*', Elsevier Scientific, Amsterdam, p. 353.
- Cai L F, Zhang Y and Shi L (2007), 'Microstructure and formation mechanism of titanium matrix composites coating on Ti-6Al-4V by laser cladding', *Rare Metals*, 26, 342–346. doi: 10.1016/S1001-0521(07)60226-5
- Chan C, Mazumder J and Chen M M (1984), 'A two-dimensional transient model for convection in laser melted pool', *Metall Trans*, 15A, 2175–2184.
- Che-Haron C H (2001), 'Tool life and surface integrity in turning titanium', *J Mater Process Technol*, 118, 231–237. doi:10.1016/S0924-0136(01)00926-8
- Chen Y and Wang H M (2003), 'Microstructure and high-temperature wear resistance of a laser surface alloyed γ -TiAl with carbon', *Appl Surf Sci*, 220, 186–192. doi:10.1016/S0169-4332(03)00816-X
- Chen Y, Liu D, Li F and Li L (2008), 'WC_p/Ti-6Al-4V graded metal matrix composites layer produced by laser melt injection', *Surf Coat Technol*, 202, 4780–4787. doi:10.1016/j.surfcoat.2008.04.057
- Cline H E and Anthony T R (1977), 'Heat treating and melting material with a scanning laser or electron beam', *J Appl Phys*, 48, 3895–3900.
- Cooper K P and Slebodnick P (1989), 'Recent developments in laser melt/particle injection processing', *J Laser Applic*, 1, 21–29.
- Coulon P A (1986), 'Erosion-corrosion in steam turbines 11; A problem largely resolved', *Lubr Eng*, 42, 357–362.
- Courant B, Hantzperque J J, Avril L and Benayoun S (2005), 'Structure and hardness of titanium surfaces by pulsed laser melting with graphite addition', *J Mat Proc Tech*, 160, 374–381. doi: 10.1016/j.jmatprotec.2004.06.025
- Covelli L, Pierdominici F, Smurov I and Tosto S (1996), 'Surface microstructure of titanium irradiated by Nd:YAG pulsed laser in presence of carbon and nitrogen', *Surf Coat Tech*, 78, 196–204. doi:10.1016/0257-8972(94)02409-X
- Deng J and Braun M (1994), 'Tribological behaviour of TiN, TiC_xN_y and TiC coatings prepared by unbalanced magnetron sputtering techniques', *Surf Coat Tech*, 70, 49–56.
- Dong L X and Wang H M (2008), 'Microstructure and corrosion properties of laser-melted deposited Ti₂Ni₃Si/NiTi intermetallic alloy', *J Alloys Comps*, 465, 83–89. doi: 10.1016/j.jallcom.2007.10.065

- Draper C W and Ewing C A (1984), 'Laser surface alloying – a bibliography', *J Mater Sci*, 19, 3815–3825.
- Draper C W and Poate J M (1985), 'Laser surface alloying', *Int Met Rev*, 30, 85–107.
- Drechsler A, Kiese J and Wagner L (1999), 'A Comparison of the Effects of Shot Peening and Roller-burnishing on the Fatigue Performance of Titanium Alloys', A. Nakonieczny (ed.), *Proc 7th Int Conf on Shot Peening*, 145–152, Warsaw, Institute of Precision Mechanics.
- Duley W W (1983), *'Laser Processing and Analysis of Materials'*, Plenum Press, New York.
- Duraiselvan M, Galun R, Siegmans S, Wesling V and Mordike B L (2007), 'Investigation of hydroabrasive erosion of laser alloyed nickel and titanium based intermetallic matrix composites with TiC reinforcement', *Surf Eng*, 23, 425–430. doi:10.1179/174329407X260609
- Eskin S, Zahavi J and Berner A (1995), 'CO₂-Laser nitriding as a result of Ti coating modification in a nitrogen atmosphere. (1) Features of nitriding process', *Lasers Eng*, 4, 85–96.
- Ettaqi S, Hays V, Hantzpergue J J, Saindrenan G and Remy J C (1998), 'Mechanical, structural and tribological properties of titanium nitrided by a pulsed laser', *Surf Coat Technol*, 100–101, 428–432. doi:10.1016/S0257-8972(97)00664-6
- Flower H M, Walker A and West D R F (1985), 'The structure of Ti-6Al-4V laser surface alloyed with carbon', *Scripta Metal*, 9, 923–926.
- Garcia I, Fluente J de la and Damborenea J J de (2002), '(Ti, Al)/(Ti, Al)N coatings produced by laser surface alloying', *Mater Lett*, 53, 44–51. doi:10.1016/S0167-577X(01)00451-7
- Gates A S (1986), 'Composition, structure and wear resistance of TiAlOC coatings deposited by chemical vapour deposition', *J Vac Technol*, A4, 2707–2712.
- Gerdes C, Karimi A and Bieler H W (1995), 'Water droplet erosion and microstructure of laser-nitrided Ti-6Al-4V', *Wear*, 186–187, 368–374. doi:10.1016/0043-1648(95)07153-9
- Grenier M, Dubé D, Adnot A and Fiset M (1997), 'Microstructure and wear resistance of CP titanium laser alloyed with a mixture of reactive gases', *Wear*, 210, 127–135. doi:10.1016/S0043-1648(97)00043-4
- Guo B, Zhou J, Zhang S, Zhou H, Pu Y and Chen J (2007), 'Phase composition and tribological properties of Ti-Al coatings produced on pure Ti by cladding', *Appl Surf Sci*, 253, 9301–9310. doi:10.1016/j.apsusc.2007.05.056
- Guo B, Zhou J, Zhang S, Zhou H, Pu Y and Chen J (2008), 'Tribological properties of titanium aluminide coatings produced on pure Ti by laser alloying', *Surf Coat Technol*, 202, 4121–4129. doi:10.1016/j.surfcoat.2008.02.026
- Guo B, Zhou J, Zhang S, Zhou H, Pu Y and Chen J (2008a), 'Microstructure and tribological properties of *in situ* synthesized Ti/TiAl₃ intermetallic matrix composite coatings on titanium by laser cladding and laser nitriding', *Mater Sci Eng*, A 480, 404–410. doi:10.1016/j.msea.2007.07.01
- György E, del Pino A P, Serra P and Morenza J L (2003), 'Depth profiling characterisation of the surface layer obtained by pulsed Nd:YAG laser irradiation of titanium in nitrogen', *Surf Coat Technol*, 173, 265–270. doi:10.1016/S0257-8972(03)00520-6
- György E, Pérez del Pino A, Serra P and Morenza J L (2004), 'Influence of the ambient gas in laser structuring of the titanium surface', *Surf Coat Technol*, 187, 245–249. doi:10.1016/j.surfcoat.2004.03.015
- Heyman F J (1992), 'Liquid Impingement Erosion', in *Wear*, ASM Handbook, 18, 221–232.

- Hirose A, Ueda T and Kobayashi K F (1993), 'Wear and oxidation properties of titanium aluminides formed on titanium surface by laser alloying', *Mater Sci Eng*, A160, 143–153.
- Howard R L and Ball A (1995), 'The solid particle and cavitation erosion of titanium aluminide intermetallic alloys', *Wear*, 186–187, 123–128. doi:10.1016/0043-1648(95)07126-1
- Hu C, Mridha S, Uhbi H S, Holdway P, Bowen A W and Baker T N (1996), 'Hardness, Dendrite Population and Microstructure Under Different Nitrogen Environments in Laser Nitrided Ti-6Al-4V Alloy', P A Blenkinsop, W J Evans and H M Flower (eds), *Titanium'95 Science and Technology*, Institute of Materials, London, 1959–1966.
- Hu C and Baker TN (1996), 'Investigation of the temperature field developed by a spinning beam in laser processing', *Metall Mater Trans*, 27A, 4039–4047.
- Hu C and Baker TN (1997), 'Overlapping tracks to produce a continuous nitrided layer in Ti-6Al-4V alloy', *J Mater Sci*, 32, 2821–2826. doi:10.1023/A:1018664231410
- Hu C, Xin H and Baker T N (1997), 'Surface MMCs on Ti-6Al-4V alloy produced by combining laser nitriding and powder alloying', Scott M.L. (ed.), *Proceedings of the Eleventh International Conference on Composite Materials, Metal Matrix Composite and Physical Properties*, Woodhead Publishing, Abington, UK Vol. 3, 80–89.
- Hu C, Xin H and Baker T N (1997a), 'Effect of processing parameters on the microstructure and properties of laser nitrided Ti-6Al-4V', *Proceedings of EUROMAT '97 Conference*, Vol 3, 99–102.
- Hu C, Stalker W L, Conroy R D and Baker T N (1997b), 'Formation of a high erosion resistant Ti-6Al-4V alloy surface by laser nitriding', A Strang, W M Banks, R D Conroy and M J Goulette (eds), *Proc. Fourth International Charles Parsons Turbine Conference on Advances in Turbine Materials, Design and Manufacturing*, Inst Mater, London, 454–464.
- Hu C, Xin H, Watson L M and Baker T N (1997b), 'Analysis of the phases developed by laser nitriding Ti-6Al-4V alloys' *Acta mater*, 45, 4311–4322. doi:10.1016/S1359-6454(97)00076-1
- Hu C, Selamat M S B, Uhbi H S and Baker T N (1998), 'Characterisation of surface MMC layers developed in Ti-6Al-4V alloy using a combination of SiC_p and dilute nitrogen environment', *Mater Sci Tech*, 14, 1045–1052.
- Hu C and Baker TN (1999), 'The importance of preheat before laser nitriding a Ti-6Al-4V alloy', *Mater Sci Eng A*, 265, 268–275. doi:10.1016/S0921-5093(98)01135-6
- Inoue A, Zang T, Nishiyaman N, Ohbak K and Masumoto T (1993), 'Preparation of 16mm diameter rod of amorphous Zr65Al7.7 Ni10 Cu17.5 alloy', *Mater Trans JIM*, 34, 1234–1237.
- Inoue A (2000), 'Stabilization of metallic supercooled liquid and bulk amorphous alloys', *Acta Mater*, 48, 279–306. doi:10.1016/S1359-6454(99)00300-6
- Ion J C, Shercliff H R and Ashby M F (1992), 'Diagrams for laser materials processing', *Acta Metall Mater*, 40, 1539–1551.
- Ion J C (2005), *Laser Processing of Engineering Materials*, Elsevier, Amsterdam.
- Jiang P, He X L, Li X, Yu L G and Wang H M (2000), 'Wear resistance of a laser surface alloyed Ti-6Al-4V alloy', *Surf Coat Technol*, 130, 24–28. doi:10.1016/S0257-8972(00)00680-0
- Jianglong L, Qiquan L and Zhirong Z (1993), 'Laser gas alloying of titanium alloy with nitrogen', *Surf Coat Technol*, 57, 191–195.
- Kasper J, Bretschneider J, Jacob S, Bonß S, Winderlich B and Brenner B (2007), 'Microstructure, hardness and cavitation erosion behaviour of Ti-

- 6Al-4V laser nitrided under different atmospheres', *Surf Eng*, 23, 99–106. doi:10.1179/174329407X169430
- Katayama S, Matsunawa A, Morimoto A, Ishimoto S and Arata Y (1983), 'Surface hardening of titanium by laser nitriding', ICALEO (1983), *Proceedings of the Fifth International Conference on Applied Laser Electro-Optics*, Laser Institute of America, 127–134.
- Katayama S, Matsunawa A, Morimoto A, Ishimoto S and Arata Y (1984), 'Surface hardening of titanium by laser nitriding', *Conf. Proc Laser Processing Materials*, Los Angeles, 159–166.
- Kloosterman A B and De Hosson J Th M (1995), 'Microstructural characterization of laser nitrided titanium', *Scripta Metall Mater*, 33, 567–573. doi:10.1016/0956-716X(95)00238-Q
- Kloosterman A B, Kool B J and De Hosson J Th M (1998), 'Electron microscopy of reaction layers between SiC and Ti-6Al-4V after laser embedding', *Acta Mater*, 46, 6205–6217. doi:10.1016/S1359-6454(98)00265-1
- Konstantino E and Altus E (1999), 'Fatigue life enhancement by laser surface treatment', *Surf Eng*, 15, 126–128. doi:10.1179/026708499101516461
- Kool B J, Kabel M, Kloosterman A and De Hosson J Th M (1999), 'Reaction layers around SiC particles in Ti: An electron microscopy study', *Acta mater* 47, 3105–3116. doi:10.1016/S1359-6454(99)00151-2
- Kustas F M and Misra M S (1994), 'Friction and Wear of Titanium alloys', *Material Property Handbook: Titanium Alloys*, ASM International, Materials Park, OH, 1169–1176.
- Langlade C, Vannes A B, Krafft J M and Martin J R (1998), 'Surface modification and tribological behaviour of titanium and titanium alloys after YAG-laser treatments', *Surf Coat Technol*, 100–101, 383–387. doi:10.1016/S0257-8972(97)00653-1
- Liu X B and Wang H M (2006), 'Modification of tribology and high temperature behaviour of Ti-48Al-2Cr-2Nb intermetallic alloy by laser cladding', *Appl Surf Sci*, 252, 5735–5744. doi: 10.1016/j.apsusc.2005.07.064 2006
- Liu X B and Wang H M (2007), 'Microstructural and tribological properties of laser clad $\gamma\text{Cr}_7\text{C}_3/\text{TiC}$ composite coatings on $\gamma\text{-TiAl}$ intermetallic alloy', *Wear*, 262, 514–521. doi: 10.1016/j.wear.2006.06.012
- Liu X B and R L Yu (2007a), 'Effects of La_2O_3 on microstructure and wear properties of laser clad $\gamma\text{Cr}_7\text{C}_3/\text{TiC}$ composite coatings on TiAl intermetallic alloy', *Mater Chem Phys*, 10, 448–454. doi:10.1016/j.matchemphys.2006.08.013
- Liu X B and R L Yu (2007b), 'Microstructure and high-temperature wear and oxidation resistance of laser clad $\gamma/\text{W}_2\text{C}/\text{TiC}$ composite coatings on TiAl intermetallic alloy', *J Alloys and Cmps*, 439, 279–286. doi: 10.1016/j.jallcom.2006.08.065
- Majumdar J D, Weisheit B L, Mordike B L and Manna I (1999), 'Laser surface alloying of Ti with Si, Al and Si plus Al for an improved oxidation resistance', *Mater Sci Eng A*, 266, 123–134. doi:10.1016/S0921-5093(99)00045-3
- Majumdar J D, Mordike B L and Manna I (2000), 'Friction and wear behavior of Ti following laser surface alloying with Si, Al and Si plus Al', *Wear*, 242, 18–27. doi:10.1016/S0043-1648(00)00363-X
- Majumdar J D, Manna I, Kumar A, Bhargava P and Nath A K (2009), 'Direct laser cladding of Co on Ti-6Al-4V with a compositional graded interface', *J Mater Proc Technol*, 209, 2237–2243. doi:10.1016/j.jmatprotec.2008.05.017.
- Man H C, Zhang S, Cheng F T and Yue T M (2001), 'Microstructure and formation mechanism of *in situ* synthesized TiC/Ti surface MMC on Ti-6Al-4V by laser cladding', *Scripta Mater* 44, 2801–2807. doi:10.1016/S1359-6462(01)00977-0

- Man H C, Cui Z D, Yue T M and Cheng F T (2003), 'Cavitation erosion behavior of laser gas nitrided Ti and Ti-6Al-4V alloy', *Mater Sci Eng*, A355, 167–173. doi:10.1016/S0921-5093(03)00062-5
- Massoud J P and Coquerelle G (1988), 'High power laser surface treatments on Ti-6Al-4V in order to improve its erosion resistance', P. Lacombe *et al.* (eds) *6th World Conf. on Titanium*, 1847–1852, Les Editions de Physique, Les Ulis Cedex, France.
- Mehlmann A, Dirfeld S F and Minkoff I (1990), 'Laser-melt injection of B₄C on titanium', *Surf Coat Technol*, 42, 275–281. doi:10.1016/0257-8972(90)90158-9
- Meng Q, Geng L and Ni D (2005), 'Laser cladding NiCoCrAlY coating on Ti-6Al-4V', *Mater Lett*, 59, 2774–2777. doi:10.1016/j.matlet.2005.03.056
- Miyoshi K and Buckley D H (1982), 'Adhesion and friction of transition-metals in contact with non-metallic hard materials', *Wear*, 77, 253–264.
- Miyoshi K and Buckley D H (1984), 'Correlation of tensile and shear strengths of metals with their frictional properties' *ASLE Trans*, 27, 15–23.
- Molian P A and Hualun L (1989), 'Laser cladding of Ti-6Al-4V with BN for improved wear performance', *Wear*, 130, 337–352.
- Mordike B L (1985), 'Laser gas alloying', Draper C W and Mazzoldi P (eds), *Laser Surface Treatment of Metals*, 389–412, Martinus Nijhoff, Dordrecht.
- Morris D G (1988), 'Glass forming conditions during laser surface melting', *Mater Sci Eng*, 97, 177–180.
- Morton P H, Bell T, Weisheit A, Kroll J, Mordike B L and Sagoo K (1992), 'Laser gas nitriding of titanium and titanium alloys', Sudarshan T S and Braza J F (eds), *Surface Modification Technologies V*, Inst Mater, 593–609.
- Moskowitz D, Turner L L and Hamenik M Jr (1986), 'Some physical and metal cutting properties of titanium carbonitride base materials', Almond E A, Brookes C A and Warren R (eds), *Science of Hard Materials*, Inst Phys Conf Ser No 75, Adam Hilger, Bristol, p. 605.
- Mridha S and Baker T N (1991), 'Characteristic features of laser-nitrided surfaces of two titanium alloys', *Mater Sci Eng*, A142, 115–124. doi:10.1016/0921-5093(91)90760-K
- Mridha S, Ubhi H S, Holdway P, Baker T N and Bowen A W (1993), 'Metal–ceramic composite layer formation on titanium surface through laser treatment', Froes FH and Caplan IL (eds), *Proceedings of the Seventh International Conference on Titanium, Titanium '92 Science and Technology Conference*, Vol III, pp 2641–2648, TMS Warrendale.
- Mridha S and Baker T N (1994), 'Crack-free hard surfaces produced by laser nitriding of commercial purity titanium', *Mater Sci Eng* A188, 229–239. doi:10.1016/0921-5093(94)90376-X
- Mridha S and Baker T N (1994a), 'Surface cracking in laser-nitrided titanium of commercial purity and possible ways of reducing these defects', *Proc Adv Mater*, 4, 85–94.
- Mridha S and Baker T N (1996), 'Metal matrix composite layers formed by laser processing of commercial purity Ti-SiC_p in nitrogen environment', *Mat Sci Technol*, 12, 595–602.
- Mridha S, Hu C, Ubhi H S, Bowen A W and Baker T N (1996), 'Characteristic features of the MMC layer formed on Ti-6Al-4V(IMI318) alloy surfaces through laser treatment by using SiC powder injection and preplacement techniques', P A Blenkinsop, W J Evans and H M Flower (eds), *Titanium '95 –Science and Technology*, Institute of Materials, London, 2835–2842.
- Mridha S and Baker T N (1997), 'Metal matrix composite layer formation with 3 µm

- SiC_p powder on IMI318 titanium alloy surfaces through laser treatment', *J Mat Proc Tech*, 63, 432–437. doi:10.1016/S0924-0136(96)02660-X
- Mridha S and Baker T N (1998), 'Effects of nitrogen gas flow rate on the microstructure and properties of laser nitrided IMI318 titanium alloy (Ti-6Al-4V)', *J Mat. Proc Tech*, 77, 115–121. doi:10.1016/S0924-0136(97)00408-1
- Mridha S and Baker T N (2007), 'Incorporation of 3 μm SiC_p into titanium surfaces using a 2.8kW laser beam of 186 and 373MJm⁻² energy densities in a nitrogen environment', *J Mat Proc Tech*, 185, 38–45. ISSN: 0924-0136. doi:10.1016/j.jmatprotec.2006.03.110
- Munteanu D and Vaz F (2006), 'The influence of nitrogen content on the properties of TiN_x thin films', *J Optoelect Adv Mater*, 8, 720–725.
- Nalla R K, Altenberger L, Noster U, Liu G Y, Scholtes B and Richie R O (2003), 'On the influence of mechanical surface treatments – deep rolling and laser shock peening – on the fatigue behavior of Ti-6Al-4V at ambient and elevated temperatures', *Mater Sci Eng*, 355A, 216–230. doi:10.1016/S0921-5093(03)00069-8
- Neville A and McDougall B A B (2001), 'Erosion and cavitation-corrosion of titanium and its alloys', *Wear*, 250, 726–735. doi:10.1016/S0043-1648(01)00709-8
- Nwobo A I P, Rawlings R D and West D R F (1999), 'Nitride formation in titanium based substrates during laser surface melting in nitrogen–argon atmospheres', *Acta Mater*, 47, 631–643. doi:10.1016/S1359-6454(98)00369-3
- Pang W, Man H C and Yue T M (2005), 'Laser surface coating of Mo-WC metal matrix composite on Ti6Al4V alloy', *Mat Sci Eng*, A390, 144–153. doi:10.1016/j.msea.2004.07.065
- Pei Y T, Ocelik V and De Hosson J Th M (2002), 'SiCp/Ti6Al4V functionally graded materials produced by laser melt injection', *Acta Mater*, 50, 2035–2051. doi:10.1016/S1359-6454(02)00049-6
- Peng T C, Sastry S M L, O'Neal J E and Tesson J F (1983), 'A correlation between dendrite-arm spacing and cooling rate for laser-melted Ti-15V-3Al-3Sn-3Cr', E A Metzbow, (ed.) *Lasers in Materials Processing*, 241–246, Amer Soc Metals, Metals Park, OH.
- Perry A J, Sharkeev Y P, Geist D E and Fortuna S V (1999), 'Dislocation network developed in titanium nitride by ion implantation', *J Vac Sci Technol A*, 17A, 1848–1853.
- Poletti C, Balog M, Schubert T, Liedtke V and Edtmaier C (2008), 'Production of titanium matrix composites reinforced with SiC particles', *Compos Sci Technol.*, 68, 2171–2177. doi:10.1016/j.compscitech.2008.03.018
- Pu Y P, Guo B G, Zhou J S, Zang S, Zhou H and Chen J (2008), 'Microstructure and tribological properties of *in situ* synthesized TiC, TiN, and SiC reinforced Ti₃Al intermetallic matrix composite coatings on pure Ti by laser cladding', *Appl Surf Sci*, 255, 2697–2703. doi:10.1016/j.apsusc.2008.07.180
- Raaf M, El-Hossary F M, Negm N Z, Khalil S M, Kolitsch A, Höche D, Kasper J, Mändl S and Schaaf P (2008), 'CO₂ laser nitriding of titanium', *J Phys D:Appl Phys.*, 41, 085208 (8pp)
- Ribeiro M V, Moréira M R V and Ferreira J R (2003), 'Optimization of titanium alloy (6Al-4V) machining', *J Mater Proc Technol*, 143–144, 458–463. doi:10.1016/S0924-0136(03)00457-6
- Robinson J M, Anderson S, Knutsen R D and Reed R C (1995), 'Cavitation erosion of laser melted and laser nitrided Ti-6Al-4V', *Mater Sci Technol*, 11, 611–618.
- Robinson J M and Reed R C (1995), 'Water droplet erosion of laser surface treated Ti-6Al-4V', *Wear*, 186–187, 360–367. doi:10.1016/0043-1648(95)07131-8

- Robinson J M, Van Brussel B A, De Hosson J Th M and Reed R C (1996), 'X-ray measurement of residual stresses in laser melted Ti-6Al-4V alloy', *Mater Sci Eng*, A208, 143–147. doi:10.1016/0921-5093(95)10158-6
- Santos E C, Morita M, Shiomi M, Osakada K and Takahashi M (2006), 'Laser gas nitriding of pure titanium using CW and pulsed Nd:YAG lasers', *Surf Coat Technol*, 201, 1635–1642. doi:10.1016/j.surfcoat.2006.02.048
- Schaaf P (2002), 'Laser nitriding of metals', *Prog Mater Sci*, 47, 1–161. doi:10.1016/S0079-6425(00)00003-7
- Schüssler A, Steen P H and Ehrhard P (1992), 'Laser surface treatment dominated by buoyancy flows', *J Appl Phys*, 71, 1972–1975.
- Selemat M S, Baker T N and Watson L M (2001), 'Study of the surface layer formed by laser processing of Ti-6Al-4V alloy in a dilute nitrogen atmosphere', *J. Mater Proc Technol*, 113, 509–515. doi:10.1016/S0924-0136(01)00595-7
- Selemat M S, Watson L M and Baker T N (2003), 'XRD and XPS studies of surface MMC layer of SiC reinforced Ti-6Al-4V alloy', *J. Mater Proc Technol*, 142, 725–737. doi:10.1016/S0924-0136(03)00814-8
- Selemat M S, Watson L M and Baker T N (2006), 'XRD and XPS studies of surface MMC layers developed by laser alloying Ti-6Al-4V using a combination of a dilute nitrogen environment and SiC powder', *Surf. Coat Technol*, 20, 724–736. doi:10.1016/j.surfcoat.2005.12.038.
- Selvan J S, Subramanian K, Nath A K, Kumar H, Ramachandra C and Ravindranathan S P (1999), 'Laser boronising of Ti-6Al-4V as a result of alloying with preplaced BN', *Mater Sci Eng*, A260, 178–187. doi:10.1016/S0921-5093(98)00964-2
- Selvan J S, Subramanian K, Nath A K (1999a), 'Laser surface alloying of (pre-placed) SiC and Ni-SiC coating on commercially pure titanium', *Mater Manufact Proc*, 14, 285–296.
- Selvan J S and Subramanian K (2003), 'High temperature thermal barrier coating formation by laser alloying of CP-Ti with pre-placed Ni-SiC coating', *J Mater Sci*, 38, 4783–4801.
- Shercliff H R and Ashby M F (1991), 'The prediction of case depth in laser transformation hardening', *Metall Trans*, 22A, 2459–2466.
- Singhal S C (1978), 'An erosion-resistant coating for titanium and its alloys', *Thin Solid Films*, 53, 375–381.
- Sproul W D, Rudick P J and Graham M E (1989), 'The effect of N₂ partial pressure, deposition rate and substrate bias potential on the hardness and texture of reactively sputtered TiN coatings', *Surf Coat Technol*, 39–40, 355–363. doi:10.1016/0257-8972(89)90068-6
- Steen P H, Ehrhard P and Schüssler A (1994), 'Depth of melt pool and heat-affected zone in laser surface treatments', *Metall Mater Trans*, 25A, 427–435.
- Sue J A and Troue H H (1988), 'Influence of residual compressive stress on erosion behaviour of arc evaporation titanium nitride coating', *Surf Coat Tech*, 36, 695–705. doi:10.1016/0257-8972(88)90010-2
- Sun R L, Yang D Z, Guo L X and Dong S L (2000), 'Microstructure and wear resistance of NiCrBSi laser clad layer on titanium alloy substrate', *Surf Coat Tech*, 132, 251–255. doi:10.1016/S0257-8972(00)00904-X
- Sun R L, Yang D Z, Guo L X and Dong S L (2001), 'Laser cladding of Ti-6Al-4V alloy with TiC and TiC + NiCr + BSi powders', *Surf Coat Tech*, 135, 307–312. doi:10.1016/S0257-8972(00)01082-3
- Sun R L, Mao J F and Yang D Z (2002), 'Microscopic morphology and distribution of

- TiC phase in laser clad NiCrBSiC-TiC layer on titanium alloy substrate', *Surf Coat Technol*, 155, 203–207. doi:10.1016/S0257-8972(02)00006-3
- Sun R L, Yang D Z, Guo L X and Dong S L (2002a), 'Microstructural characterization of NiCr1BSiC laser clad layer on titanium alloy substrate', *Surf Coat Tech*, 150, 199–204. doi:10.1016/S0257-8972(01)01512-2
- Tian Y S, Chen C Z, Li S T and Huo Q H (2005), 'Research progress on laser modification of titanium alloys', *Appl Surf Sci*, 242, 177–184. doi: 10.1016/j.apsusc.2004.08.011
- Tian Y S, Chen C Z, Wang D Y and Lei T Q (2005a), 'Surface modification of pure Ti by laser alloying with B and Ni mixed powders', *Adv Eng Mater*, 7, 629–632. doi: 10.1002/adem.200400221
- Tian Y S, Chen C Z, Wang D Y, Huo Q H and Lei T Q (2005b), 'Laser surface alloying of pure titanium with TiN-B-Si-Ni mixed powders', *Appl Surf Sci*, 250, 223–227. doi:10.1016/j.apsusc.2005.01.001
- Tian Y S, Chen C Z, Chen L X and Huo Q H (2006), 'Microstructures and wear properties of composite coatings produced by laser alloying Ti-6Al-4V with graphite and silicon mixed powders', *Mat Lett.*, 60, 109–113. doi: 10.1016/j.matlet.2005.07.082
- Tian Y S, Chen C Z, Chen L X and Huo Q H (2006a), 'Effect of RE oxides on the microstructure of the coatings fabricated on titanium alloys by laser alloying technique', *Scripta Mater*, 54, 847–852. doi:10.1016/j.scriptamat.2005.11.011
- Tian Y S, Chen C Z, Chen L B and Chen L X (2006b), 'Study on the microstructure and wear resistance of composite coatings fabricated on Ti-6Al-4V under different processing conditions', *Appl Surf Sci*, 253, 1494–1499. doi:10.1016/j.apsusc.2006.02.026
- Ubhi H S, Holdway P, Bowen A W and Baker T N (1988), 'The development of surface-modified microstructures in laser-treated titanium and titanium alloys', *Proc. 6th World Conference on Titanium*, pp 1687–1692, France.
- Vilar R (1999), 'Laser cladding' *J Laser Applic*, 11, 64–79.
- Walker A, Foulkes J, Steen W M and West D R F (1985), 'Laser surface alloying of titanium substrate with carbon and nitrogen', *Surf Eng*, 1, 23–29.
- Wang H M and Liu Y F (2002), 'Microstructure and wear resistance of laser clad Ti₅Si₃/NiTi₂ intermetallic composite coating on titanium alloy', *Mater Sci Eng*, A338, 126–132. doi:10.1016/S0921-5093(02)00076-X
- Wang Y, Li G, Wang C, Xia Y, Sandip B and Dong C (2000), 'Microstructure and wear resistance of NiCrBSi laser clad layer on titanium alloy substrate', *Surf Coat Tech*, 132, 251–255. doi:10.1016/S0257-8972(00)00904-X
- Wang Y F, Li G, Wang C, Xia Y, Sandip B and Dong C (2004), 'Microstructure and properties of laser clad Zr-based alloys coatings on Ti substrates', *Surf Coat Tech*, 176, 284–289. doi:10.1016/S0257-8972(03)00771-0
- Wang Y and Wang H M (2004), 'Wear resistance of laser clad Ti₂Ni₃Si reinforced intermetallic composite coatings on titanium alloys', *Appl Surf Sci*, 229, 81–86. doi: 10.1016/j.apsusc.2004.01.045
- Wu W L and Li X W (2006), 'Research progresses on laser cladding of titanium alloys', *Rare Metal Materials and Engineering*, 35, 850–854.
- Xin H and Baker T N (1996), 'The development of wear resistant surface on CPTi and Ti-6Al-4V alloys by laser nitriding', P A Blenkinsop, W J Evans and H M Flower (eds), *Titanium '95 Science and Technology*, Institute of Materials, London, 2031–2038.
- Xin H, Mridha S and Baker T N (1996), 'The effect of laser surface nitriding with a spinning beam on the wear resistance of commercial purity titanium', *J Mater Sci*, 31, 23–30. doi:10.1007/BF00355121
- Xin H, Watson L M and Baker T N (1998), 'Surface analytical studies of a laser nitrided

- Ti-6Al-4V Alloy: A comparison of spinning and stationary laser beam modes', *Acta Metall*, 46, 1949–1961.
- Xin H, Hu C and Baker T N (2000), 'Microstructural assessment of laser nitrided Ti-6Al-4V alloy', *J Mater Sci*, 35, 3373–3382. doi:10.1023/A:1004833018817
- Xue L, Islam A, Koul A K, Wallace W and Bibby M (1997), 'Laser gas nitriding of Ti-6Al-4V alloy', *Mater Manufac Proc*, 12, 799–817.
- Yamada M (1996), 'An overview on the development of titanium alloys for non-aerospace application in Japan', *Mater Sci Eng*, A213, 8–15. doi:10.1016/0921-5093(96)10241-0
- Ye H Q (1999), 'Recent developments in Ti₃Al and TiAl intermetallics research in China', *Mater Sci Eng*, A263, 289–295. doi:10.1016/S0921-5093(98)01159-9
- Yerramareddy S and Bahadur S (1992), 'The effect of laser surface treatments on the tribological behavior of Ti-6Al-4V', *Wear*, 142, 245–262.
- Yilbas B S, Hashmi M S J and Shuja S Z (2001), 'Laser treatment and PVD TiN coating of Ti-6Al-4V alloy', *Surf Coat Technol*, 140, 244–250. doi:10.1016/S0257-8972(01)01038-6
- Yilbas B S and Shuja S Z (2000), 'Laser treatment and PVD TiN coating of Ti-6Al-4V', *Surf Coat Technol*, 130, 152–157. doi:10.1016/S0257-8972(00)00715-5
- Zang S, Wu W T, Wang M C and Man H C (2001), 'In-situ synthesis and wear performance of TiC particle reinforced composite coating on alloy Ti6Al4V', *Surf Coat Technol*, 138, 95–100. doi:10.1016/S0257-8972(00)01133-6
- Zhecheva A, Sha W, Malinov S and Long A (2005), 'Enhancing the microstructure and properties of titanium alloys through nitriding and other engineering methods', *Surf Coat Technol*, 200, 2197–2207. doi:10.1016/j.surfcoat.2004.07.115

Laser surface modification of aluminium and magnesium alloys

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Abstract: Aluminium and magnesium alloys are choice materials for research, development and application of surface engineering techniques. Favoured for their low density and ease of fabrication, combined with good mechanical properties, they demonstrate a poor resistance to surface wear; and magnesium alloys are particularly susceptible to corrosion. Due to the flexibility and relative ease of control of laser processing techniques and the limited or negligible effect on the bulk material, the modification of surface properties by means of such methods has been extensively investigated. The range of laser surface processes applied to light alloys includes simple remelting of the alloy surface; remelting with the addition of alloying elements or ceramic particles; cladding with a layer of material having different properties; and shock processing to create residual stresses in the surface.

Key words: Aluminium alloys, magnesium alloys, laser alloying, laser cladding, surface particle composites, laser shock processing.

13.1 Introduction

Aluminium and magnesium alloys have found application in the transport industry due to their low density and ease of fabrication. However, they have poor tribological properties in terms of resistance to surface wear. Although aluminium alloys have good resistance to corrosion, magnesium alloys are particularly susceptible. In addition, there is no martensitic hardening in Al and Mg alloys and hence they cannot be deep-case hardened by induction hardening or carburising/quenching, as used for steel. Thus they are choice materials for the application of energy beam surface engineering procedures, and due to the flexibility and relative ease of control, laser assisted surface engineering processes have been extensively investigated.

The range of laser surface engineering processes applied to light alloys can be subdivided into two groups: laser surface modification by remelting (with or without the addition of material), and laser shock processing. The former, and more extensive, requires remelting of the alloy surface to a depth limited by process parameters, together with a change in material structure or composition. Following a brief section on general considerations on the laser processing of light alloys, this chapter will proceed to deal with laser remelting processes, which favourably alter the properties of the surface. The subsequent section will describe laser beam alloying, in which the

composition of the remelted surface is modified by the addition of alloying material. Laser beam cladding, in which the surface is melted to bond to a new surface layer of material deposited over it, is considered next. This first group of processes will be concluded by a section on alloying and cladding processes that produce composite surfaces reinforced with ceramic particles.

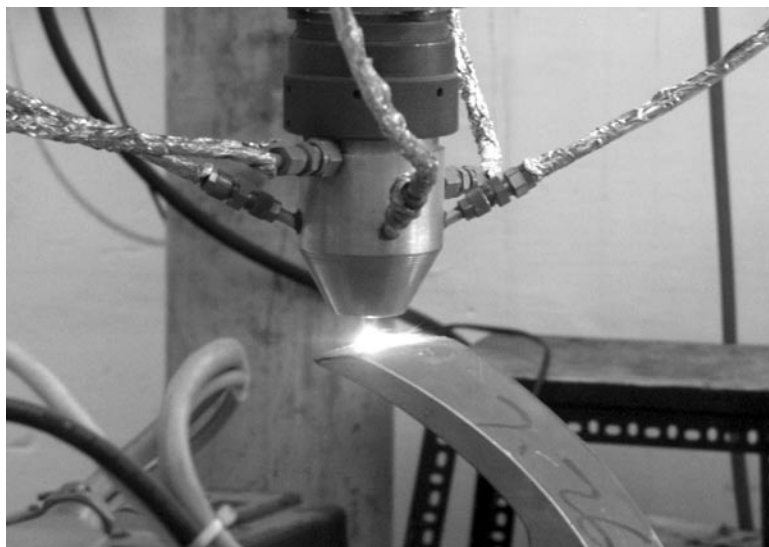
The second and less extensive group includes laser shock processing techniques, which create residual stresses in the surface that affect the mechanical properties of the material. Current and potential research trends will conclude this chapter.

13.2 General considerations on the laser processing of light alloys

Laser surface processing of materials includes a wide variety of additive, mutative or subtractive processes. Most of these are applied to high performance metal alloys or to composites with a metal matrix. Titanium, aluminium and magnesium alloys combine high performance with low density, and the potential for surface modification or augmentation by means of laser processing, combined with the limited or negligible effect of these processes on the bulk material, has contributed to the high interest generated in them. Aluminium and magnesium alloys will be considered in this chapter, whilst titanium alloys are considered in Chapter 12. To date, the laser treatment of aluminium alloys has featured more prominently in peer-reviewed publications and conferences than the laser treatment of magnesium alloys.

Laser treatment offers high-precision control over the process and the dimensions of the treated zone. Complex, three-dimensional surfaces can be treated with relative ease (Fig. 13.1) by means of Computer Numerical Control (CNC) (Wu, 2008); the treatment can be applied to selected areas, and thus only where required. CNC laser systems are highly versatile, and can be applied to a range of processes instead of being dedicated to a specific application. Competing processes such as electrochemical plating, conversion coating, anodizing, gas-phase deposition processes and the application of organic coatings (Gray and Luan, 2002) offer less flexibility than laser processes. Other processes which are in more direct competition with laser alloying and cladding include thermal spraying processes (Chapter 7). These generally require less expensive equipment, but the integrity of the coating produced by laser processes is higher; precision is higher in laser processes, and the distortion in the component equivalent or less (Ion, 2005, p. 299).

As indicated in Chapter 12, the field of laser processing is dominated by CO₂ and Nd:YAG lasers, with the former being the first to be applied and the latter increasing in popularity as their power output increased with time, due to the higher absorptivity of their wavelength by metal alloys (although



13.1 CNC laser beam cladding over a complex surface.

this is less significant for Al alloys than for steels) (Modest, 2001). Laser shock processing could only be developed once pulsed Nd:YAG lasers were available, due to the requirement for high-frequency, short-pulse laser impulses which cannot be produced by a CO₂ laser. Diode and excimer lasers are now providing competition to both of these. Table 13.1 indicates the applications identified for different types of laser in the literature.

The other system components required include material support, retention and movement systems, which are usually based on three or more axis CNC systems; and the optical components used to deliver the beam to the required location and focus it, which may include Mo-coated, water-cooled copper mirrors, ZnSe lenses, and, in the case of Nd:YAG, diode and other shorter wavelength lasers, optic fibres. In the case of laser shock treatment, the component is submerged under a shallow depth of water, and thus a containment system is required. Preplaced deposition of powder for alloying and cladding processes using a bonding agent such as polyvinyl alcohol (as used, for example, by Jaffar *et al.*, 2005) is gradually falling in disfavour, and is being replaced by direct delivery or by other pre-process coating methods such as electroless deposition (Yang *et al.*, 2005; Cui *et al.*, 2008; Gordani *et al.*, 2008; Razavi *et al.*, 2008); sol-gel coating (López *et al.*, 2009); or by thermal spray deposition (Shibata and Matsuyama, 2000) or plasma spray deposition (Carroll *et al.*, 2001).

For direct deposition laser alloying and cladding, a material delivery system transporting wire or powder is usually used, the latter being more popular due to greater ease and flexibility of application when depositing

Table 13.1 Lasers used for surface engineering of light alloys

Laser type	Applications	Alloys
CO ₂	Remelt	Aluminium Magnesium
	Alloying	Aluminium Magnesium
	Cladding	Aluminium Magnesium
	Composite surface	Aluminium Magnesium
Nd:YAG	Remelt	Aluminium Magnesium
	Alloying	Aluminium Magnesium
	Cladding	Aluminium Magnesium
	Composite surface	Aluminium Magnesium
	Shock processing Surface cleaning	Aluminium
Diode 940nm	Remelt	Aluminium
Diode*		Magnesium
Diode 940nm	Cladding	Aluminium
Excimer KrF 248nm	Remelt	Aluminium
Excimer XeCl 308nm		Magnesium
Excimer*		Magnesium

*Wavelength not specified

in complex patterns, and a far wider range of material availability, further enhanced by the possibility of blending powders.

Lateral powder delivery, as used by Ignat *et al.* (2004a) for the cladding of WE43 and ZE4 magnesium alloys with Al powder, and by Yang and Wu (2009) for the cladding of AZ91D Mg alloy with Al and Si powder, provides a cheap and simple method of powder delivery. Coaxial delivery is, however, generally preferred as the rate of powder deposited per unit area is, in this case, not altered by a change in direction of motion causing a variation in the relative velocities of the powder stream and the component being treated (as in the case of lateral deposition methods, including wire material delivery). A coaxial delivery head with powder delivery apertures surrounding the laser beam exit aperture is shown in Fig. 13.2. For all powder delivery techniques, a powder feeder with a variable powder metering system and a gas–powder transport system are required. In some cases, processes are carried out in sealed enclosures that contain an inert atmosphere, preventing reaction with atmosphere gases and also enclosing powder and metal fumes.



13.2 Coaxial nozzle showing flow of powder, with laser beam off.

These components of laser processing and other equipment, including safety equipment and process monitoring and control systems, will not be considered in detail here.

13.3 Laser surface remelting of light alloys

Laser surface remelting of aluminium alloys requires the application of a laser beam in pulsed or continuous wave (constant power with time) mode to melt a shallow depth of the material surface and allow it to resolidify by quenching by the cooler bulk of the material once the laser beam has moved on. An inert atmosphere is required if any form of reaction (usually with atmospheric oxygen or nitrogen) is to be avoided (Lindner *et al.*, 1990), and this is achieved by using a jet of shielding gas or by carrying out the process in a controlled enclosed environment. The laser remelting (or melting) process produces three beneficial results in the re-solidified material: grain refinement; a more homogeneous redistribution of alloying elements within the alloy; and the creation of intermetallic phases resulting from reactions of alloying metals in the laser-created molten pool (Ion, 2005). Grain refinement can increase surface hardness and the resistance to wear, factors of major importance for aluminium alloys (Chapter 2). The creation of intermetallic phases can produce a similar result, but this is more effectively produced by the addition of alloying elements by means of laser beam alloying. Homogenization is usually beneficial to corrosion resistance as a consequence of the elimination of isolated phases of alloying

elements from grain boundaries and their uniform dispersion by convection in the melt pool.

13.3.1 Laser surface remelting of Al alloys

Although aluminium alloys are difficult to process due to their high thermal conductivity and diffusivity, and the high reflectance at laser wavelengths (Lindner *et al.*, 1990; Joshi and Sundararajan, 1998), the potential improvement of tribological properties has encouraged research in this field. Ion (2005, p. 273) reports 35 studies carried out between 1979 and 2003 on remelting (and in some cases alloying) of Al alloys, using mainly CO₂ lasers. Although alloying and the introduction of ceramic particles can provide a greater increase in hardness, remelting remains popular due to the relative simplicity of the process, which requires no infrastructure for the addition of material.

Laser melting and resolidification of a material surface produces residual stresses due to the rapid cooling. The application of a CO₂ laser beam both in Continuous Wave (CW) (Liu *et al.*, 2005a) and Pulsed modes (Tsagkarakis *et al.*, 2002) could result in cracking in laser remelting processes. Liu *et al.* (2005a) reported cracking along grain boundaries due to the high thermal stress produced by fast scanning speeds, above 50 mm s⁻¹, avoided by using lower traverse rates. Tsagkarakis *et al.* (2002) encountered cracking across the depth of the melted zone for melted spots produced with interaction times greater than 100 µs. These were eliminated by the application of shorter pulses producing shallower melting zones; this also resulted in a beneficial finer microstructure with smaller grains.

The investigation and determination of thermal stresses is fundamental to the successful application of these processes, in particular where corrosion or fatigue conditions may be encountered. Thus, for example, Yilbas *et al.* (2009) carried out CO₂ laser pulsed remelting of an aluminium surface and modelled the stress field in the irradiated region $\dot{z}$ to determine temperature distribution and thermal stresses with laser pulse duration, the results of modelling being verified using X-Ray Diffraction (XRD). The model indicated an initial rapid increase in surface temperature followed by an almost steady increase to maximum temperature; the corresponding rate of cooling is initially high, but progressively diminishes. The result of this was a high stress field being developed in the surface of the remelted material in the early stages of cooling, although the values attained, in the order of a few MPa, were lower than required for crack formation.

Biswas *et al.* (2008) carried out remelting to increase hardness and achieved 85 HV as opposed to 55 HV for the as received Al-11Si alloy. The microstructure was changed from coarse grained Al with Al-Si lathy eutectic to a dendritic microstructure, with interdendritic Al-Si eutectic. As expected from the increased rate of cooling, the dendrite arm spacing decreased with

laser beam traverse rate. Control of dendrite arm spacing in Al-Si alloys, and consequently of the remelted material hardness, is made possible by adjustment of the quenching rate (Haddenhorst *et al.*, 1988; Lindner *et al.*, 1990). At the higher traverse rates applied by Biswas *et al.* (2008) (12 mm s⁻¹ for a 2.3 kW beam of 2 mm diameter), a cellular, refined microstructure was produced, and the Al-Si phase shape changed from lathy to globular. Pin-on-disc wear tests confirmed that the increase in hardness resulting from grain refinement improved the resistance to wear.

The effect of remelting on the resistance of aluminium alloys to corrosion is generating greater interest. In the same study mentioned above, Biswas *et al.* (2008) reported that potentiodynamic polarisation tests in 1 mole H₂SO₄, 1 mole HNO₃ or 3.5% NaCl revealed that the resistance to corrosion was increased in the remelted alloy, when compared to the untreated material, in the case of the nitric acid solution only.

In an earlier study, Yue *et al.* (2004) had used an excimer laser of 248 nm wavelength, applied in 25 ns pulses at 20 Hz, giving an energy density of 10.3 Jcm⁻², using dry air for shielding. The remelting of an AISI7075 alloy produced two superimposed layers of aluminium oxide layers at the surface of the remelted zone as a result of reaction with oxygen from the shielding air flow. These were found to be effective barriers against corrosion attack, and potentiodynamic polarization test results showed that the corrosion current was reduced by six times and a passive region was obtained. The untreated specimen suffered widespread pitting corrosion in contrast to isolated attacks on the laser-remelted surface. Xu *et al.* (2006b) applied the same process to remelt aluminium alloy AISI6013 to improve pitting corrosion fatigue resistance. In the remelted layer constituent, Al-Fe-Mn particles and grain boundary precipitates that were present in the original material were largely eliminated. AlN or Al₂O₃ layers were created at the surfaces produced by respectively using a flow of nitrogen or air over the excimer laser melt pool. Analysis of the electrochemical impedance measurements showed that these layers reduced the rate of electrochemical reaction. The corrosion fatigue lives of the air-treated and the N₂-treated specimens were two to four times longer than those of the untreated specimens, and pitting resistance was improved. The report, however, stated that the overall rate of fatigue crack propagation of the laser-treated material could have been higher than in the untreated specimens due to the development of fewer crack fronts in the former, and the consequent generation of high stress concentrations.

Liu *et al.* (2005a) used a CO₂ laser to remelt AA 2014-T6 and AA 2024-T351 alloys and investigated corrosion resistance by means of potentiodynamic anodic polarization tests in 1 M NaCl solution. The as-received material included randomly distributed intermetallic particles, such as Al₂Cu in AA 2014-T6 or Al₂CuMg in AA2024-T351, with an Al-Cu-Mn-Fe-Si phase

in both. Laser surface melting produced cellular/dendritic microstructures with refined second phase particles in both alloys. In the AA 2024-T351 alloy, some of Al_2CuMg phase was converted into Al_2Cu due to the selective vaporisation of magnesium during the process – this occurrence is relevant to elements which can vaporise easily. In this study, EPMA analysis revealed that the average concentration of magnesium was reduced from 0.61 and 1.30 wt% in the as-received AA 2024-T3 and AA 2024-T351 alloys to 0.32 and 1.05 wt% in the laser-treated surfaces. The remelting process produced an increase in copper solubility, which resulted in a higher corrosion potential. In the AA 2024-T3 alloy the cathodic nature of the Al_2Cu phase relative to the α -Al solution reduced the galvanic coupling between the intermetallic phase and the matrix, thus reducing the driving force for pitting corrosion. In the AA 2024-T351 alloy, however, due to the anodic nature of the Al_2CuMg phase relative to the α -Al matrix, the higher copper solubility in the matrix increased the driving force for pit initiation due to the higher potential difference between the two phases. The laser remelting process actually promoted pitting corrosion of the AA 2024-T351 alloy. The effect of laser remelting on pitting corrosion was thus demonstrated to be dependent on the electrochemical characteristics of second phase particles relative to the matrix, and, depending on the alloy composition, could be improved or exacerbated (Liu *et al.*, 2005a).

Yue *et al.* (2006) investigated the effect of Nd:YAG laser remelting on stress corrosion cracking performance by loading specimens in a three-point bending tester whilst immersed in a 3.5% NaCl solution. The process was applied in either air or nitrogen shielding. In both cases, coarse constituent particles present in the 7075-T651 alloy were removed and the structure was transformed to a fine cellular/dendritic one. The main difference afforded by the nitrogen shielding was the presence of an AlN phase, identified by XRD. This phase was to produce an important result: the untreated specimens were severely attacked by corrosion, with intergranular cracks forming along the grain boundaries of the specimen; the specimen treated in air presented some long stress corrosion cracks following the interdendritic boundaries, and relatively large pits; but the nitrogen-shielded specimens presented only a few, short stress corrosion cracks. This superior performance was attributed to the AlN phase formed by remelting at the surface acting as an electrical insulator and providing a film resistance higher than those of the untreated or unshielded specimens.

Laser remelting has also been applied to aluminium alloy-matrix composites. Hu *et al.* (2007a; 2007b; 2008) reported the remelting of an alumina borate whisker-reinforced composite with an Nd:YAG laser. The whisker presence was reduced, and the intermetallic CuAl_2 was eliminated and replaced by gamma alumina and boron oxide. The remelted areas were relatively defect free, and improvements to passivation depended on a balance between less

homogeneity at low power (500 W, 0.4 mm diameter beam) and a greater number of defects at higher power (900 W, 0.4 mm diameter beam). The microhardness was increased from 178 HV to 294 HV due to the creation of a fine dendritic microstructure, solid solution hardness, the presence of the hard Al_2O_3 ceramic phases and grain refinement. Rams *et al.* (2007) surface-treated A361 and A360 aluminium alloy-matrix composites reinforced with 10 and 20 vol% SiC particles. The remelting process was intended to eliminate the presence of SiC particles disrupting the continuity of the Al_2O_3 protective layer on the surface of the material. A high power diode laser was used to homogenize the surface and refine the grains. This resulted in an increase in hardness of 48–80% for the various material combinations treated. The materials showed higher polarization resistance than the original composites, and differences between the corrosion and pitting potential values reduced pitting corrosion. Care had to be taken however to avoid excessive decomposition of the SiC, and the formation of harmful aluminium carbides which reduce corrosion resistance.

The surface of a laser-remelted alloy has its texture altered (Tsagkarakis *et al.*, 2002; Biswas *et al.*, 2008) by the solidification of ripples produced by convection in the melt zone or by cratering resulting from evaporation. Pantelis (1998) describes the effect of excimer laser fluence on surface roughness, indicating that at values below plasma formation an improvement to micro-roughness is achieved by removal of grease, oxides, abrasive particles and deformation layers; whilst above plasma formation, melting produces a ridged wave morphology, increasing roughness, although further increase in fluence produces more complex but smoother surfaces. Spadaro *et al.* (2007) used the surface modification effects of laser remelting to improve the adhesion of structural joints in aluminium alloys. A general increase in adhesive fracture energy with the single-pulse beam energy was attributed to a microscale texture effect increasing the specific surface area and sites for mechanical keying between the components and the adhesive.

13.3.2 Laser surface remelting of Mg alloys

Laser remelting processes for magnesium alloys are similar in aim to those designed for aluminium alloys, and are intended mainly to refine the grains and homogenize alloy distribution in the material in order to improve resistance to wear and to corrosion. Grain refinement, solid solution hardening and increase in intermetallics resulting in an increase in surface hardness and wear resistance are reported (Wu, 2008; Mondal *et al.*, 2008).

Fundamental research on remelting requires data on physical properties of the alloys being treated; thus, Ignat *et al.* (2004b) carried out a practical investigation on the absorptivity of the Nd:YAG laser wavelength by WE43 and ZE41 with different pre-process surface treatments applied, determining

values of absorptivity between 0.2 and 0.65 for WE43 and up to 0.85 for ZE41, the specific value for each condition depending on the pre-treatment, the laser intensity and whether melting was achieved or not. Liu *et al.* (2005b) applied numerical simulation to determine a low absorption coefficient of 0.04 at the Nd:YAG laser wavelength for a Mg-Al alloy including Ce. Research is also being carried out on the remelting process to understand temperature variation and heat transfer in the area of interaction and fluid velocities in the melt zone (Abderrazak *et al.*, 2008).

Majumdar *et al.* (2003) reported high absorption of the 308 nm wavelength for investigations on the effect of an XeCl excimer laser on material homogeneity of AZ91-T4 Mg alloy. The untreated material presented a $\text{Mg}_{17}\text{Al}_{12}$ intermetallic phase at grain boundaries, and had a low hardness of 100 HV. Pulsed laser remelting resulted in the precipitation of MgO and Mg_3N_2 particles of 10–15 nm size, a grain size reduction to 200–300 nm, and an increase in hardness to 150–175 HV produced by these combined effects (Majumdar *et al.*, 2000; 2002; 2003). Jun *et al.* (2008) reported homogenisation of AZ91D as a result of pulsed Nd:YAG laser remelting, and an increase in hardness similar to the values indicated by Majumdar *et al.* An increase in hardness was reported for higher speeds and lower powers as these parameters produced a finer microstructure. Pin-on-disc testing indicated an improvement in performance resulting from grain refinement and solid solution hardening. Ghazanfar *et al.* (2006) reported similar improvement for AZ31 and AZ61 remelted with a diode laser, but achieved lower hardness values of 89–80 HV for AZ31 and 92–105 HV for AZ61. Pin-on-disc tests indicated an improvement of 2.5x over untreated alloys. Zhang *et al.* (2008a) reported an increase in hardness to 55–75 HV in CO_2 laser-remelted AM50 alloy, compared with 40 HV for the untreated material, the ball-on-flat wear volume loss being decreased by 42%.

Mondal *et al.* (2008) report characteristic grain refinement and the creation of a fine cellular and dendritic structure produced by Nd:YAG remelting of ACM720 alloy. This process is of particular interest to the automotive engine and power train industry as it enhances creep-resistance, castability and cost effectiveness. The composition of the treated alloy consisted of α -Mg, Al_8Mn_5 and $\text{Ca}_{31}\text{Sn}_{20}$ phases – the Ca being included in the alloy to increase creep resistance. The laser treatment doubled surface hardness and reduced the wear rate, due to grain refinement and solid solution strengthening.

Long-term linear polarization resistance and electrochemical impedance spectroscopy measurements on laser remelted and untreated ACM720 confirmed that the polarization resistance values of the treated alloy were twice those for untreated material. This improvement was attributed to the absence of a cathodic Al_2Ca phase at the grain boundaries of the remelted material, as well as microstructural refinement and extended solid solubility resulting from rapid solidification (Mondal *et al.*, 2008).

Liu *et al.* (2005b) laser-melted a magnesium alloy that included Ce to produce the typical fine dendritic structure and increase hardness. XRD identified β -Mg₁₇Al₁₂ and α -Mg dendrites; other unidentified intermetallics were noted. The Ce produced an oxide film that complemented the overall micro-structural refinement in enhancing corrosion resistance.

Wu (2008) reviewed laser processing of Mg alloys and listed several reports of laser remelting to improve corrosion resistance by means of dissolution of intermetallics and re-solution of alloying elements in solid solution, for example in Mg-Y-Zn alloys. Grain refinement was reported to assist corrosion resistance as it reduces the anode-to-cathode area ratio, diminishing initiation of corrosion. Finer grains also permit formation of a more homogeneous surface film, reducing tendency for pitting. Examples of corrosion resistance enhancement by grain refinement include the laser surface remelting of Mg-Li alloy MA21.

13.3.3 Conclusions on laser surface remelting processes

Laser beam remelting is the simplest of the processes described. It is the most easily adaptable to surface processing of complex shapes as no powder delivery is required (as in alloying and cladding); nor does the component need to be submerged (as in laser shock treatment). For similar reasons it is also the cleanest, as no powder materials or liquids are required. The process is however limited as it produces limited effects on the material as the composition of the latter is unchanged, unless volatile elements evaporate. Laser surface alloying (Section 13.4), cladding (Section 13.5) and surface particle composite fabrication (13.6) overcome this limitation by means of the addition of other materials to the original alloy.

13.4 Laser surface alloying of light alloys

Laser alloying can be an unintentional result of laser remelting: the reaction of the remelted substrate with atmospheric oxygen or with nitrogen from the atmosphere or shielding gas has previously been indicated (Lindner *et al.*, 1990; Yue *et al.*, 2006; Xu *et al.*, 2006b). The alloying process is, in fact, laser remelting with the addition of alloying material, usually in powder form. Several elements have been considered including Si, Fe, Ni, Cu, Zr, Mn and Bo, separately and combined (Kovalenko, 2001, p. 284). Some of the reported alloying processes use ceramic materials such as SiC and Al₂O₃, producing particles embedded in a matrix. These will be considered in a subsequent section. Table 13.2 lists materials used for alloying, cladding and particle reinforcement.

Table 13.2 Materials used for laser alloying, cladding and composite surface fabrication applied to Al and Mg alloys

	Al alloys	Mg alloys
Materials for alloying	Si, Fe, Ni, Cr, Cu, Zr, Mn, Bo; Al-Nb; Al-Cr-Mo-Nb; Ni-P; Fe ₃ O ₄	Al, Cu, Ni, Si
Materials for cladding	Ni; Al-Si; Ni-Al; Cu-Al; Cr-Al	Al, Zr; Al-Si; Al-Mn
Materials for composite surfaces	SiC, Al ₂ O ₃ , TiC, TiB ₂ ; SiC-Ni, SiC-Al, WC-Mo; Mo-Si-C; Ti-WC-NiAl; Ti-W-C-NiAl; Ti-Al-Fe-B	SiC; SiC-Al; Al ₂ O ₃ -Al; Al ₂ O ₃ -Al-Si

13.4.1 Laser surface alloying of Al alloys

The choice of alloying material may be constrained by process parameters or performance requirements. Zirconium and titanium, for example, form intermetallics with aluminium; however, their melting point is relatively high, and effective melting of these elements may result in the evaporation of some of the aluminium, potentially creating pores in the surface layer. The alloying of aluminium with iron produces useful intermetallic phases, but lowers the corrosion resistance of the surface. Carroll *et al.* (2001) reported several potential metastable iron–aluminium intermetallics that could be formed by rapid solidification of aluminium alloyed with iron powder, but investigated mechanical improvement rather than corrosion resistance, and managed to attain a hardness between 200 and 700 HV (compared to 90 HV for the as-cast alloy), and a threefold improvement of wear resistance.

The addition of chromium to aluminium alloys does not produce a similar disadvantage, but the acicular morphology of the intermetallics makes it less popular than nickel for this purpose. The latter produces a fine feathery eutectic that increases strength, retains ductility, and also improves the high-temperature performance of the surface. Manganese is particularly suited for alloying with the popular Al-Si alloys as the manganese silicides produced have a high hardness (Lindner *et al.*, 1990). Silicon is another useful alloying element which, if added in a quantity greater than the eutectic proportion, can precipitate to form dispersed, hard silicon crystals (Blank *et al.*, 1987; Pei and de Hosson, 2000).

As in the case of remelting, investigations on the process dynamics and heat transfer are still the subject of ongoing research. Almeida and Vilar (2008) have modelled temperatures in the melt pool formed when alloying commercially pure aluminium with blends of aluminium and the transition metals Cr, Mo or Nb. Some undissolved particles of the transition metals survived the process due to their high melting temperatures, and sank to the bottom of the melt pool. A diffusion zone formed around these, creating undesirable brittle intermetallics and resulting in the nucleation of cracks. Effective alloying was achieved only when the temperature (as indicated

by the model) exceeded the melting temperature of the readily-formed intermetallics. Almeida *et al.* (2001) had reported similar problems when alloying commercial purity Al with an Al and Nb blend of powders, but overcame the difficulty by applying a laser remelting process to the alloyed surface to obtain fine dendritic Al_3Nb with interdendritic $\alpha\text{-Al}$. Nayak *et al.* (2005) used infra-red imaging to analyse exothermic alloying reactions of A319 alloy with Fe_3O_4 . The temperature estimated using high spatial resolution IR thermography revealed that the reactions between the iron oxide and aluminium produced a higher heat of reaction than the remelting of the aluminium alloy or an alloying process using FeO instead of Fe_3O_4 .

Alloying procedures have been applied to provide dispersion strengthening of surfaces or the more resistant presence of intermetallic phases. Ni-alloying improved creep and erosion resistance; and a 3x improvement in fretting resistance and decrease in coefficient of friction was obtained by alloying AA6061 with Ni30Cr. A hardness increase to 325 HV compared to 60–70 HV for the substrate was produced (Joshi and Sundararajan, 1998). The use of Ni or Ni-based materials for alloying has been extensively investigated at least since the late 1980s (Kreutz *et al.*, 1987; Jobez *et al.*, 1989; Shibata and Matsuyama, 1990), and interest in these has still not waned (Yang *et al.*, 2005; Cui *et al.*, 2008; Gordani *et al.*, 2008; Razavi *et al.*, 2008).

Interest has however transferred from improvements to mechanical properties to surface engineering for enhancing corrosion resistance, and a current trend common to all recent publications mentioned above is the treatment of electroless Ni-P deposited over commercially pure Al or Al alloys. This process lies on the border between remelting and alloying. Yang *et al.* (2005) and Cui *et al.* (2008) applied Nd:YAG laser remelting to Ni-P plated on commercially pure aluminium. The process improved surface smoothness and homogenized the surface layer, and improved adhesion to the Al substrate at low power density values, which resulted in melting and flow of aluminium but not of the Ni-P. The surface was transformed from an amorphous state to a crystalline one with improved corrosion resistance. Alloying occurred at higher power densities. Gordani *et al.* (2008) reported the presence of NiAl, NiAl_3 and Ni_3Al_2 intermetallics in Nd:YAG laser remelted electroless Ni-P deposited over Al-356 alloy. The as-received alloy and the electroless coated samples suffered from severe pitting corrosion during testing in 3.5% NaCl solution, the latter due to cracks and porosities in the Ni-P layer. The corrosion potential of the laser remelted/alloyed specimen was higher than of the other specimens. This was attributed to the presence of elemental Ni; the fine Ni–Al intermetallic phases; and a Ni-rich aluminium solid solution in the surface layer. Razavi *et al.* (2008) reported similar results, but indicated that if the electroless films are too thin or the traverse rate too low (and the interaction time consequently high), excessive alloying with Al occurs, resulting in a reduced resistance to corrosion.

In spite of the difficulties encountered in alloying Al with transition metals described above, alloying with chromium is reported in a review by Joshi and Sundararajan (1998), who mention alloying of 7175 with Cr to increase corrosion resistance by the creation of a chrome oxide layer resistant to pitting. Ferreira *et al.* (1997) report the modification of crevice corrosion behaviour of Al7175 by CO₂ laser surface alloying with a powder blend of aluminium and chromium. The creation of a fine, chromium-rich microstructure and a chrome oxide layer resulted in increased resistance to crevice corrosion in 3% NaCl solution.

13.4.2 Laser surface alloying of Mg alloys

The laser alloying of magnesium alloys is applied mainly to increase hardness and resistance to wear; the presence of magnesium at the surface diminishes corrosion resistance, generally making laser surface cladding, a process which deposits a new surface over the substrate, a better proposition. Dutta Majumdar *et al.* (2002) applied CO₂ laser alloying with a blend of Al and Mn powder to MEZ alloy. The surface produced consisted predominantly of Al+Mn and Al+Mg dendrites, and a hardness of 250–350 HV was attained compared to 35 HV for the untreated alloy. The corrosion rate in 3.56 wt% NaCl solution was significantly reduced from 1520 mpy to 250 mpy. This was not attributed to the change in microstructure and alloying of the Mg with Al and Mn, however, but to the formation of an Al₂O₃ and Mn₃O₄ layer on the surface produced by reaction of the alloying elements with atmospheric oxygen.

Joshi and Sundararajan (1998) report alloying of magnesium alloy Al80 with Al, Cu, Ni or Si to increase its wear resistance. Alloying with aluminium failed to increase hardness, whilst nickel and silicon produced hard but brittle intermetallics. Alloying with copper, however, afforded significant improvement.

In his review of laser surface treatments, Wu (2008) indicated reports of Mg alloys being alloyed with Al, Zn, Mn, Si, rare earths, Ni, Cu, Al+Si, Al+Cu, Al+Ni. Specific mention is made of some metal additions, in particular Al, which gives a high resistance to pitting when >20% is added. However, this can also result in the formation of Mg-Al intermetallics, which can have a hardness of 200 HV but which may be brittle and could promote galvanic corrosion. The addition of Si was reported to promote formation of an Mg-Si intermetallic which contributed to an increase in hardness and resistance to wear.

13.4.3 Conclusions on laser surface alloying processes

Laser surface alloying is an extrapolation of the laser surface remelting process that adds a variety of complex permutations and possibilities to the

design of laser surface treatment for light alloys. This obviously implies added costs in the form of the added material and the delivery system. One limitation to the flexibility of material modification made possible by alloying is the required presence of the substrate material, which can limit some of the desirable effects, a case in point being the presence of magnesium alloys or intermetallics in the surface decreasing resistance to galvanic corrosion. This can be overcome by the creation of a new surface, as is the case in laser surface cladding (Section 13.5).

13.5 Laser surface cladding of light alloys

Laser cladding of aluminium and magnesium alloys is intended to create a surface with properties differing from those of the substrate. Cladding of aluminium alloys is often applied to create metal matrix composite surfaces that can offer a high resistance to wear; these will be considered in the following section.

As in the other processes discussed, an essential requirement is an understanding of the process by empirical means and by modelling. Several models exist to describe laser cladding processes, and these will not be considered here. Empirical investigations are usually carried out to verify models, determine material parameters or determine the effects of process parameters in terms of measures such as energy coupling, which is the ratio of absorbed beam energy to input laser energy (Ott *et al.*, 2000).

13.5.1 Laser cladding on Al alloys

Joshi and Sundararajan (1998) describe the application of Ni alloy FP-5 on Al alloy AA333. This application is of particular interest as its aim was to combine the low density of the Al alloy with the higher temperature mechanical properties of the Ni alloy. The process, however, introduced hard but brittle Ni_xAl_y intermetallics as a result of dilution by the substrate alloy. This could be avoided by depositing an intermediate layer of copper or bronze over the aluminium prior to depositing the nickel alloy layer.

Brandt *et al.* (2002) describe Nd:YAG laser cladding of an Al/Si blend and Al7075 over Al7050 and Al7075 substrates, and highlight a potential problem encountered in laser processes that include aluminium-based powders: the creation of porosity, resulting from the liberation of hydrogen produced from moisture captured by powder which has been incorrectly stored or insufficiently dried prior to processing. In this instance, the Al/Si blend was more hygroscopic than the alloy powder, and produced a higher porosity. The study also considered cracks produced by thermal stresses, a defect encountered in remelting and alloying, and which could be limited by reducing process traverse rate. Although surface properties could have

been altered by grain refinement, the scope of this research was to investigate process and material parameters for deposition of a metal alloy surface, which leads to material deposition for component modification and direct fabrication; repair by cladding is also mentioned in the context of Mg alloys by Wu (2008). The latter topic of great interest is an extrapolation of the laser surface cladding process, but is beyond the scope of this section.

López *et al.* (2009) applied a sol–gel coating process as a precursor to the laser process, aiming to reduce corrosion of an A380/SiC composite. Sol–gel coatings are usually densified by means of a thermal treatment at temperatures above 500°C. This may result in a decrease in substrate mechanical properties of low melting temperature substrates. López *et al.* used a diode laser to consolidate sol–gel silica coatings on the surface of the composite, creating a crack-free ceramic layer. This process is hard to categorize, as it could be defined as remelting or sol–gel consolidation, but it is included here as it is intended to create a new surface layer. Damage to the substrate was successfully avoided, and for optimum laser parameters the samples proved to be 45% harder than those conventionally cured. The laser-consolidated specimens furthermore proved to have a corrosion resistance higher than those consolidated in an oven, resisting contact with 3.5 wt% NaCl over a seven day period. Excessive heat input, however, produced coatings with reduced corrosion protection, due to dilution and cracking of the surface.

13.5.2 Laser cladding on Mg alloys

Cladding of magnesium alloys is a more popular process. Wu (2008), in a review of Mg surface engineering with lasers, listed reports of cladding of magnesium alloys with an impressive range of blends of powders, including Mg–Zr, Al–Si, Al–Cu, Al–Zn, Cu–Zn, stainless steel and Al–Ti–C, with other blends indicated for the production of ceramic reinforced layers. The border between cladding processes that form metallic or intermetallic phases and those that produce composite surfaces is admittedly indistinct for both Al and Mg alloys: hypereutectic blends of Al and Si applied to both Al and Mg substrates produce a hard, crystalline Si phase in what practically amounts to a composite surface; and the Al–Ti–C blend indicated above results in both Ti–Mg and Ti–Al intermetallics and a TiC ceramic phase, all of which improved hardness and wear resistance. Cladding with Zr–Mg improves corrosion resistance, as the alloy is shifted to the more noble end of the galvanic series. Al–Cu and Al–Si blends have also been shown to improve corrosion resistance, and high bond strength can be achieved. Excessive dilution has to be avoided however, as diffusion of Mg from the substrate reduces the resistance to corrosion that could be attained. The application of these blends, together with Al–Zn and Cu–Zn, on ZK60/SiC composite

substrate has also been investigated. The application of a stainless steel clad layer was found to be more effective in resisting corrosion, although intermediate brass or Cu layers had to be applied due to the large difference between the steel and Mg melting points, which resulted in cracking and heavy melting of the substrate. Generic issues reported by Wu include:

- surface cracking due to a wide solidification temperature range, high shrinkage, high coefficient of thermal expansion – this could be limited by the application of high power or low traverse rate;
- porosity resulting from the boiling of magnesium – in this case high traverse rates again prove undesirable as the resulting high speed of the solidification front could entrap evaporating metal to create pores;
- cratering and material loss at high powers, again due to evaporation of Mg;
- poor mixing and low homogeneity at low powers; and
- reaction with atmospheric oxygen or nitrogen due to high reactivity of the Mg during cladding – this could be limited by using argon shielding, but is reportedly only effectively eliminated by cladding in an enclosed, controlled-atmosphere environment.

Gao *et al.* (2006) and Yang and Wu (2009) described Nd:YAG laser cladding of AZ91HP and AZ91D respectively with Al-Si blends. Gao *et al.* reported the formation of a dendritic Mg_2Si phase and acicular Mg_2Al_3 dispersed in an $\text{Mg}_{17}\text{Al}_{12}$ matrix, which gave a hardness of 300–450 HK, a 340% increase with respect to the substrate, due to grain refinement and phase hardness. Magnesium in the clad was present as a consequence of substrate dilution. The clad layer gave a 90% decrease in wear volume compared to the substrate. The corrosion resistance of the clad layer was a significant improvement over that of the substrate, again due to grain refinement and the formation of the intermetallic phases. Yang and Wu reported the formation of similar phases, and an increase in hardness from 35 HV to above 170 HV, together with a corresponding increase in wear resistance. Variation in the Si content of the powder blend used for cladding indicated an increase in wear resistance with increase in Si content. Volovitch *et al.* (2008) applied a similar cladding process to ZE41 alloy, but reported corrosion issues for multiple clads, resulting from differences in clad track composition due to variations in heat transfer and dilution between tracks straddling their previously-deposited counterparts.

Ignat *et al.* (2004b) reported Nd:YAG laser cladding (and alloying) of Mg alloys WE43 and ZE4 with aluminium powder, to produce a surface consisting of Al_3Mg_2 and $\text{Al}_{12}\text{Mg}_{17}$ – the same intermetallic phases indicated above, in this case without the presence of Si. One reported problem frequently encountered in the processing of aluminium alloys is the formation of plasma at low traverse rates or high power, altering absorption of the laser beam and

possibly resulting in process discontinuity. Some important differences were observed between clads on the two different substrates: the clad obtained on the WE43 alloy presented higher dilution due to the lower thermal conductivity of WE43 compared to ZE41 and the ease of heat dissipation in the latter. Increases in hardness of around 200 HV0.05 in the single run layers or 120 HV0.05 for overlapping runs were obtained. In the latter instance, the heat input of subsequent runs increased the size of the melt pool after the first run was completed, resulting in greater dilution. Consequently, the less brittle (and hard) $\text{Al}_{12}\text{Mg}_{17}$ was present in a greater proportion than Al_3Mg_2 when compared to the isolated runs.

13.5.3 Conclusions on laser surface cladding processes

Laser surface cladding creates a new surface over the existing substrate, thereby contributing the desired surface properties. Thus, for example, the magnesium bulk material can be entirely isolated from a corroding environment by means of a clad layer. Like alloying, the process requires investment in added materials and delivery systems, as well as the corresponding issues of health, safety and cleanliness. Although impressive improvements to the material surface properties are possible, the resistance to wear can be enhanced still further by the inclusion of ceramic particles, as discussed in Section 13.6.

13.6 Laser surface particle composite fabrication processes

Processes that aim to create a composite surface consisting of a metal matrix reinforced with ceramic particles can be divided into two categories analogous to alloying and cladding. Laser particle dispersion or injection is similar to alloying, and consists of ceramic particles being injected into a surface as this is remelted by means of a laser. Laser cladding can be designed to create a composite surface either by including ceramic particles in the powder blend or by delivering elemental or compound powders which react to form a ceramic phase – an example of the latter was given in the previous section, the deposition of Al-Ti-C over a magnesium substrate described by Wu (2008), which produced a TiC phase. The survival of ceramic particles injected into an Al or Mg alloy substrate or deposited with Al-based powder is high, due to the disparity in melting points of Al and Mg and ceramics; and particle injection of borides and, in particular, carbides is a popular process for Al alloys (Kovalenko, 2001, p. 284). Ion (2005 p. 311) also reports use of Si or Al_2O_3 particles. Lindner *et al.* (1990) indicate alumina and zirconia, which are not chemically attacked by molten aluminium. The main aim of these processes is to improve tribological properties due to the high hardness of the ceramic particles. They are not usually applied to

corrosion resistance enhancement due to the variety of phases present in the surface layer produced, although Dutta Majumdar *et al.* (2006) investigated the corrosion resistance of Al+SiC or SiC alone deposited over commercially pure Al. Gasser *et al.* (1990) dispersed SiC and TiC in Al and Ti alloys, and observed that particle size has an effect on penetration of the particles in the substrate melted by the beam, with larger particles having greater momentum and therefore greater ease of insertion. The wettability of a ceramic material is another factor that affects ease of particle injection; thus, for example, the wetting of SiC by aluminium is poor, and high kinetic energies are needed to ensure effective dispersion (Liechti and Blank, 2000).

Liechti and Blank (2000) discussed another difficulty in reinforcing aluminium-based alloys with SiC: although the latter has a high melting point, it also reacts readily to form Al_4C_3 and Al_4SiC_4 , which are brittle and undesirable. In order to avoid this, blends of Al-Si powder with pure Si and SiC were deposited over Al alloys. The Si content of the cladding material had a marked effect on the solidified material. When less than 30 wt% Si was used, the SiC particles reacted with the aluminium and produced carbides; when more than 30 wt% Si was included, no carbides other than SiC itself were detected.

Hu *et al.* (1996) attempted SiC particle or alumina fibre dispersion in a small range of Al and Mg alloys (as well as a Co and a Ti alloy). Although the particles survived the process, all experiments with the Al_2O_3 fibres resulted in their dissolution due to the higher absorptivity and lower thermal conductivity (and therefore reduced heat dissipation) of alumina compared to SiC. The SiC-reinforced surfaces presented detrimental Al-Si carbides, however. Dutta Majumdar *et al.* (2006; 2007) deposited Al + SiC or SiC over commercially pure Al and encountered the same difficulty. A hardness of 700–800 HV was measured for the particles, contrasting with the hardness of 75–110 HV measured on the matrix. The original hardness of the Al was 25 HV, and the increased matrix hardness was attributed to grain refinement and the formation of an Al–Si lamellar eutectic phase. Si peaks, resulting from the decomposition of SiC, were detected. Corrosion resistance tests in a 3.56 wt% NaCl solution indicated that the performance of the clad surface was marginally inferior to that of the untreated material.

Ni and SiC were deposited over an Al8Si alloy substrate (Jaffar *et al.*, 2005) in order to provide a high hardness matrix reinforced further with ceramic particles. Several phases, including AlSi, Ni_3C , AlNi_2Si , Al_2O_3 , AlNi, Ni, SiC and Al_4SiC_4 , were identified, but the more brittle AlC_4 was not found. A hardness of 400–575 HVN was achieved in the composite layer. When varying the proportion of SiC to Ni in the cladding powder blend, it was noted that the an increase in SiC resulted in greater heat absorption; this is explained by the higher absorptivity of SiC (0.2) as opposed to Ni (0.05) at the CO_2 laser wavelength of 10.6 μm .

The high hardness of WC and the wear resistance performance imparted by it made it an inevitable inclusion in research oriented towards tribological performance, and although it is more frequently used with steels, nickel alloys or cobalt alloys, it has been applied in cladding processes to Al alloys as well. Chong *et al.* (2000) report a range of hardness values between 220–750 HV for cladding with WC-Mo blends, and a wear resistance improvement of 40x when more than 40 vol% WC was used in the powder blend. Some melting of WC occurred however, and dilution with Al and Si from the substrate was observed; some of the WC reacted to form W_2C and the undesirable Al_4C . Man *et al.* (2004) preplaced Ti, W and C powders or Ti and WC powders over Al6062 and deposited NiAl or $NiAl_2O_3$ over these. The intention was to have the Ti react with and scavenge the C liberated from decomposing WC and avoid the formation of brittle aluminium carbides. This was successful, and a high hardness range of 800–1100 HV was obtained, a great improvement over the 80 HV hardness of the substrate. Cladding in both the above two cases was carried out with a Nd:YAG laser.

The *in-situ* synthesis of a ceramic phase described above for cladding with W and C powder by Man *et al.* (2004), and cladding experiments with Fe-coated boron, Al and Ti blends (Xu *et al.*, 2006a; Xu and Liu, 2006), were designed to counter the poor wetting between ceramic particles and the molten metal, and the large differences in thermal expansion coefficient between them. In the latter cases, the CO_2 laser cladding process generated TiB_2 , Ti_3B_4 , Al_3Ti , Al_3Fe and α -Al in a pore- and defect-free layer, the aluminium being introduced by dilution by the substrate. The surface hardness of the coating was increased to a range between 265 HV to 908 HV, the value varying with composition in the composite surface but increasing with the proportion of added boron and titanium powders, which determined the amount of hard TiB_2 and Ti_3B_4 phases. In pin-on-ring wear tests, the unmodified substrate lost fifteen times as much weight of worn material as the best-performing coating. Wear performance under high loads was however, less effective due to detachment of particles resulting in aggressive 3-body abrasion.

Yang *et al.* (2001) investigated the possibility of creating a molybdenum silicide matrix reinforced with SiC, and applied a CO_2 laser cladding process over commercially pure aluminium using elemental Mo, Si and C powder. XRD analysis indicated that the resulting clad included $MoSi_2$, SiC and Mo_5Si_3 ; a hardness of 1200 HV was attained at the surface, varying between this value and 1000 HV to a depth of around 0.5 mm.

As in the case of Al alloys, the reinforcement of Mg alloys by ceramic particles is mainly intended to improve tribological properties. In his review on laser processing of Mg alloys, Wu (2008) described the cladding of Mg alloys with Al- Al_2O_3 and Al-Si- Al_2O_3 . Cladding with an Al-based component was preferred to alloying, as Si and Al_2O_3 form a poor interface with Mg; Al was preferred to Mg powder as it enhances corrosion resistance. Cladding

with Al and Al_2O_3 gave a hardness of 350 HV compared to 35 HV for the substrate. Cladding with elemental powders is applied to Mg alloys as well, and one solution described by Wu was the creation of a clad including TiC with Ti-Mg and Ti-Al intermetallics by cladding with Ti-Al-C.

One of the more popular powder combinations for ceramic-reinforced cladding of magnesium alloys is aluminium and alumina. A homogeneous and defect-free microstructure consisting of a dispersion of Si and Al_2O_3 particles in a hypoeutectic Al matrix was produced by Jun *et al.* (2006) by a pulsed Nd:YAG laser deposition of Al, Si and Al_2O_3 over an AZ91D alloy substrate. $\text{Mg}_{17}\text{Al}_{12}$ and Mg were identified in the bonding zone, where diffusion of magnesium produced the intermetallic phase. The microhardness of the clad layer was of 210 HV0.05 compared with 60–70 HV0.05 for the substrate. Similar results were obtained by Liu *et al.* (2006) and Dutta Majumdar *et al.* (2004), although the latter reported hardnesses between 90 to 350 HV, decreasing with both laser power and traverse rate. The wear rate was significantly reduced, due to this increase in microhardness resulting from the ceramic phases.

Another popular combination is a blend of aluminium and silicon carbide. Dutta Majumdar *et al.* (2003) reported that close control of the process parameter envelope was required to ensure survival of the particles and their dispersion in the Al matrix: this was due to the lower density and higher CO_2 laser wavelength absorptivity of the SiC. A maximum hardness of 270 HV was obtained for the optimum parameters, and pin-on-disc tests indicated a reduction of mass loss due to wear by almost two orders of magnitude. Chen *et al.* (2008) reported a smaller increase in hardness (140–160 H), depending on the presence of the $\text{Mg}_{17}\text{Al}_{12}$ intermetallic and surviving SiC (deposited with Al as a nano-sized powder), the latter reported to be smaller than 100 nm. Partial dissolution could explain the lower hardness reported here. Material loss due to wear was reduced, and the presence of aluminium increased corrosion resistance in 3.5% NaCl solution.

In contrast to the above cladding methods, Hu *et al.* (1996) investigated dispersion of SiC particles directly in a magnesium alloy (WE43) substrate. The low solubility of the carbide assisted particle survival in the melt pool.

13.6.1 Conclusions on laser surface particle composite fabrication processes

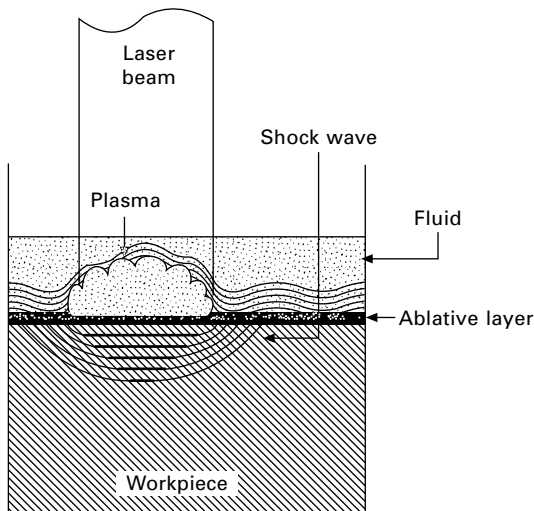
This group of processes greatly enhances resistance to wear, but shares the limitations of alloying (Section 13.4) and cladding (Section 13.5) processes as regards equipment, and health and safety requirements. The family of remelting and deposition processes also require very precise control of process parameters, thermal conditions and material addition for a specific and useful

surface to be produced. Laser shock treatment reduces the complexity of microstructural evolution and eliminates material addition and delivery.

13.7 Laser shock treatment of Al alloys

Laser shock treatment, or laser peening, is a process in which a pulsed laser is used to generate the expansion of hot plasma over a metal surface to create a shock wave in the material, which creates residual stresses and increases hardness and resistance to cracking and fatigue failure. The material composition is not altered. A dielectric material, in most cases water, is used to contain the expansion of hot plasma increasing the duration of the plasma blow-off and increasing the pressure generated. A protective coating may be applied to the material being treated to avoid melting. The process (Fig. 13.3) has some advantages over conventional mechanical peening, including the formation of lower surface stresses; graded stress with depth; and a 1–2 mm depth of effect (Berthe *et al.*, 1998).

In order to generate the shock waves, a pulsed power modulation is required. Berthe *et al.* (1998) indicate the use of Nd:YAG 25 ns pulses, with a beam diameter of 3–5 mm. The pressure produced by the shockwaves in the surface is independent of the material being treated, but increases up to a threshold with fluence; the induced residual stresses behave similarly. The threshold occurs at breakdown of the water above the component, and the pressure value at this turning point is lower for shorter wavelengths. The pressure is increased by use of very short pulses, but short pulses restrict the depth due to shock attenuation; since the plastic deformation rate is identical



13.3 Schematic diagram describing laser shock treatment.

but is concentrated in a shallow depth, higher stresses are generated with short pulses. The residual stress can also be increased by applying repeated pulsing over the same area (Peyre *et al.*, 1996; Berthe *et al.*, 1998). Increase in hardness resulting from residual stresses was found to be in the range of +10 to +20 HV for nanoseconds and GW cm^{-2} intensities (Berthe *et al.*, 1998).

Laser shock processing was also found to improve the corrosion resistance of materials such as Al alloy AISI2024 by an anodic shift of pitting potential and reduction of the passive current density; this is probably due to the effect of the compressed state of the surface on inclusions, or modification of the growth kinetics of passive films (Berthe *et al.*, 1998).

The creation of compressive stresses at the surface of a component is conducive to resistance to fatigue failure. Peyre *et al.* (1996) applied the process to A356, A112Si and 7075 aluminium alloys. A conventional shot peening treatment applied to these materials produced high surface hardness accompanied by a detrimental increase in roughness not produced by the laser process. High cycle (10^7) fatigue tests were carried out on laser-processed, shot-peened and untreated notched specimens: laser shock processing produced a +22% improvement in performance compared to a +10% improvement resulting from conventional shot peening, the performance improvement being mainly in the crack initiation stage of failure. Similar results were obtained by Berthe *et al.* (1998) on AISI 2024 and 7075 Al alloys, although a greater improvement (+20–40% increase) was reported in cast A356 or wrought 7075-T7351. The performance enhancement in the latter was again reported to be better than the result of shot peening, and with the added advantage of no increase in surface roughness. The crack propagation rate was reduced by a factor of five or six times, and was attributed to a 7x improvement in the initiation stage and a 3x improvement in the propagation stage. Luong and Hill (2008) reported a high cycle fatigue life improvement by a factor of 5.6 relative to as-machined samples of 7085-T7651 aluminium, and by a factor of at least 6.4 relative to anodised samples.

A reduction in fatigue crack growth can also be achieved in welds by means of laser shock processing. Hatamleh (2008) investigated the fatigue crack growth performance of untreated, shot peened and laser shock treated friction stir welded 2195 aluminium–lithium alloy. The results obtained indicated a significant reduction in crack growth rates measured in laser-treated welds compared to shot peened or untreated weld specimens, comparable to the rate of crack growth in unwelded 2195 alloy. In this application, both sides of the specimen were shock treated using the same parameters, and through-thickness residual stress measurements indicated that laser shock processing introduced higher compressive stresses more deeply into the weld material compared to shot peening.

A specific application of the process, using a Q-switched laser of 1054

nm wavelength, is described by Zhang *et al.* (2008b). The blade roots and edges of aircraft gas turbine blades experience fatigue loading in flight. Fatigue samples and turbine blades of LY2 aluminium alloy were coated with ablative 7075 aluminum foil and submerged under 3 mm of water. A stressed layer more than 2 mm-thick was generated by the application of repeated laser-induced shockwaves. Micro-indenters were generated at the surface by the shock process; the surface roughness was however lower than that of the untreated specimens. Testing revealed that low cycle fatigue performance of the specimens was increased by the high compressive residual stresses generated.

In contrast with aluminium alloys, no reports of laser shock hardening of Mg alloys have been identified.

13.7.1 Conclusions on laser shock treatment of Al alloys

Whilst not as flexible as laser deposition processes, laser shock treatment offers an excellent contribution to the range of laser surface processes, and permits effective control over surface properties by careful selection of process parameters. The main disadvantages are the need for immersion of the material; the application of protective coating, which requires an extra process step; and the lack of applicability to magnesium alloys. The possibility of processing aluminium alloys potentially without even melting their surface is, of course, a great advantage as the surface finish of the component can be retained.

13.8 Future trends

Continued interest in light materials to reduce the weight of structures and (for transport applications) fuel consumption implies that aluminium and magnesium alloys will remain in demand. Competition by other low density materials, particularly composites, means that these alloys may require improvement of their surface properties to remain desirable or to widen their range of application, and laser surface treatments offer a variety of possibilities. Tribological, corrosion and fatigue performance can be enhanced by laser beam remelting or its derived additive processes – alloying, cladding, and ceramic surface reinforcement – or by laser shock peening. The potential for fine process control and selective application, together with the minimal to negligible damage to the bulk material, makes these high value-added processes attractive. These features, together with the high flexibility of lasers, guarantee continuity of research in this area of surface engineering.

Research is currently moving away from fundamental, generic investigations towards dedicated application, as described for laser shock processing of aluminium alloys (Zhang *et al.*, 2008), although the empirical verification

of models (Abderrazak *et al.*, 2008; Almeida and Vilar, 2008; Yilbas *et al.*, 2009) is still on the agenda. It is clear that interest is generated by processes that can maximise performance. Thus, particle inclusion is currently preferred for the improvement of mechanical and tribological properties, whilst remelting, alloying and cladding are applied to the improvement of corrosion resistance. In this area, laser beam cladding appears to have an edge in magnesium alloy processing, as the corrosion-prone magnesium is completely coated by the surface layer produced and isolated from the corroding medium. Laser shock processing has the advantage of producing low surface roughness, and does not require the powder-handling systems and powder and metal vapour containment equipment, although it is limited by requirements for component coating pre-process and for submerging the component. Its distinct advantages over shot peening (a greater depth of action and lower surface roughness) ensure the continuity of interest in this process.

Targets of future research opportunity must include process control systems dedicated to the laser processing of these high-reflectivity alloys; the extrapolation of deposition of layers of material to direct fabrication processes, possibly with graded composition of the deposited material; and the incorporation of fibre reinforcement by means of combined preplaced and direct laser deposition.

13.9 Sources of further information and advice

Publications on these processes are readily available in journals, conference proceedings and books. The Laser Institute of America (LIA) regularly includes mention of these processes, and describe some of them in the *LIA Handbook of Laser Materials Processing* (ed. Ready, 2001), a classic text, which, although now becoming dated, is still useful. *The International Congress on Applications of Lasers & Electro-optics (ICALEO®)* is an annual event in which light alloy-oriented laser surface processes regularly feature. LIA's *Laser Additive Manufacturing Workshop (LAM)* is oriented to laser additive processes, including cladding and rapid manufacturing. The website of major interest is that of the Laser Institute of America (LIA); it provides links to courses and events organised by the Institute. The site is located at <http://www.laserinstitute.org/>.

The closest European counterpart is the *Laser Assisted Net-shape Engineering (LANE) Conference*, organised by the Bavarian Laser Centre in cooperation with the Chair of Manufacturing Technology, University of Erlangen/Nuremberg, Germany, although this focuses on direct fabrication rather than surface engineering. The next LANE will be held in September 2010.

Other useful publications include:

- The dated but still valid *Lasers in Surface Engineering, Surface Engineering Series Vol.1* (Dahotre, 1998).
- The more recent *Laser Processing of Engineering Materials* (Ion, 2005), which is a very useful and more up-to-date volume, although process detail provided is less specific.
- *Laser Cladding* (Toyserkani *et al.*, 2004) describes the cladding process and is a very useful compilation dedicated solely to this process.
- An as-yet to be published potentially useful book is *Advances in Laser Materials Processing Technology* (Lawrence *et al.*, 2010 to be published by CRC Press, Boca Raton, FL).

Although papers on the processes may be found in several journals, two of these, dedicated to laser materials processing, should be mentioned: the LIA's *Journal of Applications*, and *Lasers in Engineering* published by Old City Publishing.

13.10 References

- Abderrazak K., Kriaa W., Ben Salem W., Mhiri H., Lepalec G., Autric M., 2008. Numerical and experimental studies of molten pool formation during an interaction of a pulse laser (Nd:YAG) with a magnesium alloy. *Optics Laser Technology*, doi:10.1016/j.optlastec.2008.07.012
- Almeida A., Nogueira I., Vilar R., 2001. Aluminium–niobium alloys produced by laser surface alloying: Their structure and properties. In *ICALEO (International Congress on Applications of Lasers & Electro-Optics) ICALEO 2001*. Jacksonville, Florida, October 2001. Laser Institute of America: Orlando, FL
- Almeida A., Vilar R., 2008. Alloy formation in laser surface alloying of Al with transition metals. *Lasers in Engineering*, 18(1–2), pp. 49–60
- Berthe L., Peyre P., Schepereel X., Fabbro R., Jeandin M., 1998. Laser shock surface processing of materials. In: Dahotre N.B. (ed.), *Lasers in Surface Engineering, Surface Engineering Series, Vol.1*. Ontario: ASM International, Ch. 12
- Biswas A., Mordike B.L., Manna I., Dutta Majumdar J., 2008. Studies on laser surface melting of Al-11%Si alloy. *Lasers in Engineering*, 18(1–2), pp. 95–106
- Blank E., Hunziker O., Mariaux S., 1987. Load bearing capability of laser surface coatings for aluminium silicon alloys. In: Mordike B.L. (ed.), *Laser Treatment of Materials*. Oberursel: DGM Informationsgesellschaft-Verlag, pp. 193–198
- Brandt M., Durandet Y., Liu Q., 2002. Nd:YAG laser cladding of Al/Si and Al7075 powder on Al7050 and Al7075 substrates. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2002*. Scottsdale, Arizona 14–17 October 2002. Laser Institute of America: Orlando, FL
- Carroll J.W., Liu Y., Mazumder J., Perry T.A., 2001. Laser surface alloying of aluminum 319 alloy with iron. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2001*. Jacksonville, Florida, October 2001. Laser Institute of America: Orlando, FL
- Chen C., Zhang M., Chang Q.-M., Zhang S., Ma H.-Y., Yan W.-Q., Wang M., 2008. Laser cladding of ZM5 magnesium base alloy with Al+nano-SiC powder. *Lasers in Engineering*, 18(1–2), pp. 85–94

- Chong P.H., Man H.C., Yue T.M., 2000. Laser surface cladding of Mo-WC on AA6061 aluminium alloy. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2000*. Dearborn, Michigan 2–5 October 2000. Laser Institute of America: Orlando, FL
- Cui C., Hu J., Yang Y., Wang H., Guo Z., 2008. The structure and phase transformation behaviour of laser melted electroless Ni-P coating on Al after various tempering treatments. *Lasers in Engineering*, 18(1–2), pp. 61–70
- Dutta Majumdar J., Maiwald T., Galun R., Mordike B.L., Manna I., 2002. Laser surface alloying of an Mg alloy with Al+Mn to improve corrosion resistance. *Lasers in Engineering*, 12, pp. 147–169
- Dutta Majumdar J., Ramesh Chandra B., Galun R., Mordike B.L., Manna I., 2003. Laser composite surfacing of a magnesium alloy with silicon carbide. *Composites Science and Technology*, 63, pp. 771–778
- Dutta Majumdar J., Ramesh Chandra B., Mordike B.L., Galun R., Manna I., 2004. Laser surface engineering of a magnesium alloy with Al+Al₂O₃. *Surface and Coatings Technology*, 179, pp. 297–305
- Dutta Majumdar J., Ramesh Chandra B., Nath A.K., Manna I., 2006. Compositionally graded SiC dispersed metal matrix composite coating on Al by laser surface engineering. *Materials Science and Engineering A*, 433, pp. 241–250
- Dutta Majumdar J., Ramesh Chandra B., Manna I., 2007. Friction and wear behavior of laser composite surfaced aluminium with silicon carbide. *Wear*, 262, pp. 641–648
- Ferreira M.G.S., Li R., Almeida A., Vilar R., Watkins K.G., Steen W.M., 1997. Modification of the Crevice Corrosion Behaviour of Al7175 Alloy by Surface Alloying. [online] *Journal of Corrosion Science and Engineering*, Vol. 1. Available at: <http://www.jcse.org/volume1/paper5/v1p5.php> [Accessed 8 May 2009]
- Gao Y., Wang C., Lin Q., Liu H., Yao M., 2006. Broad-beam laser cladding of Al–Si alloy coating on AZ91HP magnesium alloy. *Surface & Coatings Technology*, 201, pp. 2701–2706
- Gasser A., Kreutz E.W., Krönert W., Lohmann K., Wissenbach K., Zografou C., 1990. Dispersion of hard particles in light alloys with CO₂ laser radiation. *ECLAT '90 (European Conference on Laser–Metal Treatment)*, pp. 651–660
- Ghazanfar A., Li L., Ghazanfar U., Liu Z., 2006. Effect of high power diode laser surface melting on wear resistance of magnesium alloys, *Wear*, 260, pp. 175–180
- Gordani G.R., Shojarazavi R., Hashemi S.H., Isfahani A.R.N., 2008. Laser surface alloying of an electroless Ni–P coating with Al-356 substrate. *Optics and Lasers in Engineering*, 46, pp. 550–557
- Gray J.E., Luan B., 2002. Protective coatings on magnesium and its alloys – a critical review. *Journal of Alloys and Compounds*, 336, pp. 88–113
- Haddenhorst H., Hornbogen E., Vollmer H.W., 1988. Investigation of laser-treated surfaces of aluminium silicon alloys by scratch-, friction- and wear-tests. In: *ECLAT (European Conference on Laser–Metal Treatment) ECLAT'88*, pp. 97–99.
- Hatamleh O., 2008. A comprehensive investigation on the effects of laser and shot peening on fatigue crack growth in friction stir welded AA 2195 joints. *Int J Fatigue*, doi:10.1016/j.ijfatigue.2008.03.029
- Hu C., Barnard L., Mridha S., Baker T.N., 1996. The role of SiC particulate and Al₂O₃ (Saffil) fibres in several alloys during the forming of *in situ* MMCs developed by laser processing. *Journal of Materials Processing Technology*, 58, pp. 87–95
- Hu J., Liu G. Li Z.J., Kong L.C., 2007a. Improvement in the corrosion resistance of Al₁₈B₄O₃₃w/2024Al composite by laser surface treatment. *Applied Surface Science*, 253, pp. 4524–4530

- Hu J., Wu P.L., Kong L.C., Liu G., 2007b. The effect of YAG laser surface treatment on corrosion resistance of $\text{Al}_{18}\text{B}_4\text{O}_{33}\text{w}/2024\text{Al}$ composite. *Materials Letters*, 61, pp. 5181–5183
- Hu J., Kong L.C., Liu G., 2008. Structure and hardness of surface of $\text{Al}_{18}\text{B}_4\text{O}_{33}\text{w}/\text{Al}$ composite by laser surface melting. *Materials Science and Engineering A*, 486, pp. 80–84
- Ignat S., Sallamand P., Grevey D., Lambertin M., 2004a. Magnesium alloys laser (Nd:YAG) cladding and alloying with side injection of aluminium powder. *Applied Surface Science*, 225, pp. 124–134
- Ignat S., Sallamand P., Grevey D., Lambertin M., 2004b. Magnesium alloys (WE43 and ZE41) characterization for laser applications. *Applied Surface Science*, 233, pp. 382–391
- Ion J.C., 2005. *Laser Processing of Engineering Materials*. Oxford: Elsevier – Butterworth Heinemann
- Jaffar M.J.M., Sastikumar D., Nath A.K., 2005. Metal–ceramic composite layer formation on Al–Si alloy by laser processing. *Lasers in Engineering*, 15(3–4), pp. 267–283
- Jobez S., Pelletier J.M., Vannes A.B., 1989. Surface engineering of aluminium base alloys with high power laser beams: Improvement of mechanical properties. In *Surface Engineering with High Energy Beams, The Proceedings of the 2nd IFHT Seminar, Lisbon, Portugal*. Lisbon: Center of Mechanics and Materials of the Technical University of Lisbon, pp. 317–323
- Joshi S.V., Sundararajan G., 1998. Lasers for metallic and intermetallic coatings. In: Dahotre N.B. (ed.), *Lasers in Surface Engineering, Surface Engineering Series Vol. 1*. Ontario: ASM International, Ch. 4
- Jun Y., Sun G.P., Wang H.-Y., Jia S.Q., Jia S.S., 2006. Laser (Nd:YAG) cladding of AZ91D magnesium alloys with Al + Si+ Al_2O_3 . *Journal of Alloys and Compounds*, 407, pp. 201–207
- Jun Y., Sun G.P., Jia S.S., 2008. Characterization and wear resistance of laser surface melting AZ91D alloy. *Journal of Alloys and Compounds*, 455, pp. 142–147
- Kovalenko V.S., 2001. Enhanced Surface Properties. In Ready J.F. (ed.) *LIA Handbook of Laser Materials Processing*. Orlando, FL: Laser Institute of America, Ch. 8, 6.4
- Kreutz E.W., Pirch N., Rozsnoki M., 1987. Solidification in laser surface alloying of Al and AlSi10Mg with Ni and Cr. In: Mordike B.L. (ed.), *Laser Treatment of Materials*. Oberursel: DGM Informationsgesellschaft-Verlag, pp. 269–279
- Liechti T., Blank E., 2000. Laser processing of MMC coatings for aluminium alloys. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2000*. Dearborn, Michigan, 2–5 October 2000. Laser Institute of America: Orlando, FL
- Lindner H., Bergmann H.W., Endres Th., 1990. Remelting and alloying of Al–Si alloys. In: *ECLAT (European Conference on Laser–Metal Treatment) ECLAT’90*, pp. 661–670.
- Liu S.Y., Hu J.D., Yang Y., Guo Z.X., Wang H.Y., 2005b. Microstructure analysis of magnesium alloy melted by laser irradiation. *Applied Surface Science*, 252, pp. 1723–1731
- Liu Y.H., Guo Z.X., Yang Y., Wang H.Y., Hu J.D., Li Y.X., Chumakov A.N., Bosak N.A., 2006. Laser (a pulsed Nd:YAG) cladding of AZ91D magnesium alloy with Al and Al_2O_3 powders. *Applied Surface Science*, 253, pp. 1722–1728
- Liu Z., Chong P.H., Butt A.N., Skeldon P., Thompson G.E., 2005a. Corrosion mechanism of laser-melted AA 2014 and AA 2024 alloys. *Applied Surface Science*, 247, pp. 294–299

- López A.J., Ureña A., Rams J., 2009. Laser densification of sol–gel silica coatings on aluminium matrix composites for corrosion and hardness improvement. *Surface & Coatings Technology*, 203, pp. 1474–1480
- Luong H., Hill M.R., 2008. The effects of laser peening on high-cycle fatigue in 7085–T7651 aluminum alloy. *Materials Science and Engineering A*, 477, pp. 208–216
- Majumdar B., Galun R., Mordike B.L., 2000. Excimer laser treatment of magnesium alloy surface. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2000*. Dearborn, Michigan 2–5 October 2000. Laser Institute of America: Orlando, FL
- Majumdar B., Galun R., Mordike B.L., Weisheit A., 2002. Formation of embedded nanoparticles in an Excimer laser treated Mg alloy surface. *Lasers in Engineering*, 12(2), pp. 103–115
- Majumdar B., Galun R., Mordike B.L., Weisheit A., 2003. Influence of Processing Parameters on Morphology and Structure of Single Spot Excimer Laser Melted Mg Alloy Surfaces. *Lasers in Engineering*, 13(2), pp. 75–90
- Man H.C., Yang Y.Q., Lee W.B., 2004. Laser induced reaction synthesis of TiC+WC reinforced metal matrix composites coatings on Al 6061. *Surface & Coatings Technology*, 185, pp. 74–80
- Modest M.F., 2001. Reflectivity and absorptivity of opaque surfaces. In Ready J.F. (ed.), *LIA Handbook of Laser Materials Processing*. Orlando, FL: Laser Institute of America Ch. 5.3
- Mondal A.K., Kumar S., Blawert C., Dahotre N.B., 2008. Effect of laser surface treatment on corrosion and wear resistance of ACM720 Mg alloy. *Surface & Coatings Technology*, 202, pp. 3187–3198
- Nayak S., Wang H., Kenik E.A., Anderson I.M., Dahotre N.B., 2005. Observation of exothermic reaction during laser-assisted iron oxide coating on aluminum alloy. *Materials Science and Engineering A*, 390, pp. 404–413
- Ott A., Dausinger F., Hugel H., 2000. Energy coupling in the cladding process of aluminium alloys. *Proceedings of ICALEO 2000*, Laser Institute of America.
- Pantelis D.I., 1998. Excimer laser surface modification of engineering metallic materials: Case studies. In Dahotre N.B. (ed.), *Lasers in Surface Engineering, Surface Engineering Series, Vol. 1*. Ontario: ASM International, Ch. 5
- Pei Y.T., De Hosson J.Th.M., 2000. Producing Functionally Graded Coatings by Laser-Powder Cladding. [online] *Journal of Materials JOM-e*, 52 (1) (2000) Available at: <http://www.tms.org/pubs/journals/JOM/0001/Pei/Pei-0001.html> [Accessed 8 May 2009]
- Peyre P., Fabbro R., Merrien P., Lieurade H.P., 1996. Laser shock processing of aluminium alloys. Application to high cycle fatigue behaviour. *Materials Science & Engineering A*, 210, (1–2), pp. 102–113
- Rams J., Pardo A., Ureña A., Arrabal R., Viejo F., López A.J., 2007. Surface treatment of aluminum matrix composites using a high power diode laser. *Surface & Coatings Technology*, 202, pp. 1199–1203
- Razavi R.Sh., Salehi M., Monirvaghefi M., Gordani G.R., 2008. Laser surface treatment of electroless Ni–P coatings on Al356 alloy. *Journal of Materials Processing Technology*, 195, pp. 154–159
- Shibata K., Matsuyama H., 1990. Surface alloying of aluminum by CO₂ laser irradiation. In: *ECLAT (European Conference on Laser–Metal Treatment) ECLAT'90*, pp. 681–688
- Spadaro C., Sunseri C., Dispenza C., 2007. Laser surface treatments for adhesion

- improvement of aluminium alloys structural joints. *Radiation Physics and Chemistry*, 76, pp. 1441–1446
- Tsagkarakis M., Villareal F., Hall D.R., Baker H.J., 2002. Surface melting of aluminium alloys using an ultra-super-pulsed CO₂ laser. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2002*. Scottsdale, Arizona 14–17 October 2002. Laser Institute of America: Orlando, FL
- Volovitch P., Masse J.E., Fabre A., Barrallier L., Saikaly W., 2008. Microstructure and corrosion resistance of magnesium alloy ZE41 with laser surface cladding by Al–Si powder. *Surface & Coatings Technology*, 202, pp. 4901–4914
- Wu W.L., 2008. Research progress of laser surface modification of magnesium alloys. *Lasers in Engineering*, 18(1–2), pp. 71–84
- Xu J., Liu W., Kan Y., Zhong M., 2006a. Microstructure and wear properties of laser cladding Ti–Al–Fe–B coatings on AA2024 aluminum alloy. *Materials and Design*, 27, pp. 405–410
- Xu J., Liu W., 2006. Wear characteristic of *in situ* synthetic TiB₂ particulate-reinforced Al matrix composite formed by laser cladding, *Wear*, 260, pp. 486–492
- Xu W.L., Yue T.M., Man H.C., Chan C.P., 2006b. Laser surface melting of aluminium alloy 6013 for improving pitting corrosion fatigue resistance. *Surface & Coatings Technology*, 200, pp. 5077–5086
- Yang S., Zhong M., Liu W., Chen N., Zhang Q., 2001. *In-situ* synthesis of MoSi₂/SiC composite coating by laser cladding. In *ICALEO (International Congress on Applications of Lasers & Electro-optics) ICALEO 2001*. Jacksonville, Florida, October 2001. Laser Institute of America: Orlando, FL
- Yang Y., Wang H.Y., Liu S.Y., Li Y.X., Guo Z.X., Vasiliev M.N., 2005 Surface modification of a Ni–P layer deposited on an aluminium substrate by Nd:YAG pulsed laser irradiation. *Lasers in Engineering*, 15(3–4), pp. 147–156
- Yang Y., Wu H., 2009. Improving the wear resistance of AZ91D magnesium alloys by laser cladding with Al–Si powders. *Materials Letters*, 63, pp. 19–21
- Yilbas B.S., Arif A.F.M., Karatas C., Raza, K., 2009. Laser treatment of aluminium surface: Analysis of thermal stress field in the irradiated region. *Journal of Materials Processing Technology*, 209, pp. 77–88
- Yue T.M., Yan L.J., Chan C.P., Dong C.F., Man H.C., Pang G.K.H., 2004. Excimer laser surface treatment of aluminum alloy AA7075 to improve corrosion resistance. *Surface and Coatings Technology*, 179, pp. 158–164
- Yue T.M., Yan L.J., Chan C.P., 2006. Stress corrosion cracking behavior of Nd:YAG laser-treated aluminum alloy 7075. *Applied Surface Science*, 252, pp. 5026–5034
- Zhang Y., Chen J., Lei W., Xu R., 2008a. Effect of laser surface melting on friction and wear behavior of AM50 magnesium alloy. *Surface & Coatings Technology*, 202, pp. 3175–3179
- Zhang Y.K., Lu J.Z., Ren X.D., Yao H.B., Yao H.X., 2008b. Effect of laser shock processing on the mechanical properties and fatigue lives of the turbojet engine blades manufactured by LY2 aluminum alloy. *Journal of Materials Design*, doi:10.1016/j.matdes.2008.07.017

13.11 Bibliography

- Ion J.C., 2005. *Laser Processing of Engineering Materials*. Oxford: Elsevier – Butterworth Heinemann

- Laser Institute of America, 2009. *Journal of Laser Applications*. [printed, online order] Laser Institute of America. Available at: <http://www.laserinstitute.org/subscriptions/jla/> [Accessed 8 May 2009]
- Mordike B.L. ed., 2009, *Lasers in Engineering*. [printed, online order] Old City Publishing. Available at: <http://www.oldcitypublishing.com/LIE/LIE.html> [Accessed 8 May 2009]
- Ready J.F. ed., 2001. *LIA Handbook of Laser Materials Processing*. Orlando, FL: Laser Institute of America
- Toyserkani E., Corbin S., Khajepour A., 2004. *Laser Cladding*. Boca Raton, FL: CRC Press

Ceramic conversion treatment of titanium-based materials

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Abstract: Ceramic conversion treatment (CCT) is a cost-effective, environmentally friendly new surface engineering technology developed specifically for titanium-based alloys, including titanium and its alloys, TiAl intermetallics and TiNi shape memory alloys. To date, the potential of the new ceramic conversion technology is being realised in the motor sport, automotive, aerospace, biomedical and off-shore oil industries. This chapter starts with a brief introduction to ceramic conversion treatment, followed by three sections devoted to CCT of Ti and its alloys, TiAl intermetallics and TiNi shape memory alloys; and it ends with conclusions and future trends.

Key words: ceramic conversion treatment, titanium and its alloys, TiAl intermetallics, TiNi shape memory alloy.

14.1 Introduction

14.1.1 Driver for cost-effective surface treatment

Owing to their unique physical, mechanical, chemical and biological properties, titanium-based materials, including Ti and its alloys, TiAl intermetallics and TiNi shape memory alloys, have been the material of choice for many industrial sectors to address technological challenges, to promote wealth creation and to increase the quality of life. For example, titanium alloys have found important applications in aerospace, power generation, marine, off-shore, automotive, biomedical, performance sports, general engineering and architecture because of their unusual combination of high strength-to-weight ratio, excellent resistance to corrosion and outstanding bio-compatibility.

However, as discussed in Chapter 3, titanium-based materials are characterised by, especially in sliding situations, poor tribological properties, including high and unstable friction coefficients, severe adhesive wear and susceptibility to fretting wear. This problem could be, to a varying degree, addressed by applying surface engineering technologies initially developed for steel such as ion implantation, electric plating, PVD, thermal spraying, plasma nitriding and laser surface alloying. However, the bonding between coatings and titanium-based materials is normally weak because of the inherent surface oxide film formed on the substrate, and the load-bearing capacity (LBC) of coatings on Ti-based materials is low due to the soft substrate.

Such surface modification technologies as plasma nitriding and laser

surface alloying can address the bonding and LBC issues associated with thin coatings. However, plasma nitriding will reduce the fatigue strength by 10–30% and cause distortion of components with complex geometries due to the relatively high treatment temperatures (Lanagan *et al.*, 1986). Laser melting, laser nitriding and laser cladding normally produce a relatively rough surface and post-machining is needed. Duplex surface treatments can provide combined enhancements in wear resistance and LBC, but they are costly.

It is well-known that titanium-based materials are expensive compared with most ferrous materials, which is a barrier for their wider application. Therefore, it is desirable to develop cost-effective surface engineering technologies tailored for titanium-based materials.

14.1.2 Development of ceramic conversion treatment

Over the past 50 years, there has been extensive research into oxidation of titanium alloys, which is generally viewed as a problem rather than as a surface engineering treatment. It was observed in the early 1950s that the surface of commercially pure titanium (CP-Ti) was effectively hardened when heated in the range of 850 to 1000°C in air at a pressure between 10^{-3} to 10^{-2} mmHg (Worner, 1950). However, subsequent research met with little enthusiasm since, at temperatures high enough to achieve an appreciable hardening effect, a considerable amount of scale was formed and fatigue strength was also reduced (Hanzel, 1954). As a result, this process was considered not to be commercially feasible and was hence commonly ignored.

In view of the difficulties associated with the severe scaling of titanium alloys heated in air, the possibility of controlled oxidising in molten salt baths was explored in the middle of the 1960s (Mitchell and Brotherton, 1964/65). It was found that when titanium specimens were heated in lithium carbonate salt baths at temperatures between 600 and 900°C for 2 to 4 hours, satisfactory layers were formed. However, corrosion of the Ti substrate and the environmental impact are major concerns of this method.

Gaucher and Zabinsky (1975) developed an oxidising process, naming it ‘Tifran’, to treat Ti-6Al-4V at 750°C for 10 h. However, such a treatment produced a porous, poorly adherent oxide layer. Similarly, Mushiake *et al.* (1991) investigated the possibility of improving the wear resistance of Ti-22V-4V beta titanium alloy by thermal oxidation at 850°C in air. They found that the bonding between the surface oxide and the substrate was very weak and therefore the oxide layer formed was removed by grinding before application.

A new surface engineering technique based on thermal oxidation has recently been developed specifically for titanium-based materials by Dong *et al.* (1997; 1998). The technique is a thermochemical process, usually carried

out in a controlled atmosphere containing oxygen. During the treatment, the surface of the titanium-based material reacts with oxygen to convert *in-situ* into titanium oxides (hence comes the name ceramic conversion). Unlike some previous processes, the newly developed ceramic conversion process can effectively harden titanium-based materials without causing scaling or surface damage (Dong *et al.*, 1998). While the term ‘thermal oxidation (TO)’ describes the process, the term ‘ceramic conversion (CC)’ emphasises the results of thermal oxidation. Therefore, in this chapter, CC is used instead of TO from a surface engineering viewpoint.

Since then, many researchers are exploring the potential of CCT for different titanium materials, such as CP Ti (Bloyce *et al.*, 1998; Qi, 2000; Krishna *et al.*, 2007; Dahm, 2009), Ti-6Al-4V (Borgioli *et al.*, 2005; Guleryuz and Cimenoglu, 2005; Yazdanian *et al.*, 2007; Biswas and Majumdar, 2009), Timet 550 (Boettcher *et al.*, 2002), SP700 (Komotori *et al.*, 2001; Kim *et al.*, 2008), Ti-10Ta-10Nb (Ahn *et al.*, 2008), Ti-6Al-17Nb (Meydanoglu *et al.*, 2008) to achieve a variety of surface properties. The CCT technology has also been applied to TiAl intermetallics (Xia, 2004) and TiNi shape memory alloys (Ju, 2007).

More recently, some researchers have used different oxygen-containing atmospheres for CCT treatment at relatively high temperatures (750–950°C), including a gas mixture of O₂/Ar (Stratton, 2002), CO/Ar (Kim *et al.*, 2008; Stratton and Graf, 2008) and CO₂/Ar (Kim *et al.*, 2006; Stratton and Graf, 2008),

14.2 Ceramic conversion treatment (CCT) of titanium and titanium alloys

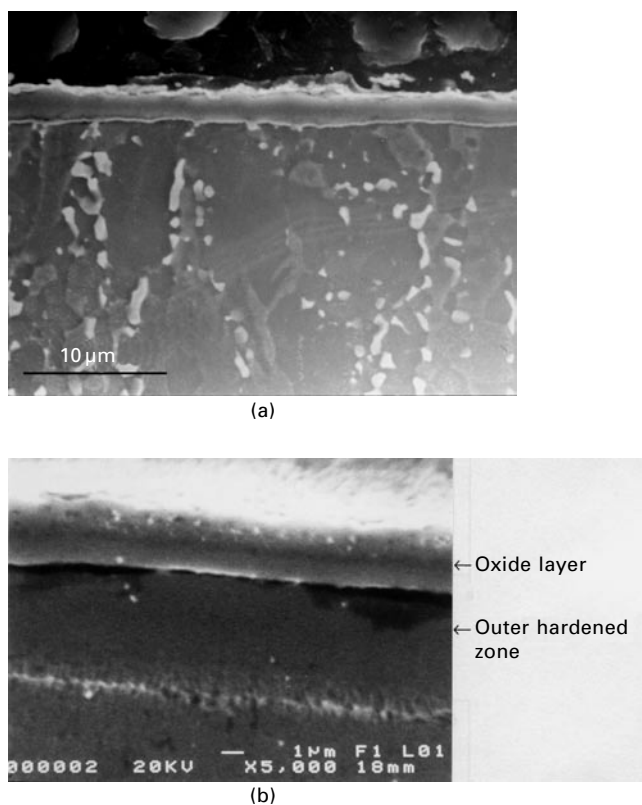
14.2.1 Treatment and microstructure

Ceramic conversion treatment (CCT) is a patented, cost-effective and environmentally friendly surface engineering technique developed by Dong *et al.* (1997) initially for titanium and titanium alloys. In essence, this technique is a thermochemical process based on thermal oxidation and therefore it was initially named as thermal oxidation (TO) treatment in our early publications. The CCT is usually carried out in a controlled medium containing oxygen (e.g. in air) at 550–650°C for 50–120 hours. However, some researchers conducted the CCT at higher temperatures (700–900°C) for a shorter period of time (a few hours). The reported gas compositions include 20%O₂–80%N₂ (Dong *et al.*, 1997), Ar-20%CO₂ and Ar-20%O₂ (Kim *et al.*, 2006) and Ar-5%CO (Kim *et al.*, 2008). In addition to gas mixtures, CCT can be carried out in plasma to enhance the process (Borgioli *et al.*, 2004; Ju and Dong 2006).

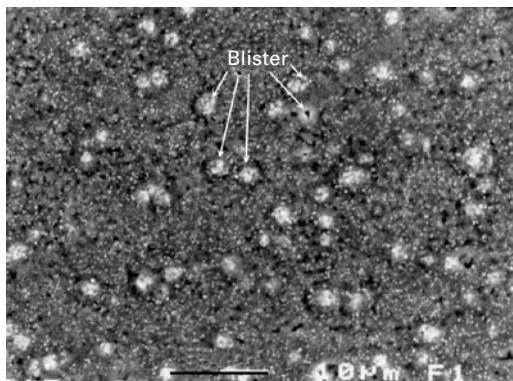
During CCT, oxygen reacts with titanium to convert the surface into a

titanium oxide layer. Meanwhile, oxygen also diffuses into the titanium to form an oxygen hardened case via interstitial solid solution hardening. Figures 14.1a and b show respectively typical SEM cross-sectional microstructures of 600°C/65h CC-treated Ti-6Al-4V alloy and 600°C/100h CC-treated CP-Ti in an atmosphere containing about 80% oxygen and 20% nitrogen. The CCT produces a thin (a few microns), dense, adherent oxide layer supported by a strong and relatively thick (a few tens of microns) oxygen diffusion zone.

When treated at temperatures above 600°C, the surface oxide layer developed by the CCT is dominated by TiO_2 of rutile modification. The thicknesses of both the surface ceramic layer and the oxygen diffusion zone increase with the treatment temperature and/or time; however, high-temperature and long treatment time will form porous, poorly adherent oxide layers or end up with severely damaged surfaces (Fig. 14.2). The optimal treatment conditions depend mainly on the oxidation behaviour and thus composition of the titanium materials.



14.1 SEM micrograph showing cross-sectional microstructures of (a) 600°C/65h CCTed Ti-6Al-4V and (b) 600°C/100h CCTed CP-Ti.



14.2 SEM micrograph showing surface blisters in surface oxide on high-temperature oxidised Ti-6Al-4V.

14.2.2 Hardening effect

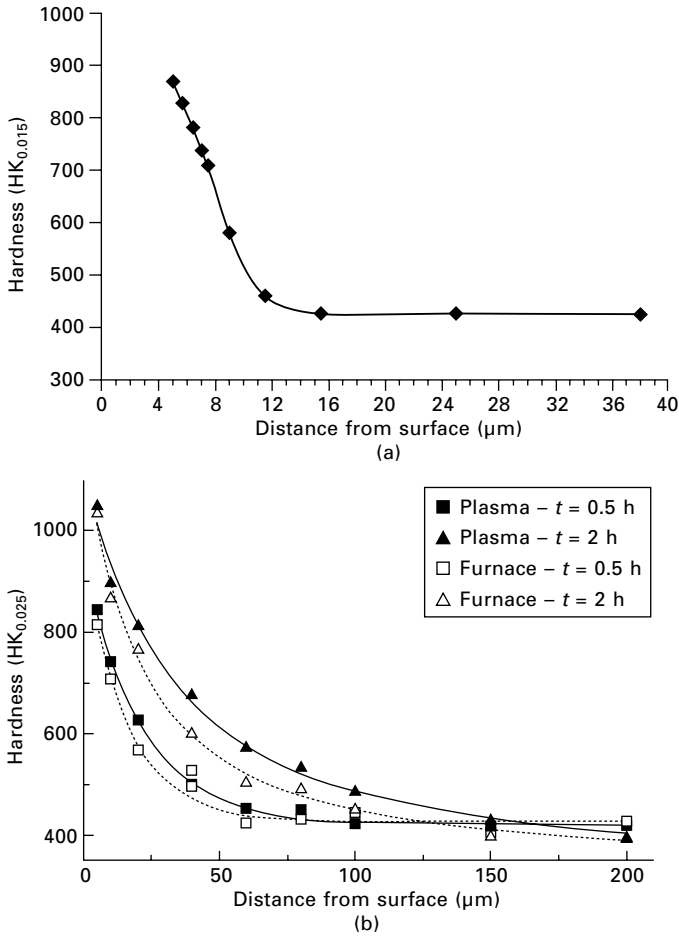
Significant surface hardening of Ti and its alloys can be achieved by CC treatment because of the formation of the surface ceramic layer and the oxygen diffusion hardened case. For example, the hardness (H) and Young's modulus (E) of the surface oxide layer formed on Ti-6Al-4V during CCT are 10.6 and 146.7 GPa, respectively (Dong *et al.*, 1997). The E/H ratio can thus be reduced from 26.9 for as-received Ti-6Al-4V to 13.8 for the CC treated material.

The hardness depth distribution across the oxygen diffusion zone (ODZ) beneath the oxide layer depends mainly on alloy composition and treatment conditions (such as temperature, time and oxygen-containing medium). The thickness of the ODZ for 600°C/50 h CC treated Ti-6Al-4V is about 15 μm (Fig. 14.3a) while that of material treated at 900°C for 0.5 and 2 h increased to 50 and 150 μm , respectively (Fig. 14.3b) (Borgioli *et al.*, 2004). However, it should be pointed out that such high-temperature CCT would severely reduce the bonding between the surface oxide layer and the ODZ, and the fatigue properties.

14.2.3 Tribological properties

Friction coefficient

As discussed in Chapter 3, untreated Ti and its alloys are characterised by a high and unstable coefficient of friction because of their high adhesion to most engineering materials. The rutile oxide layer formed during CCT is very effective in reducing the coefficient of friction of Ti and its alloys, especially under oil lubricated conditions. For example, the friction coefficient of Ti-6Al-4V sliding against a WC ball can be reduced from 0.5–0.6 (dry) and



14.3 Hardness depth profiles of (a) 600°C/50h (Dong *et al.*, 1997) and (b) 900°C/0.5 and 2h CCT (Borgioli *et al.*, 2004) treated Ti-6Al-4V.

0.4–0.5 (lubricated) for the untreated material to 0.2–0.3 (dry) and 0.1–0.2 (lubricated) after CCT, in ball-on-disc tests (Dong *et al.*, 1997). A similar friction reduction effect has also been observed when applying CCT to Timet 550 (Ti-4Al-4Mo-2Sn-0.4Si) alloy (Boettcher *et al.*, 2002) and CP-Ti (Taheri and Zahrani, 2008; Krishna *et al.*, 2007).

The friction reduction effect conferred by CCT can be attributed to the reduced E/H ratio, thus limiting the degree of plastic deformation. In addition, Gardos (1988) has reported that because of its layered structure, rutile possesses a low shear strength and thus low friction. Research has also revealed that the rutile oxide layer can effectively increase wettability with oil and hence improve the effectiveness of lubrication on the titanium surfaces (Dong and Bell, 1999).

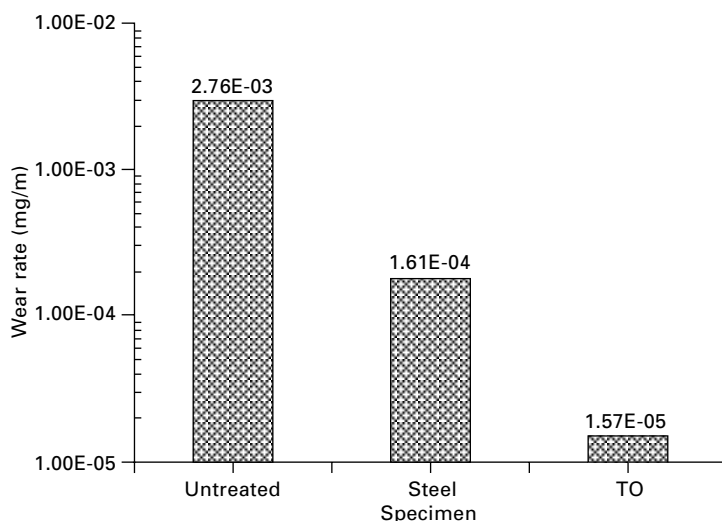
Wear resistance

CCT can also successfully improve the wear resistance of Ti and its alloys under scratch, sliding and rolling–sliding conditions. The abrasive wear resistance of CC-treated and TiN-coated Ti-6Al-4V and SP700 (Ti-4.5Al-3V-2Fe-2Mo) as well as the untreated materials, was evaluated by Komotori *et al.* (2001) by scratching these samples with a diamond Rockwell ‘C’ indenter with an indentation load of 500 g at a scratch speed of 0.25 mm s^{-1} . As evidenced in Table 14.1, the CCT treated Ti alloys outperform both the untreated and TiN coated materials under the abrasion conditions.

Dong and Bell (2000) compared the wear resistance of an untreated and a CC treated Ti-6Al-4V wheel under a combined 90% rolling/10% sliding contact. The counterpart was a hardened (600 HV10) 709M40 steel wheel under oil lubricated conditions, for 450 000 revolutions. As shown in Fig. 14.4, the steady wear rate of the CC treated Ti-6Al-4V wheel ($1.57 \times 10^{-5} \text{ mg m}^{-1}$) is two orders of magnitude lower than that for the untreated wheel

Table 14.1 Comparison of scratch wear scar areas (μm^2) (Komotori *et al.*, 2001)

Treatment	SP700	Ti-6Al-4V
Untreated	28	29
TiN coated	27	37
CC treated	15	15



14.4 Wear rate of CC treated Ti-6Al-4V as well as untreated Ti-6Al-4V and hardened steel counterpart for comparison (Dong and Bell, 2000).

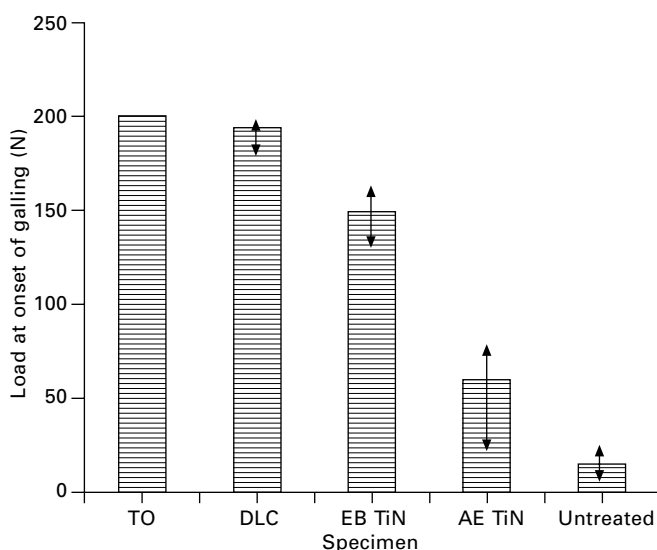
($2.76 \times 10^{-3} \text{ mg m}^{-1}$) and more than ten times lower than that for the hardened steel wheel ($1.61 \times 10^{-4} \text{ mg m}^{-1}$). This indicates that the CC treated Ti-6Al-4V wheel can outperform the hardened steel wheel. Comparable results have been obtained by Yazdanian *et al.* (2007) when sliding a $600^\circ\text{C}/60\text{h}$ CC treated Ti-6Al-4V against a hardened 52100 steel ball under 2 N at 0.05 m s^{-1} in air and in vacuum.

Equally, CCT can effectively improve the wear resistance of CP-Ti. For example, the wear of CP-Ti can be reduced by 6–8 times by $850^\circ\text{C}/5\text{h}$ CCT when unidirectionally sliding against a 6 mm alumina ball under 2 N at a speed of 0.1 m s^{-1} in air (Krishna and Sun, 2007).

Anti-galling and anti-scuffing capacity

Titanium and its alloys are notoriously susceptible to scuffing (localised surface damage under lubrication) and galling (gross surface damage under poor or no lubrication conditions). CCT can effectively improve the resistance of titanium and its alloys to galling and scuffing.

Wiklund and Hutchings (2001) independently compared the anti-galling capacity of CCT with CVD DLC coating, ion implanted (IonSlip), and Arc- (AE) and electron-beam (EB) vaporised TiN coatings, using a galling test in which two crossed cylinders of 6.35 mm in diameter are slid over each other under a steadily increasing contact load up to 200 N. As shown in Fig. 14.5, galling occurred to the untreated Ti-6Al-4V at a very low load



14.5 Summary showing the critical load for onset of galling: Mean values and the range (Wiklund and Hutchings, 2001).

(6–18N). On the other hand, no galling occurred to the CCT samples up to the maximum load, 200 N (equivalent to a maximum Hertzian pressure of 5 GPa), on the test rig. This indicates that the CC treatment provides the best protection against galling, followed by CVD DLC and EB TiN coatings, whereas the AE TiN coating showed the lowest critical galling load. The high anti-galling capacity of the CC treated Ti-6Al-4V can be explained by the fact that, unlike these thin coatings, the thin ($\sim 2\text{ }\mu\text{m}$) rutile layer formed during the CCT is mechanically supported by a relatively thick (15–20 μm) oxygen diffusion hardened case. In addition, because of the *in-situ* conversion nature, the bonding between the surface rutile layer and the hardened case beneath is much stronger than these PVD and CVD coatings on the soft Ti-6Al-4V substrate.

The anti-scuffing capacity of untreated, 750°C/20h plasma nitrided (PN) and 600°C/95h CC treated Ti-6Al-4V has been assessed using a block-on-wheel configuration on an Amsler wear test machine. During the test, the En19 steel wheel (HV800) rotated at a speed of 400 rpm against the titanium block specimen in oil-lubricated conditions. The load was increased step by step and kept for 5 min at each load level until a large increase in friction force occurred, which indicated the failure or scuffing of the surface layer. The corresponding load was taken as the anti-scuffing capacity of the tested material. The results indicate that scuffing occurred to the untreated Ti-6Al-4V at a load as low as 5 N, while the critical loads for the PN and CC treated materials were 1450 and 1470 N, respectively.

14.2.4 Corrosion and corrosion wear

It is known that, in general, titanium and its alloys possess very good corrosion resistance in many different corrosive media. However, the corrosion resistance of Ti and its alloys can be further enhanced by CCT.

CCT can effectively increase the corrosion resistance of CP-Ti both in electrochemical and immersion corrosion tests. The results of anodically potentiodynamic polarisation measurements in 3.5% NaCl solution demonstrated that the CC treated CP-Ti exhibit much better electrochemical corrosion behaviour than the as-received material in terms of the more noble corrosion potential and the much lower anodic current density. The results also revealed that the anodic current density of CCT treated CP-Ti is 1–2 orders of magnitude lower than that for plasma nitrided material (Qi, 2000).

Equally, the CCT can increase the corrosion resistance of CP-Ti in boiling HCl solutions, and the results are summarised in Table 14.2. It can be seen that the corrosion resistance of the CC-treated CP-Ti is much better than as-received CP-Ti and Ti-0.05Pd (well-known corrosion-resistant Ti) in boiling 10% HCl solution; the lifetime for the protective surface layer of the

Table 14.2 Corrosion resistance of CP-Ti in HCl solutions (Bloyce *et al.*, 1998)

Material and treatment	Weight loss, mg (cm ⁻² ·h ⁻¹) in boiling 10% HCl solution	Time-to-breakdown (h) in boiling 20% HCl
Untreated CP-Ti	4.14	Breakdown before boiling
Untreated Ti-0.05Pd	1.75	Breakdown before boiling
Plasma nitrided CP-Ti	Nil	2
CC treated CP-Ti	Nil	20

CC-treated CP-Ti is about ten times that of plasma nitrided CP-Ti in boiling 20% HCl (Bloyce *et al.*, 1998).

Recently, Ahn *et al.* (2008) also reported that, after CCT at 650°C for 30 min, the corrosion current of Ti-10Ta-10Nb in 0.9% NaCl solution can be reduced. In addition, they found from cytotoxicity tests in a MTT assay treated L929 fibroblast that the CCT can lower the cytotoxicity of Ti-10Ta-10Nb alloy as well.

Komotori *et al.* (2001) have studied the corrosion-wear of as-received PVD TiN coated and CC-treated Ti-6Al-4V and SP700 (Ti-4.5Al-3V-2Fe-2Mo) alloys by combining scratching and cyclic polarisation in 0.89% NaCl solution at 37°C. They found that the exterior surface oxide layer produced by the CCT was very stable; at high applied potential (>1.0 V Ag/Ag/Cl), the TiN-coated Ti alloys were inherently prone to pitting and blistering while the CC-treated materials had a superior repassivation capacity following break-down. Prior abrasion damage from multi-directional scratching made the TiN-coated alloys more vulnerable to subsequent corrosion of the substrate but this was not observed for the CC-treated alloys. Therefore, the CC-treated samples offered the best resistance to the sequential actions of mechanical damage and corrosion. The improved corrosion-wear resistance of CC-treated Ti alloys can be attributed to the formation of a dense, stable and wear resistant TiO₂ oxide layer.

14.2.5 Fatigue and fretting fatigue properties

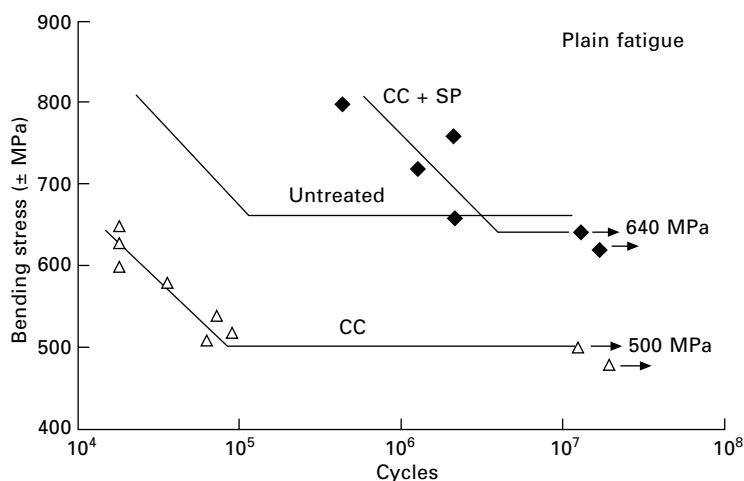
It should be mentioned that although CCT can effectively improve the tribological and corrosion properties of Ti and its alloys, such treatment will, to a lesser or greater extent, reduce their fatigue properties. For instance, the fatigue limit of Ti-6Al-4V and Ti-6Al-7Nb was reduced by 30 and 10% respectively after 600°C/60 h CCT in air (Meydanoglu *et al.*, 2008). Cingi *et al.* (2007) reported that the rotating bending fatigue strength of Ti-6Al-4V alloy at 5×10^6 cycles decreased from 610 to 400 MPa (i.e. a 34% reduction) following 600°C/60 h CCT in air. This is echoed by the findings of Li *et al.* (2007) that, following CCT at 600°C for 100 h, the fatigue limit of Ti-6Al-4V alloy was reduced from 660 MPa to 500 MPa (representing

a 24% reduction). However, it is also reported by Ebrahimi *et al.* (2008) that CCT can marginally improve the fatigue limit of 600°C/2 h treated Ti-4Al-2V alloy.

Detailed investigation indicates that the reduction in fatigue properties could be attributed to the formation of a surface oxide layer, a roughened surface (from 0.07 to 0.21 μm) and residual tensile stress (~ 100 MPa). There is a significant difference in elastic modulus between the surface rutile oxide layer (~ 230 GPa) and the core material (~ 114 GPa). In such a composite system, the stress developed at a given bending load will be much higher in the oxide than in the substrate. Since the ceramic oxide is relatively brittle, premature fatigue cracking can be expected to occur from the rutile layer, as well as from the interface between the oxide and the oxygen diffusion zone at a lower stress. Multiple fatigue origins and the oxide layer spallation on a fatigue fractured sample are reflections of crack initiation from the oxide layer and from the interface (Li *et al.*, 2007).

However, the detrimental effect of CC treatment on rotating-bending fatigue properties could be recovered by an additional shot peening (SP) after CC treatment (Fig. 14.6). Fatigue-like failures of CC treated titanium and its alloys have also been observed in reciprocating pin-on-plate sliding wear (Dahm, 2009) and wheel-on-wheel rolling-sliding wear tests (Dong and Bell, 2000). Interfacial fatigue was observed, as evidenced by the bench marks, when the applied load is above a critical value (Dong and Bell, 2000). It has been found that interfacial fatigue progressed from isolated blisters, through widespread blistering, to final rupture of the oxide layer (Dahm, 2009).

In contrast to its detrimental effect on plain fatigue properties, CC treatment



14.6 Effect of shot peening on the fatigue properties of CC treated Ti-6Al-4V (Li *et al.*, 2007).

can improve the fretting fatigue strength (FFS) at 10^7 cycles of Ti-6Al-4V alloy by approximately 10%. This is attributed to the hard ceramic oxide layer on the surface and the oxygen-hardened diffusion zone underneath, which reduces fretting wear, fretting surface damage and fretting-induced fatigue crack initiation (Li *et al.*, 2007).

14.2.6 Applications

The new ceramic conversion technology can offer combined improvements in hardness, tribological properties, corrosion resistance and biocompatibility for titanium alloys, thus paving the way towards high-performance, dynamically-loaded titanium components in demanding design situations. For example, the CCT technology initially invented from the Surface Engineering Research Group at the University of Birmingham has been transferred to Ad.Surf. Eng.Ltd (www.adsurfeng.com), a spin-off company of the University of Birmingham. To date, the potential of these novel technologies has been realised in motorsport (Dong *et al.*, 1999a) and off-shore industries (Dong and Bell, 1999); and CCT treated titanium bone fixation devices are being tested *in vivo*.

Great efforts have been made to reduce the weight of engines, especially reduction in the reciprocating mass of internal components. This allows greater acceleration of the lighter component or assembly, thus achieving better fuel efficiency and a higher upper limit of the engine speed. The development of the cost-effective, environmentally friendly CCT has provided a golden opportunity for replacing steel components with titanium alloy in racing car engines (Dong *et al.*, 1999a).

Another successful application example is CC-treated CP-Ti valves used in the off-shore industry. Because of the corrosive environments, such valves are required to be made from corrosion-resistant CP-Ti. However, galling occurs on the untreated CP-Ti disc due to the high contact pressure and low open-close cycles. This problem can be addressed by applying CCT to the CP-Ti disc and such surface treated valves have been successfully used for years.

Dong *et al.* (1999b) have also explored the possibility of reducing wear of UHMWPE by the damage of titanium surface in UHMWPE-on-Ti artificial hip joints. It has been reported that although UHMWPE cups are much softer than titanium heads, severe wear occurs to the head of retrieved UHMWPE-on-Ti artificial hip joints. This seemingly abnormal wear of Ti by UHMWPE is believed to be caused by hydrogen-induced embrittlement of the Ti surface (Li *et al.*, 2001). The Ti wear debris is embedded into the soft polymer, thus abrading the Ti surface. When a relatively thick, dense and adherent oxide layer on the Ti is formed by CCT, the diffusion of hydrogen is retarded or stopped, thus preventing the Ti surface from hydrogen-induced

damage. Therefore, CCT offers significant promise for combating the wear of Ti surfaces by polymers in artificial hip and knee joints.

14.3 CCT for TiAl intermetallics

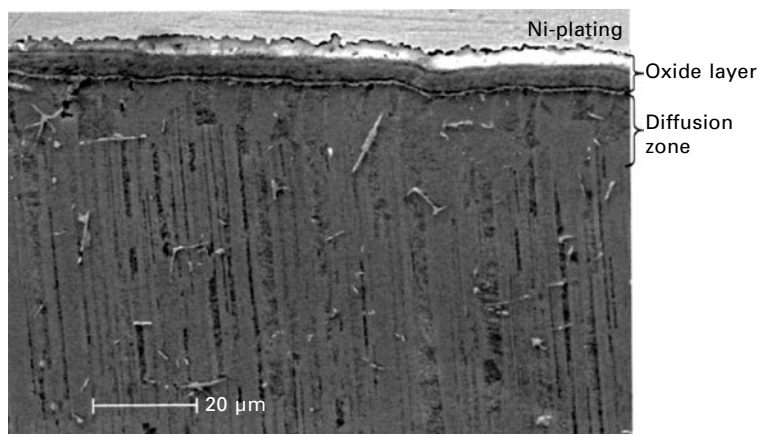
Titanium-based intermetallics have great potential for high-tech applications, owing to their high specific strength, stiffness and creep resistance at elevated temperatures. For example, higher operating temperatures of gas turbine and car engines allow more efficient fuel energy conversion with lower toxic emissions. However, it has been found that these aluminides have very poor tribological behaviour (Chapter 3). This has been a serious impediment to their uptake as steel component replacements. Chu and Wu (1996) and Raskar (2000) have used plasma nitriding to improve the tribological properties of TiAl. Stimulated by the success of ceramic conversion treatments in improving the tribological, load-bearing and corrosion properties of titanium and its alloys, researchers have recently explored the potential of CCT for TiAl intermetallics because they contain at least 50 at% of titanium.

14.3.1 Treatment and microstructure

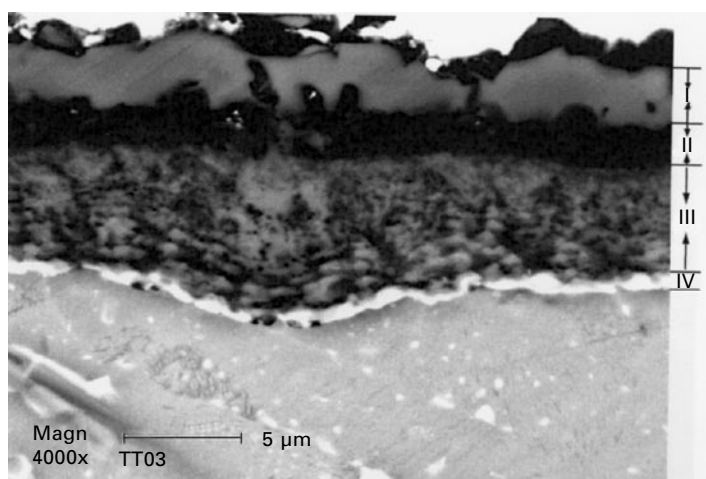
Although a great deal of work has been devoted to studying the oxidation behaviour of titanium aluminides, these studies have focused on oxidation resistance rather than on using the beneficial effect of the oxide layer to improve wear resistance. It is obvious that TiAl contains high amounts of Al and Ti; therefore, an oxide layer of Al_2O_3 and/or TiO_2 could be formed when applying CCT originally developed for titanium and its alloys.

The CCT treatment of γ -TiAl based alloys is normally carried out at temperatures ranging from 750–950°C, depending on the amounts and types of the alloying elements. This is because, if the treatment temperature is too low, no practically useful hardening effect can be produced; on the other hand, severe scaling occurs to TiAl at temperatures near 1000°C (Xia, 2004).

Figure 14.7 shows a typical SEM cross-sectional microstructure of 850°C CC treated γ -TiAl based Ti-48Al-2Nb-2Cr-1B alloy. Similar to the CC treated titanium alloys, the CCT produced a surface oxide layer followed by an oxygen diffusion zone (ODZ) beneath. XRD analyses revealed major diffraction peaks of TiO_2 and Al_2O_3 from the CC-treated surfaces. More detailed SEM and TEM characterisation indicated that the CCT surface was multi-layered (Xia *et al.*, 2004a). For example, the 850°C/100 h CC treated Ti-48Al-2Nb-2Cr-1B contained four sublayers (Fig. 14.8): (i) top rutile TiO_2 , (ii) α - Al_2O_3 , (iii) mixture of α - Al_2O_3 and TiO_2 and (iv) $\text{Ti}_2\text{AlN/TiN}$. The sublayer (i) was thicker than sublayer (ii) because TiO_2 grows much more rapidly than Al_2O_3 (Tortorelli and DeVan, 1996). The thickness of the ODZ increased from 7 to 16 μm when the treatment time increased from 8



14.7 SEM cross-section image of 850°C/50h treated Ti-48Al-2Nb-2Cr-1B (Xia *et al.*, 2004a).



14.8 High magnification SEM back-scatter electron image of 850°C/100h treated Ti-48Al-2Nb-2Cr-1B.

to 100 h. The ODZ is thinner when formed in TiAl intermetallics than in titanium alloys.

14.3.2 Surface property enhancement

Significant improvement in the surface hardness of titanium aluminides can be achieved through the ceramic conversion treatment. The surface hardness of 850°C/100 h CCT treated Ti-48Al-2Nb-2Cr-1B can be more than four

times higher than that of the untreated surface because of the formation of surface oxide layers; the ratio of E/H is about three times lower than that of the untreated material. Therefore, CCT cannot only increase hardness but can also reduce the plastic deformation due to the reduced E/H ratio.

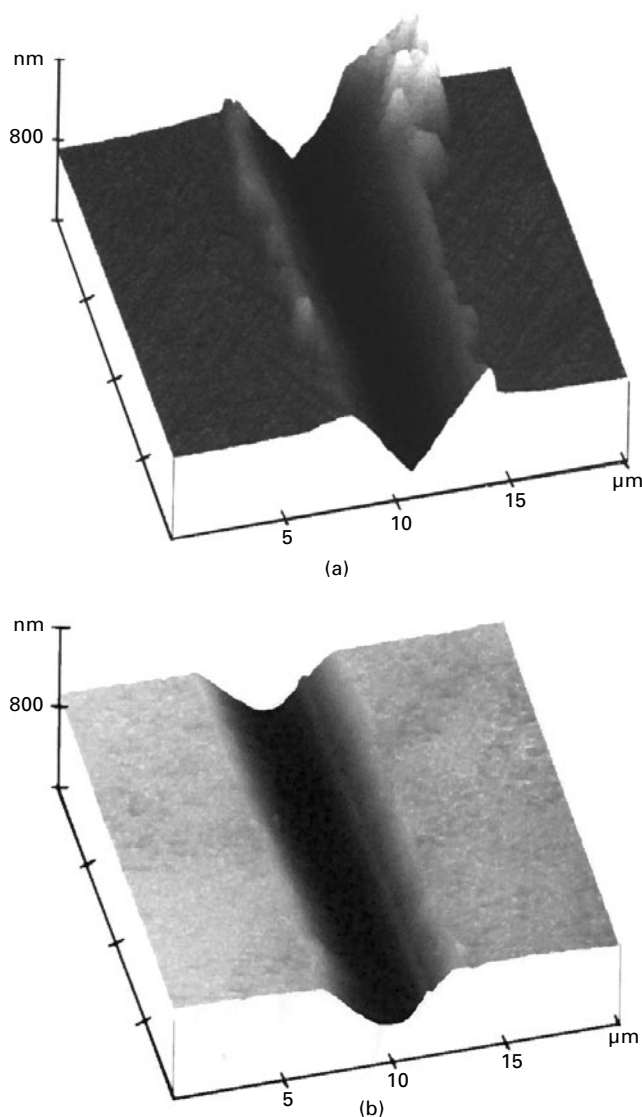
Because of the formation of surface oxide layers of α -Al₂O₃ and TiO₂, the scratch resistance of TiAl intermetallics can be effectively increased. For example, when scratched by a diamond indenter under a load of 100 mN, the residual scratch depth reduced from 400 nm for the untreated Ti-48Al-2Nb-2Cr-1B to less than 350 nm following the CCT. Atomic force microscopy (AFM) measurements demonstrated no cracking or spallation of the oxide layer (Fig. 14.9), implying that the surface oxide layer has reasonable toughness and adherence to the substrate (Xia *et al.*, 2006).

The tribological properties of TiAl intermetallics can be greatly enhanced by ceramic conversion treatment. The critical load to scuffing, determined from the Amsler block specimen-on-hardened wheel (780 HV) testing, was about 40 kgf for the as-received Ti-48Al-2Nb-2Cr-1B, and increased to 180 kgf following CC treatment. The friction coefficient of Ti-48Al-2Nb-2Cr-1B disc sliding against a WC ball (8 mm in diameter) under 10 N in air was scattered in the range of 0.5–0.7, whereas the friction coefficient of CC treated material was much smaller and stable, with an average value of 0.22. The average wear rate in the steady stage of the as-received material was $2.55 \times 10^{-3} \text{ mm}^3 \text{ m}^{-1}$, which is more than two orders magnitude greater than that of the as-received material ($6.76 \times 10^{-6} \text{ mm}^3 \text{ m}^{-1}$) (Xia *et al.*, 2004b).

14.3.3 Applications

It has long been the target of all new engine development to improve the efficiency of the engines, thus reducing fuel consumption and CO₂ emissions. The use of TiAl valves could contribute to achieve this target, mainly because of their light weight and thus reduced moving mass. In addition, TiAl intermetallics possess relatively high oxidation resistance and high strength at high temperature, which is particularly beneficial for exhaust valves in view of the ever-increasing service temperature.

One of the technical barriers to the potential use of TiAl as engine valves is the poor wear resistance of TiAl and the wear of valves at the tip of stem, stem and the seat. Gebauer (2006) has explored the possibility of using CCT to protect TiAl exhaust valves from wear. Figure 14.10 compares the wear of CCT treated (left) and PVD coated (right) TiAl exhaust valves after 600 h testing. It can be seen that the distance between the groove and the tip is much smaller for the PVD coated valve than for the CC treated one. Indeed, the tip of the PVD coated valve was worn by 1.5 mm in 20 h, but no significant wear to the CCT treated tip was observed. Therefore, CCT is



14.9 AFM images of the scratch track on (a) as-received and (b) CCT TiAl under a load of 100 mN (Xia *et al.*, 2006).

a cost-effective surface engineering technology for the wear protection of TiAl valves.

TiAl intermetallics are initially developed for aerospace applications and their high specific strength and high resistance to creep and oxidation make them good candidate materials for low-pressure turbine blades. As has been discussed in Chapter 3, gamma-TiAl is prone to adhesion, material transfer



14.10 Comparison of the wear of (a) CCT and (b) PVD treated TiAl valves (Gebauer, 2006).

and fretting damage (Miyoshi *et al.*, 2003). It is thus expected that CCT could be a promising surface engineering technology for combating fretting wear and fretting fatigue of gamma-TiAl turbine blades.

14.4 CCT of TiNi shape memory alloys

TiNi shape memory alloys (SMAs) are ordered intermetallic compounds based on the equiatomic composition. Because of their shape memory effect and superelasticity effect, TiNi SMAs have found many important applications. For example, as biomaterials, TiNi SMAs are used in dentistry and medicine as body implants and surgical devices (Hassters *et al.*, 1990); as smart materials, TiNi SMAs are used to make actuators to actively sense and control the action of some important devices. Although TiNi shape memory alloys can exhibit fairly good wear resistance under some conditions, resulting from their rapid work hardening and superelasticity characteristics (Li, 2000), wear is still a major concern for many demanding biomedical and actuator applications (Ju and Dong, 2007).

14.4.1 Treatment and microstructure

TiNi shape memory alloys are attractive materials for biomedical applications owing to their unique shape memory and superelasticity characteristics, as well as acceptable biocompatibility as bulk materials. However, concerns over the release of potentially toxic nickel ions caused by such surface degradation processes as wear and corrosion have, to a large extent, restricted their wider applications. As smart materials, TiNi shape memory alloys are

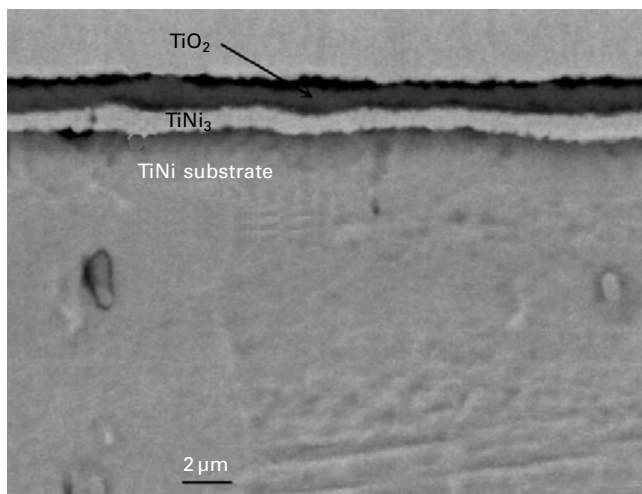
also used to make actuators for some important devices. For many such applications, sliding wear would occur, which could impair the effectiveness and reliability of TiNi actuators.

Some surface treatments, such as excimer laser treatment, mechanical polishing, electropolishing, nitric acid passivation and steam autoclaving, have been used to thicken the surface oxide layer on TiNi SMAs (Shabolovskaya, 2002). Although these surface treatments can improve, to some extent, the corrosion resistance of TiNi alloys, the oxide layer formed during these treatments is too thin to withstand wear, or the synergistic effect of corrosion and wear.

Recently, Ju (2007) has conducted systematic work to address the above wear and metal ion release problems by applying the ceramic conversion treatment to TiNi SMAs. This is because, mechanically, TiO_2 has high hardness and wear resistance, and biologically, the rutile TiO_2 formed can act as a barrier to Ni ion release. Both thermal oxidation treatment in air at 300–500°C for 50 h and 550–750°C for 1–9 h (Ju, 2007), and plasma oxidation in a gas mixture of air and hydrogen at 400–650°C for 4–16 h (Ju and Dong, 2007) were investigated to identify the optimal conditions for CCT of TiNi SMA surfaces. The comparative studies (Ju, 2007) indicated no apparent advantages for plasma oxidation over thermal oxidising treatment in terms of the thinner oxide layer and lower scratch critical load, probably due to the sputtering effect of plasma. In addition, oxidation of plasma facility associated with plasma oxidation treatment at high-temperature could be a practical problem.

Ju and Dong's detailed research (Ju, 2007; Ju and Dong, 2007) into CCT of TiNi SMAs revealed that, when treated at 300°C in air for 50 and 100 h, a very thin single layer of anatase TiO_2 was formed. When the treatment temperature rose to 400°C, rutile TiO_2 was identified in conjunction with anatase TiO_2 . A new phase, Ni_3Ti , was formed at 400°C when increasing the treatment time from 50 to 100 h. The phase composition of 500°C/(50 and 100 h) and 550°C/(4–16 h) treated samples were the same as the 400°C/100 h treated one but the intensity of rutile TiO_2 and Ni_3Ti increased while that of anatase TiO_2 decreased. A new phase, NiTiO_3 was detected along with rutile TiO_2 , anatase TiO_2 and Ni_3Ti in the surface of TiNi SMAs after CCT at 650°C or above.

All the samples after 50 and 100 h CCT at 300, 400 and 500°C had a similar cross-section structure with a single layer formed on the surface. The thickness of the ceramic layer increased with the treatment temperature and time, but it was normally less than 1 micron. A two-layer cross-section structure, a top TiO_2 layer followed by a TiNi_3 -enriched layer (Fig. 14.11), was observed in the surface of TiNi SMAs when CC treated at 550°C for more than 2 hours, or at 650°C for 1–4 hours. Further increase in temperature and/or time led to the formation of a three-layer cross-section structure with



14.11 Cross-sectional two-layer structure of CCT SMAs (Ju and Dong, 2007).

a Ni-rich intermediate layer between the top TiO_2 layer and bottom TiNi_3 layer. Scratch test results demonstrated that CCT treated surfaces with a relatively thick single layer or relatively thin double layers possessed high scratch critical loads.

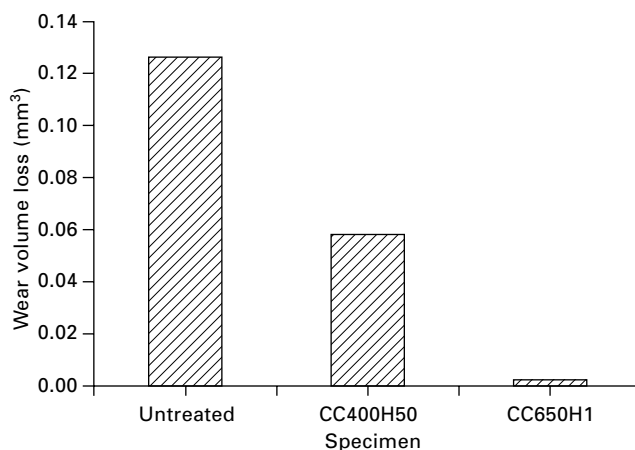
14.4.2 Surface property enhancement

Corrosion resistance

Optimally CC treated TiNi SMA samples demonstrate a much better corrosion resistance in Ringer's physiological solution when tested using the potential dynamic corrosion method (Ju, 2007). This is because the TiO_2 oxide layer formed by CCT is chemically inert in neutral or acidic media, and therefore can effectively protect the substrate from corrosion provided the oxide layer is dense, adherent and free of defects (such as flaws, pinholes, scratches or pores).

Dry unidirectional sliding wear

The sliding wear resistance of TiNi SMAs can be effectively improved by optimal CCT. As shown in Fig. 14.12, the wear of $400^\circ\text{C}/50\ \text{h}$ (CC400H50) and $600^\circ\text{C}/1\ \text{h}$ (CC650H1) CCT treated TiNi SMAs is significantly reduced when unidirectionally sliding against an 8 mm hardened (853 HV) SAE52100 ball in air under 6 N. The wear mechanism changed from adhesive and abrasive wear for the untreated materials to mild abrasive wear for the CC



14.12 Comparison of wear volume of the untreated and CC treated TiNi alloys samples under 6N (Ju and Dong, 2007).

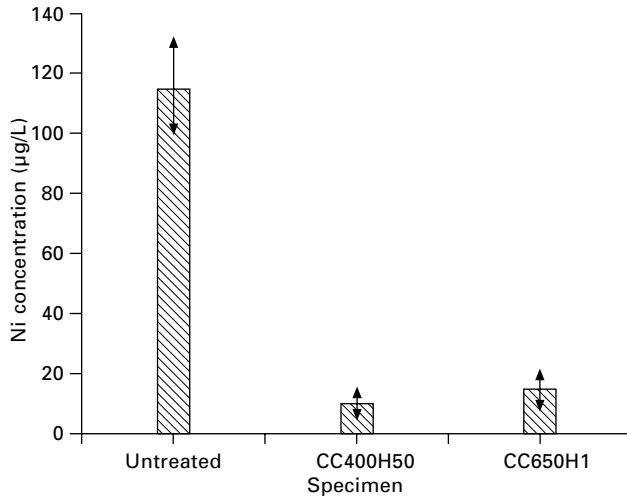
treated samples. This is partially because of the increased surface hardness and thus abrasive wear resistance and partially because of the reduced E/H ratio and thus reduced adhesive wear.

Reciprocating corrosion-wear

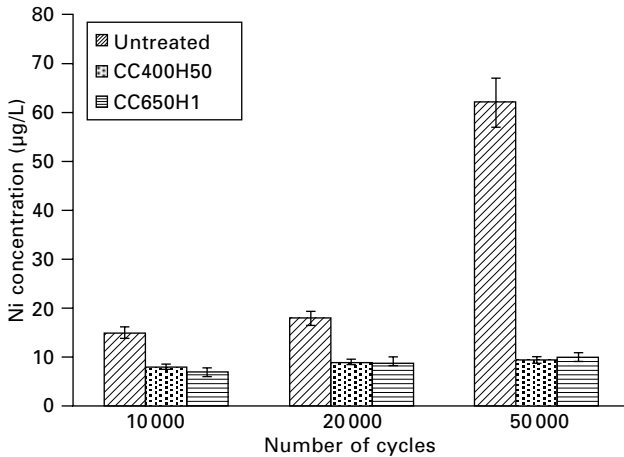
Similar improvement in wear resistance was also found when the CCT surfaces reciprocated against a 12.5 mm WC/Co ball in Ringer's physiological solution. As shown in Fig. 14.13, after CC treatment, the Ni ion released into the solution during wear tests greatly decreased from about $115 \mu\text{g L}^{-1}$ for the untreated NiTi alloy samples to around $14 \mu\text{g L}^{-1}$ for the $600^\circ\text{C}/1 \text{ h}$ samples and $11 \mu\text{g L}^{-1}$ for the $400^\circ\text{C}/50 \text{ h}$ ones, which represents a more than 8 and 10 times decrease, respectively.

Fretting corrosion

Recently, Dong *et al.* (2008) have carried out fretting-corrosion tests in Ringer's solution to investigate the effect of ceramic conversion treatments on the surface damage and nickel ion release of NiTi alloys under fretting corrosion conditions. This is because some SMA implants, such as orthodontic arch wires and orthopaedic bone fixation devices, need to withstand the combined attack of corrosion from body fluid and mechanical fretting. Their experimental results have shown that CC treatment can effectively improve the fretting corrosion resistance of TiNi SMA and reduce Ni ion release into the Ringer's solution. As shown in Fig. 14.14, while nickel ion concentration increases rapidly with the fretting cycles for as-received material, there is



14.13 Nickel concentration in the Ringer's solution after wear tests for the untreated and CC treated samples (Ju and Dong, 2007).



14.14 Nickel concentration in the Ringer's solution as a function of fretting cycles (Dong *et al.*, 2008).

almost no further release of nickel ions after the 10 000 running-in stage. After 50 000 fretting cycles, the maximum release of nickel ions was reduced from about 65 µg/L for the untreated sample to about 10 µg/L for the CC treated CC400H50 and CC650H1 samples. The reasons for the significantly reduced Ni ion release are threefold: (i) the hard surface rutile layer can increase wear resistance, (ii) the surface rutile layer is almost Ni-free and (iii) the surface rutile layer can act as a barrier to Ni ion release.

14.4.3 Applications

It is clear from the above discussion that the dry sliding wear of TiNi SMAs can be effectively addressed by CC treatment. Therefore, it is expected that the wear of load-bearing smart actuators could be reduced by CC treatment and their reliability and durability would thus be increased.

Surface damage-induced rapid nickel ion release and the associated allergic hypersensitivity are major concerns over the SMA body implants. Therefore, CCT could be used to reduce the cytotoxicity of TiNi implants such as orthodontic arch wires and novel bone fixation devices.

14.5 Summary and conclusions

Ceramic conversion treatment is a new surface engineering technology developed specifically for titanium-based alloys, including titanium and its alloys, TiAl intermetallics and TiNi shape memory alloys. During ceramic conversion treatment, the surface of titanium-based materials can be converted *in-situ* into oxide ceramic layers by reacting with oxygen. Unlike plasma electrolytic oxidation, a hardened case beneath the oxide layer is also formed when oxygen diffuses into the substrate during the ceramic conversion treatment.

Ceramic conversion treatment can effectively enhance the tribological, corrosion, fretting-fatigue and biocompatibility of titanium-based alloys, mainly due to the formation of dense and adherent surface oxide ceramic layers, which are mechanically supported by the oxygen diffusion hardened case.

Ceramic conversion treatment is cost-effective and environmentally friendly. To date, the potential of the new treatment has already been realised in the motor sports, automotive and off-shore industries. A number of new applications are being explored, for example, TiNi and titanium body implants, TiAl aero engine components and TiNi actuators.

14.6 Future trends

Ceramic conversion treatment has proved to be one of the most cost-effective surface engineering technologies to combat wear of titanium-based materials under low to medium loads. However, the total hardened case for typical CC treatments conducted in air at relatively low-temperatures (600–650°C) is thin (20–30 microns). In order to increase the load-bearing capacity of surface treated titanium-based alloys, a deep-case hardening technique (~300 microns) has been invented by Dong *et al.* (Dong and Li, 2000; Dong *et al.*, 2001) based on oxygen boost diffusion (OBD). However, although OBD treatment can improve abrasive wear of Ti-based alloys, it cannot eliminate

the high adhesion tendency of titanium alloys. This is because the surface oxide layer formed during the first boost step of OBD is dissolved during the second step diffusion step (~850/20h) in vacuum. Therefore, duplex treatments have been developed to apply a low-friction; anti-adhesion surface layer on the OBD hardened case (Bell *et al.*, 1998; Zhang *et al.*, 2008) but these duplex treatments are not cost-effective. Recent work by Stratton and Graf (2008) has revealed that a deep-hardened case (~200 microns) with a surface ceramic layer can be produced by one-step CCT at high-temperatures (850–900°C) using a gas mixture of carbon monoxide and argon. This could be a promising surface engineering process for medium-to-high loaded titanium components. However, the effect of such high-temperature treatments on the fatigue properties of treated materials needs to be assessed. In addition, such treatments are more expensive than typical CCT treatments in open air because of the need for the gas supply and a control system.

It is known that the response of titanium-based materials is strongly composition dependent, and the properties of CCT treated titanium-based alloys are sensitive to the processing conditions, such as the gas composition, treatment temperature and processing period. Currently, the screening of optimal processing conditions is mainly based on empirical or trial-and-error methods, which is both time- and labour-consuming. In addition, it is difficult, if not impossible, to identify the optimal CCT window for a given material and application conditions within a short period of time. Therefore, modelling-based process optimisation and service performance prediction methods need to be developed.

It is known that CC treatment will, more or less, reduce the fatigue properties of titanium-based alloys. Therefore, it is important to develop effective masking methods to treat selected surface areas of components. In addition, it is also important to compare the surface properties of CC treated titanium-based alloys with those produced by other surface engineering techniques (such as plasma electrolytic oxidation) to provide a database for titanium component designers.

Our work (Qi *et al.*, 2001) has demonstrated that new, multifunctional surfaces can be achieved by developing modified CC treatment. For example, when the ceramic layer on CP-Ti is doped with Pd, its corrosion resistance in boiling 20% HCl solution can be significantly improved (Table 14.2). Furthermore, CCT technology has recently been applied to zirconium-based alloys to combat wear (Ji *et al.*, 2010).

14.7 Acknowledgements

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14.8 References

- Ahn H, Lee D, Lee KM, Lee K, Beak D and Park SW (2008), 'Oxidation behaviour and corrosion resistance of Ti-10Ta-10Nb alloy', *Surf. Coat. Technol.*, 202, 5784–5789.
- Bell T, Dong H and Sun Y (1998), 'Realising the potential of duplex surface engineering', *Tribology International*, 31, 127–137.
- Biswas A and Majumdar JD (2009), 'Surface characterization and mechanical property evaluation of thermally oxidized Ti-6Al-4V', *Materials Characterization*, 513–518.
- Bloyce A, Qi P-Y, Dong H and Bell T (1998), 'Surface modification of titanium alloys for combined improvements in corrosion and wear resistance', *Surface and Coatings Technology*, 107, 125–132.
- Boettcher C (2001), *Development of a surface engineering treatment for the Timet 550 titanium alloy*, PhD thesis, The University of Birmingham, UK.
- Boettcher C, Bell T and Dong H (2002), 'Surface engineering of Timet 550 with oxygen to form a rutile-based, wear-resistant coating', *Metallurgical and Materials Transactions A*, 33A, 1201–1211.
- Borgioli F, Galvanetto E, Iozzelli F, Pradelli G (2005), 'Improvement of wear resistance of Ti-6Al-4V alloy by means of thermal oxidation', *Materials Letters*, 59, 2159–2162.
- Borgioli F, Galvanetto E, Fossati A and Pradelli G (2004), 'Glow-discharge and furnace treatments of Ti-6Al-4V', *Surf and Coat Technol*, 184, 255–262.
- Chu CL and Wu SK (1996), 'Ion nitriding of titanium aluminides with 25–53 at% Al', *Surface and Coating Technology*, 78, 211–218.
- Cingi M, Meydanoglu O, Guleryuz H, Baydogan M, Cimenoglu H and Kayali ES (2007), 'High cycle fatigue behaviour of thermally oxidised Ti6Al4V alloy', *Materials Science Forum*, 561–565, 2179–2182.
- Dahm KL (2009), 'Fatigue-like failure of thermally oxidised titanium in reciprocating pin-on-plate wear tests', *Wear*, 267, 409–416.
- Dong H, Bloyce A, Morton PM and Bell T (1997), 'Surface engineering to improve tribological performance of Ti-6Al-4V', *Surface Engineering*, 13, 402–406.
- Dong H, Morton PH and Bloyce A (1998), *European Patent EP0722510*.
- Dong H and Bell T (1999), 'Designer surfaces for titanium components', *Industrial Anti-Corrosion Methods and Materials*, 46, 338–345.
- Dong H, Bell T and Mynott A (1999a), 'Surface engineering of titanium alloys for the motorsports industry', *Sports Engineering*, 2, 213–219.
- Dong H, Shi W and Bell T (1999b), 'Potential of improving tribological performance of UHMWPE by engineering the Ti6Al4V counterfaces', *Wear*, 225–229, 146–153.
- Dong H and Bell T (2000), 'Enhanced wear resistance of titanium surfaces by a new thermal oxidation treatment', *Wear*, 238, 131–137.
- Dong H and Li X Y (2000), 'Oxygen boost diffusion for the deep-case hardening of titanium alloys', *Materials Science and Engineering*, A280, 303–310.
- Dong H, Bloyce A, Morton PM and Bell T (2001), 'Methods of case hardening of titanium alloys', *European Patent EP1000180*.
- Dong H, Ju X, Yang H, Qian L and Zhou Z (2008), 'Effect of ceramic conversion treatments on the surface damage and nickel ion release of NiTi alloys under fretting corrosion conditions', *J Mater Sci: Mater Med*, 19, 937–946.

- Ebrahimi AR, Zarei F and Khosroshahi RA (2008), 'Effect of thermal oxidation process on fatigue behaviour of Ti-4Al-2V alloy', *Surf. Coat. Technol.*, 203, 199–203.
- Gardos MN (1988), 'The effect of anion vacancies on the tribological properties of rutile (TiO_{2-x})', *STLE Tribology Transactions*, 31, 427–436.
- Gaucher A and Zabinski B (1975), 'Nouvelles possibilites de frottement des alliages de titane: le Tifranö', *Entropie*, Nû 63, 36–41.
- Gebauer K (2006), 'Performance, tolerance and cost of TiAl passenger car valves', *Intermetallics*, 14, 355–360.
- Guleryuz H and Cimenoglu H (2005), 'Surface modification of a Ti-6Al-4V alloy by thermal oxidation', *Surf. Coat. Technol.*, 192, 164–170.
- Hanzel RW (1954), 'Surface hardening process for titanium and its alloys', *Metal Progress*, 89–96.
- Hassters J, Salis-Solio VG, *et al.* (1990), 'The use of Ni-Ti as an implant material in orthopaedics', in *Engineering Aspects of Shape Memory Alloys*. (T. W. Duerig, K. N. Melton, D. Stockel and C. M. Wayman, eds) London, Butterworth-Heinemann: 427–444.
- Ji R, Li X Y and Dong H (2010), 'Ceramic conversion treatment of Zr702 and Zr705 to combat wear', *Surface Engineering*, 26, 32–39.
- Ju X (2007), *The ceramic conversion treatment and tribological characterisation of NiTi shape memory alloy*, PhD thesis, The University of Birmingham, UK.
- Ju X and Dong H (2006), 'Plasma surface modification of NiTi shape memory alloy', *Surf. Coat. Technol.*, 210, 1542–1547.
- Ju X and Dong H (2007), 'Tribological characteristics of ceramic conversion treated NiTi shape memory alloy', *Journal Physics D: Applied Physics*, 40, 5452–5462.
- Kim YZ, Murakami T, Narushima T and Ouchi C (2008), 'Evaluation of sliding wear resistant property of CP titanium and SP-700 titanium alloy surface-hardened by Ar-5%CO gas', *ISIJ International*, 48, 89–98.
- Kim YZ, Murakami T, Narushima T, Iguchi Y and Ouchi C (2006), 'Surface hardening treatment for titanium and titanium alloys in use of CO₂ gas', *Journal of the Iron and Steel Institute of Japan*, 92, 1–9.
- Komotori J, Lee BJ, Dong H and Dearnley PA (2001), 'Corrosion response of surface engineered titanium alloys subjected to prior abrasion damage', *Wear*, 251, 1239–1249.
- Krishna DSR, Brama YL and Sun Y (2007), 'Thick rutile layer on titanium for tribological applications', *Tribology International*, 40, 2, 329–334.
- Lanagan J, Morton PH and Bell T (1986), 'Surface engineering of titanium with glow discharge plasma', The Institute of Metals, *Design with Titanium*, London, The Institute, 136–150.
- Li DY (2000), 'Development of novel wear-resistant materials: TiNi-based pseudoelastic tribomaterials', *Materials and Design*, 21, 551–555.
- Li CX, Horspool D and Dong H (2007), 'Effect of ceramic conversion surface treatment on fatigue properties of Ti6Al4V alloy', *International Journal of Fatigue*, 29, 2273–2280.
- Li XY, Dong H and Shi W (2001), 'New insights into wear of Ti6Al4V by UHMWPE under water lubricated conditions', *Wear*, 250, 553–550.
- Meydanoglu O, Cingi M, Baydogan M and Cimenoglu H (2008), 'The effect of thermal oxidation on the fatigue behavior of Ti6Al4V and Ti6Al7Nb alloys', *TMS 2008 Annual Meeting Supplemental Proceedings, Vol 1: Materials Processing and Properties*, TMS, USA, 411–415.

- Mitchell E and Brotherton PJ (1964/1965), 'Surface treatments for improving wear-resistance and friction properties of titanium and its alloys', *Journal of the Institute of Metals*, 93, 381–386.
- Miyoshi K, Lerch BA and Draper SL (2003), 'Fretting wear of Ti-48Al-2Cr-2Nb', *Tribology International*, 36, 145–153.
- Mushiaki M, Asano K, Miyamura N and Nagano S (1991), *SAE Technical Report Series*, No. 910428, 41–49.
- Qi P-Y (2000), *Development of novel surface modification techniques for combined improvements in corrosion and wear resistance of titanium*, PhD thesis, The University of Birmingham, UK.
- Qi P-Y, Li XY and Dong H (2001), 'Characterisation of the palladium-modified thermal oxidation-treated titanium', *Materials Science & Engineering A*, A326, 330–342.
- Rastkar AR (2000), *Surface engineering of titanium aluminides to combat wear*, Ph.D Thesis. The University of Birmingham, UK.
- Shabolovskaya SA (2002), 'Surface, corrosion and biocompatibility aspects of Nitinol as an implant materials', *Biomedical Materials and Engineering*, 12, 69–109.
- Stratton P and Graf M (2008), 'Thermochemical surface treatment of titanium', *International Heat Treatment and Surface Engineering*, 2, No. 3/4.
- Stratton P (2002), 'Titanium – making the hard harder', *Materials World*, 10 (No. 11), 11–12.
- Taheri M and Zahrani EM (2008), 'Effect of novel thermal oxidation process on wear resistance of commercial pure titanium', *Surface Engineering*, 24, 475–478.
- Tortorelli PF and DeVan JH (1996), 'Oxidation and Other Corrosion Phenomena at Intermediate Temperatures', *Oxidation and Corrosion of Intermetallic Alloys*, ed. by G. Welsch P.D. Desai, (eds) Purdue Research Foundation, West Lafayette, Indiana 47907, 267–331.
- Wiklund U, Hutchings IM (2001), 'Investigation of surface treatments for galling protection of titanium alloys', *Wear*, 251, 1034–1041.
- Worner HW (1950), 'Surface hardening of titanium', *The Australian Engineer*, No 7, 52–55.
- Xia J (2004), *Development of novel surface engineering technology to combat wear of Al-containing intermetallics*, PhD thesis, the University of Birmingham, UK.
- Xia J, Li XY, Li CX and Dong H (2004a), 'The structural and mechanical property characterisation of thermal oxidation treated g-based titanium aluminide', *Thin Solid Films*, 458, 212–222.
- Xia J, Li CX, Dong H and Bell T (2004b), 'Ceramic conversion treatment of titanium aluminide for improved tribological properties', *Transactions of Materials and Heat Treatment*, 25, 1056–1059.
- Xia J, Li CX, Dong H and Bell T (2006), 'Nanoindentation and nanoscratch properties of a ceramic conversion treated g-TiAl based alloy', *Surface and Coatings Technology*, 200, 4755–4762.
- Yazdani MM, Edrissy A and Alpas AT (2007), 'Vacuum sliding behaviour of thermally oxidised Ti-6Al-4V alloy', *Surf. Coat. Technol.* 202, 1182–1188.
- Zhang ZX, Dong H, Bell T and Xu BS (2008), 'The effect of deep-case oxygen hardening on the tribological behaviour of a-C: H coatings on titanium alloys', *Journal of Alloys and Compounds*, 464, 519–525.

Duplex surface treatments of light alloys

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Abstract: Duplex or hybrid surface engineering is the sequential application of two (or more) established surface technologies to produce a surface composite with combined properties which are unobtainable through any individual surface technology. Low friction coatings such as DLC, nitrides and oxides can be used as the top coating layer, which can not only increase wear resistance but also diminish interfacial shear stress and strain, and reduce the tendency for debonding of top coatings. A deep case-hardened layer can be used as the bottom layer, which can significantly enhance the load-bearing capacity and improve the coating/film adhesion. In this chapter, the mechanisms, potential techniques, and applications of the duplex and hybrid treatments of titanium and aluminium alloys have been summarized.

Key words: duplex treatment, load bearing capacity, adhesion, hard coating, case hardening, Ti alloys, Al alloys.

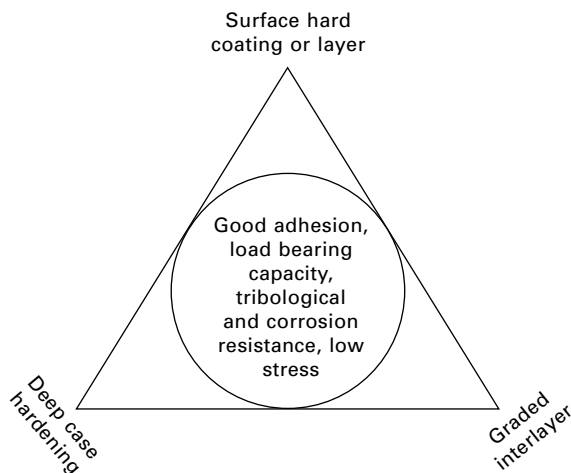
15.1 Introduction

The rapid development in engineering demands materials with good mechanical properties, resistance to friction, wear, corrosion and erosion, etc. Many components will operate under severe conditions, such as high loads, high speeds and harsh environments, in order to achieve high productivity, high power efficiency and low energy consumption (Bell *et al.*, 1994). These demands can be satisfied by applying various surface engineering techniques which permit modification of the chemical properties, composition, microstructure, and/or phases of the surface layers of the treated parts (Bell, 1987).

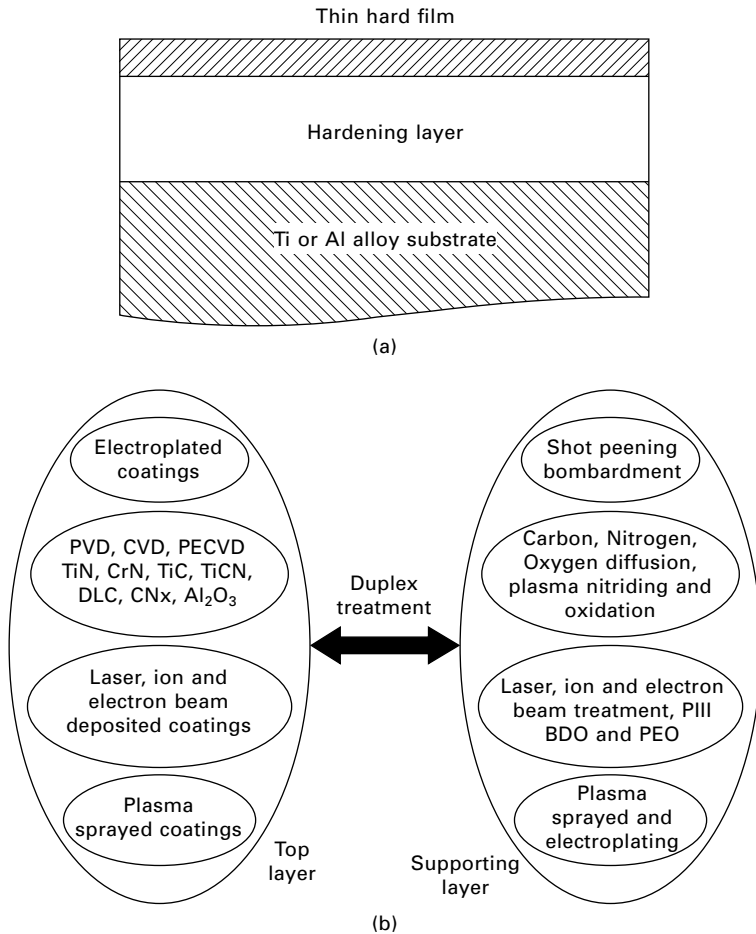
There is increasing interest in the applications of titanium and aluminium alloys in such sectors as automotive, medical, power generation and general engineering. Titanium and aluminium alloys show a relatively high strength-to-density ratio and good corrosion resistance (Budinski 1991; Gadow and Scherer *et al.*, 2002). Their main disadvantage in many applications is low hardness and hence low resistance to abrasive wear. Over the past twenty years, significant progress has been made to overcome the inherent tribological problems of titanium and aluminium alloys by means of surface engineering techniques, including sputtering, plasma nitriding, and/or electron beam surface alloying techniques (Bell *et al.*, 1994). TiN, CrN or DLC thin films have been frequently used in coatings of titanium and aluminium alloys, which can provide surfaces with dramatically improved tribological

properties in terms of low friction and high resistance to wear (Wierzchon, 2003). However, they often exhibit limited tribological performance due to (i) the low yield strength and severe plastic deformation of the substrate; (ii) being too thin to support the heavy load and protect the substrate in the contact conditions. Deposition of thick (more than 10 μm) PVD coatings usually results in large compressive stresses, and thus low adhesion (Wanstrand *et al.*, 2000).

In most coating systems that are subjected to relatively high intensity loading, plastic deformation normally initiates in the substrate near the coating–substrate interface, and plastic deformation does not initiate in the coating until a large plastic zone has been developed in the substrate (Zhang *et al.*, 2005 a and b). The load bearing capacities of coating–substrate systems depend significantly upon the substrate properties. Deep case hardening can significantly enhance the load bearing capacity of a coating–substrate system; for example, surface nitriding and oxidation (Kessler *et al.*, 2002). However, in some applications, these deep hardened layers alone exhibit higher friction and wear rates when compared with most ceramic thin film/coatings. These new challenges can be met only through realising the potential of duplex or hybrid surface engineering (see Fig. 15.1) (Bell and Dong *et al.*, 1998). Duplex or hybrid surface engineering involves the sequential application of two (or more) established surface technologies to produce a surface composite with combined properties that are unobtainable through any individual surface technology (Bell *et al.*, 1994). For example, in Fig. 15.2a, low friction coatings such as DLC, nitrides and oxides, can be used as the top coating layer, which may not only increase wear resistance but also diminish interfacial shear stress and strain, and reduce the tendency



15.1 Illustration of duplex surface engineering system.



15.2 (a) Illustration of the cross-section of a duplex treatment example. (b) Typical examples of surface engineering technologies used in the duplex surface treatment.

for debonding of the top coatings. On the other hand, a deep case-hardened layer beneath the hard coatings can significantly enhance the load bearing capacity and improve the coating/film adhesion.

The possible combinations of surface technologies and duplex surface technologies could be endless; however, to date only a limited number of duplex treatments have been developed and used in real applications (Staines, 1991; Sun and Bell, 1992; Stappen and Kerhofs, 1993; Bell and Sun, 1990). Some potential surface engineering technologies for the duplex treatment are shown in Fig. 15.2b. The common mechanisms for the enhancement of duplex or hybrid treatment can be summarized as follows (Fu *et al.*, 2000c):

- (i) To synthesise thin/hard film/coatings, it is important to provide a structural template to seed their growth. Take the crystalline carbon nitride as one example, an ideal structural template is the one with at least one low free-energy plane lattice matched to some low free-energy plane of carbon nitride (C_3N_4). TiN is a reasonable substrate to realise this purpose (Li *et al.*, 1995). By depositing carbon nitride films on plasma nitrided Ti-6Al-4V (from which TiN can be produced), it is easy to obtain an optimum chemical (both are nitrides) and structural transition between plasma nitrided layer and carbon nitride film (Fu *et al.*, 2000c).
- (ii) The case-hardening diffusion layer produces a graded hardened case that serves as an excellent supporting layer for the hard film/coating. It also increases the hardening depth, provides compressive stress and imparts better stability for the top thin film/coating (Kaestner *et al.*, 2001; Fu *et al.*, 2000c).
- (iii) Hard thin films/coatings can produce wear resistant and low-friction surfaces without impairing the beneficial effects of the case-hardened diffusion layer. Smooth and low friction film/coatings can effectively reduce both the tangential stress and the interfacial stresses, thus providing good tribological behaviour (Bailey and Sayles, 1991). For example, it was reported that in the zone near the PVD TiN-plasma nitrided substrate interface, the highest stresses were only half as large as the values that occurred at the same depth in the film on the untreated case (Dong *et al.*, 1997). This reduction in stress contributes to the improved tribological and bonding strength of engineering components.
- (iv) For some films/coatings, such as DLC, MoS_2 , or CN_x films, if small amount of film debris is generated, it might play an important role during wear processes depending on whether it is soft (graphitic) or hard (diamond-like), and how easily it is detached from the surface. The spalled films can act as a solid lubricant during sliding, i.e. as a third lubricating body between the two surfaces. Mechanical–chemical interactions between the sliding interfaces and the environment can lead to micro-graphitisation of the interlayer at the microcontacts, thus improving the tribological performance (Meletis *et al.*, 1995; Liu *et al.*, 1996). Alternatively, harder debris can do considerable damage.

In this chapter, the mechanisms, potential techniques, and applications of the duplex and hybrid treatment of titanium and aluminium alloys are summarized.

15.2 Duplex surface treatment of titanium (Ti) alloys

Titanium and its alloys have many attractive properties, including high specific strength and modulus, excellent corrosion resistance, and, in some

cases, good cryogenic properties (Park, 1984; Polmear, 1989). They are widely used in aerospace applications and many corrosive environments (Budinski, 1991). Ti-6Al-4V alloy has also been frequently used for orthopaedic devices and other engineering components due to its beneficial properties, such as low density, low elastic modulus, excellent corrosion resistance and biocompatibility (Man and Zhang, 2001). However, titanium and titanium alloys are notorious for their poor tribological properties, such as poor abrasive and adhesive wear resistance, being prone to fretting wear and fretting fatigue, a tendency to galling and seizure, etc. (Budinski, 1991). Many surface engineering techniques have been investigated and applied to titanium alloys, such as laser surface treatments, physical vapor deposition (PVD), chemical vapor deposition (CVD), plasma nitriding, plasma spraying, plasma immersion ion implantation (PIII) and plasma oxidising (Bell *et al.*, 1986; Fu *et al.*, 1998b, 2000b, 2000f; Yan *et al.*, 1999; Fu and Batchelor, 1998; Fan *et al.*, 1997; Chandra *et al.*, 1996; Heinrich *et al.*, 1997; Grill, 1997).

Thin/hard films/coatings deposited on 'hard' substrates (ceramics and hardened steels) have generally displayed excellent tribological performance. However, when they are deposited on 'soft' substrates, such as pure titanium and Ti6Al4V alloy, the soft substrate will deform plastically and may not be able to provide adequate support for the hard films. In other cases, the repeated local deformation or deflection of the coating can cause fractures or fatigue cracks that eventually destroy the film. Recently, novel duplex or hybrid systems have been designed and applied to solve this problem for Ti alloys (Kwiatniewski *et al.*, 2001). Duplex process, consisting of low temperature plasma nitriding followed by *in situ* deposition of a film/coating, can significantly increase the composite hardness, adhesion and load bearing capacity (Rahman *et al.*, 2007).

15.2.1 Duplex treatment based on plasma nitriding and CN_x

Amorphous CN_x films show attractive mechanical and tribological properties, characterised by high hardness, high elastic recovery, good adhesion to substrate and low friction coefficient. They have already been applied in the magnetic recording industry, rivalling amorphous DLC films due to their superior heat conductivity, and low friction coefficient (Grill and Patel, 1993; Koskinen *et al.*, 1996). Amorphous carbon nitride films have also been prepared on Ti alloys for improving their tribological properties and biocompatibility (Grill, 1997; Narayan *et al.*, 1994). Higher coating hardness and lower coefficient of friction are desirable for the good tribological performances of CN_x films. However, high hardness usually corresponds with brittleness and high stress in the coating, which may mean reduced load bearing capacity and tribological

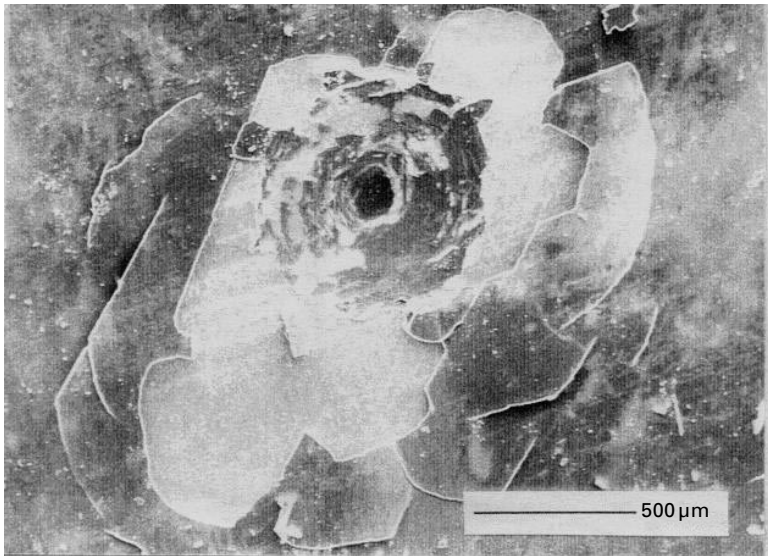
performance (Khurshudov *et al.*, 1996). The soft Ti alloys may not be able to provide adequate support for the hard DLC or CN_x films. An approach to solve this problem is to design and develop duplex diffusion/coating treatments (Rie *et al.*, 1995; Marumo *et al.*, 1996; Dong *et al.*, 1998; Huang *et al.*, 1994; Michler *et al.*, 1999; Lai *et al.*, 1996). The best design should combine high hardness, low coefficient of friction and high load bearing capacity (not only the high adhesion strength) (Ronkainen *et al.*, 1999). In the following sections, the duplex treatment of Ti based alloys combining plasma nitriding and carbon nitride films will be characterised.

15.3 Load bearing capacity of duplex surface treatments

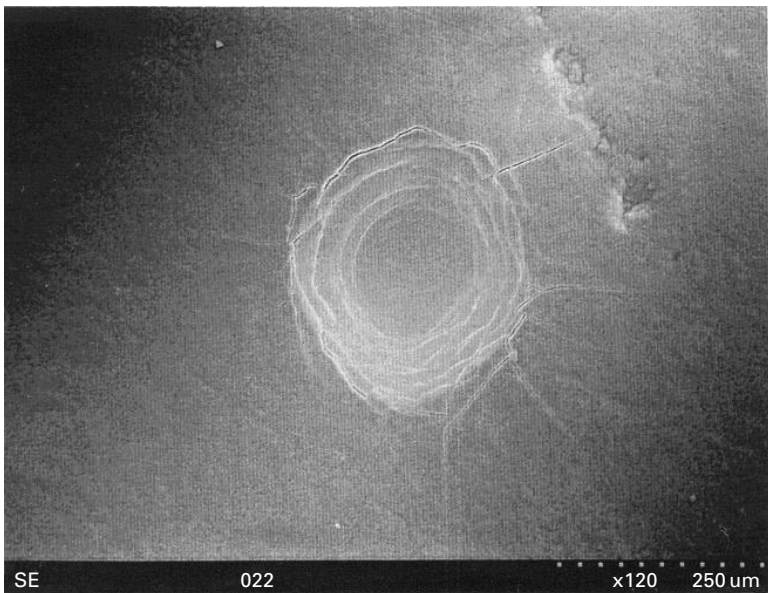
15.3.1 Indentation tests

Indentation tests are often used to measure the static load bearing capacity of a coating–substrate system (Fu *et al.*, 2000b). Figure 15.3 shows SEM micrographs of the indentation impressions of magnetron sputtered CN_x films deposited on Ti-6Al-4V and plasma nitrided Ti-6Al-4V. For the CN_x films deposited directly on Ti-6Al-4V substrate, there is usually large-area cracking and spallation occurring after indentation, due to the brittle nature of the CN_x film and poor load bearing capacity. Figure 15.3a shows surface cracking and discrete debonding (Grill and Patel, 1993). This situation corresponds to a film with a relatively poor load bearing capacity. When there are large stresses existing in the film due to sharp differences in elastic modulus or hardness between coating and substrate, the compressed film may buckle at the interface, and these buckles are susceptible to crack propagation along the interface, followed by large-area spallation, as shown in Fig. 15.3a. The poor load bearing capacity of CN_x films on Ti-6Al-4V is attributed to: (i) the high hardness, brittleness and large high internal stresses in the thin film; (ii) the significant differences in elastic modulus and hardness between the CN_x film and Ti alloy; (iii) the high contact pressure during indentation, which causes the severe plastic deformation of the soft substrate, thus inducing the cracking and spallation in the thin and hard CN_x film.

Under a normal load of 60 kgf, for a 2 μm CN_x film deposited on plasma nitrided Ti-6Al-4V substrate, there are some small ring cracks within the impression, and radial cracks formed at the circumference of the indentation, indicating the brittle nature of the deposited CN_x films, as shown in Fig. 15.3b. During indentation, the circular surface wave-like topographic deformation serves as the driving force for these lateral cracks. Under a higher normal load of 150 kgf, severe radial and ring cracks (but no spallation) are observed, indicating a high load bearing capacity of CN_x films deposited on plasma nitrided substrates.



(a)



(b)

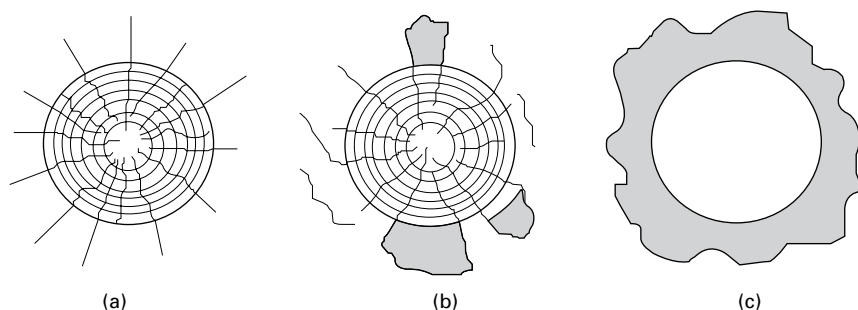
15.3 SEM micrographs of the Rockwell indentation impressions of CN_x films deposited on (a) Ti-6Al-4V and (b) plasma nitrided Ti-6Al-4V (Fu *et al.*, 2000f, with permission from Springer Publishing).

Figure 15.4 summarizes the indentation failure modes for different load bearing capacities of thin films, obtained from the results in Fig. 15.3. These results indicate that, with the application of a plasma nitrided interlayer between the substrate and coating, the static load bearing capacity has been improved significantly (Wei *et al.*, 1992; Evans and Hutchinson, 1995).

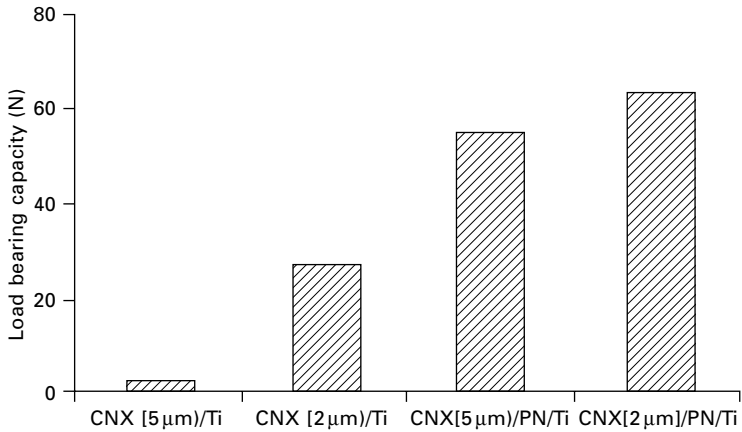
15.3.2 Scratch tests

Scratch testing was used to evaluate the dynamic load bearing capacity of coatings under both normal and tangential forces. For the scratch tests on CN_x films, the load–friction curves of coated samples often show a linear increase at the beginning period, with an abrupt increase at a critical load, corresponding to coating failure. The critical loads, i.e. the load bearing capacity of CN_x films on untreated and plasma nitrided Ti-6Al-4V substrate are shown in Fig. 15.5. Compared with that of carbon nitride film deposited directly on the Ti-6Al-4V substrate, the load bearing capacity is improved dramatically with the application of the plasma nitrided layer between the Ti-6Al-4V substrate and CN_x film.

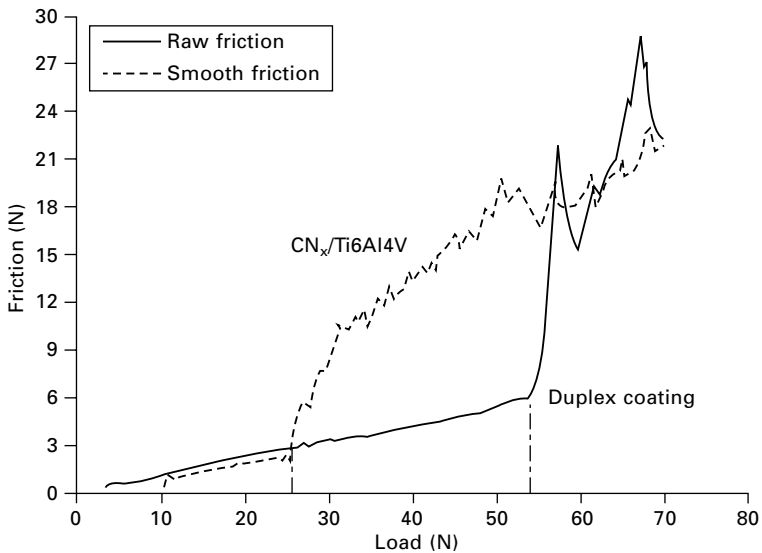
Figure 15.6 shows typical friction–load curves of scratch tests for CN_x films deposited on Ti-6Al-4V substrate and pre-nitrided layer. Figure 15.7 shows the curves of the coefficient of friction vs. normal load for different specimens. For stylus scratching on Ti-6Al-4V substrate, the coefficient of friction is extremely high (>0.6). Examination on the scratch track reveals typical severe abrasive wear (i.e. ploughing) (see Fig. 15.8). With stylus scratching on the plasma nitrided Ti-6Al-4V substrate, the coefficient of friction is low and stable (around 0.15). Examination of the wear track shows that there is not much wear and only slight scratching lines on the track,



15.4 Indentation failure modes for CN_x films deposited on different substrates (a) cracking but there is no spallation, showing good load-bearing capacity of the films; (b) cracks and debonding showing the load-bearing capacity is not good; (c) large area spallation showing poor adhesion with substrate and poor load-bearing capacity. (Fu *et al.*, 2000f, with permission from Springer Publishing).



15.5 Load bearing capacity of CN_x films on untreated and plasma nitrided Ti-6Al-4V substrate, obtained by scratch tests (Fu *et al.*, 2000f, with permission from Springer Publishing).



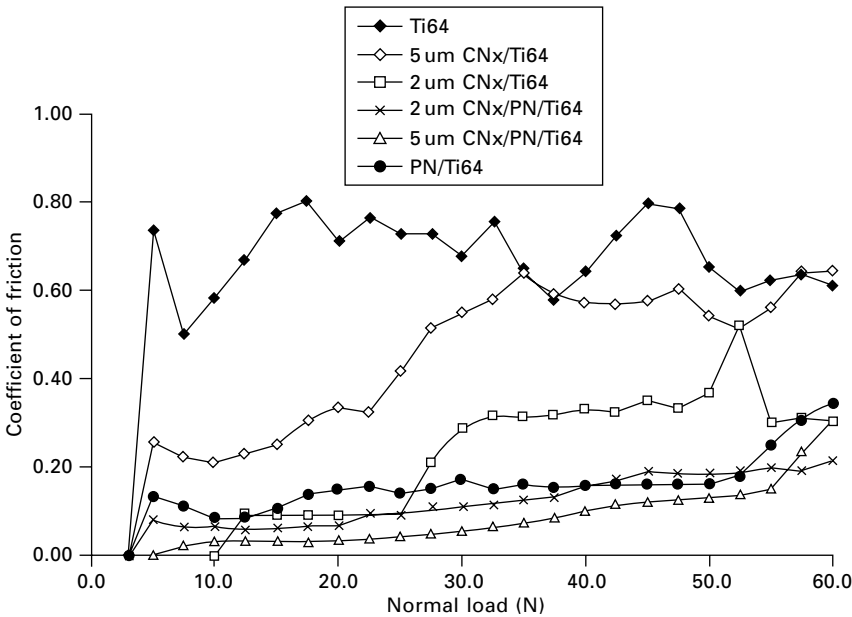
15.6 Typical friction-load curves for scratch tests on a CN_x film deposited on untreated and on plasma nitrided Ti-6Al-4V (Fu *et al.*, 2000d, with permission from Elsevier).

indicating a good wear resistance. When the load is increased to about 55 N, there is a large variation in the coefficient of friction, probably caused by the collapse of the nitrided layer under high normal load.

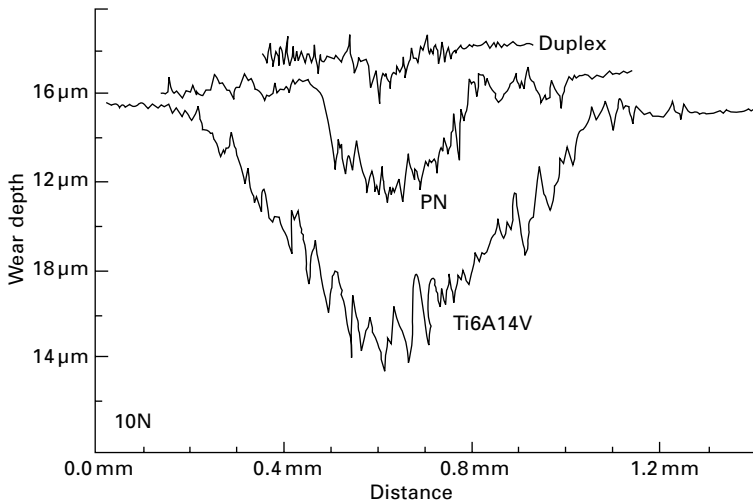
For the scratch test of CN_x film deposited on Ti-6Al-4V substrate, during the beginning period the coefficient of friction is very low (see Fig. 15.6),

indicating a good lubricating effect of the CN_x film. However, after a short period, the coefficient of friction increases abruptly. This is attributed to the spallation of the CN_x film, due to its poor adhesion strength and load bearing capacity on the Ti-6Al-4V substrate.

The duplex treated coating shows excellent load bearing capacity and tribological performance. For a 2 μm CN_x film deposited on the pre-nitrided specimen, the long-term coefficient of friction is rather low and stable as shown in Fig. 15.7. A typical scratch morphology on the duplex treated surface indicates mild wear on the CN_x film (see Fig. 15.8). Then there is a sudden jump in the friction force, occurring at a critical load of around 55 N, as shown in Fig. 15.7. SEM examination reveals that the film cannot endure the combination of the high normal load and frictional force, so it collapses and causes the large-area spallation of the film. The relatively low coefficient of friction under a higher normal load is probably related to graphitisation of the CN_x coating under high load and sliding conditions (Liu *et al.*, 1996). In brief, hard and low-friction CN_x films can effectively reduce the coefficient of friction, thus providing good tribological behaviour. Provision of a reinforcing plasma nitrided layer before deposition of CN_x films can improve the wear resistance significantly (Bailey and Sayles, 1991).



15.7 Curves of coefficient of friction with increase of normal load for Ti-6Al-4V substrate, plasma nitrided layer, CN_x film deposited on Ti-6Al-4V substrate and on pre-nitrided layer (Fu *et al.*, 2000f, with permission from Springer Publishing).



15.8 Wear surface morphology on different samples: Ti-6Al-4V, plasma nitrided (PN) and duplex treated Ti-6Al-4V alloy (Fu *et al.*, 2000d, with permission from Elsevier).

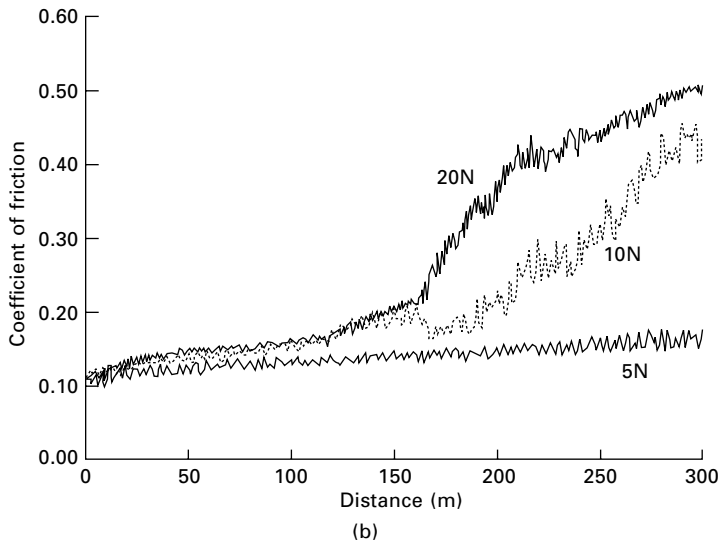
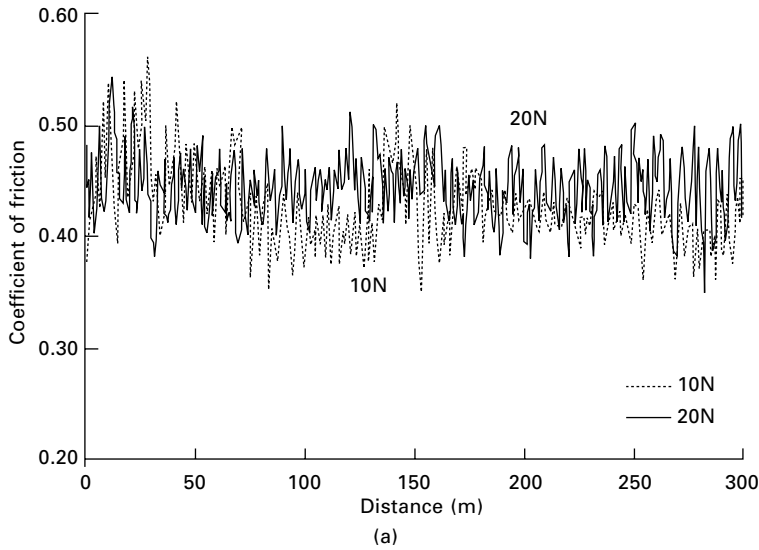
15.4 Tribological properties of duplex surface treatments

15.4.1 Dry sliding condition

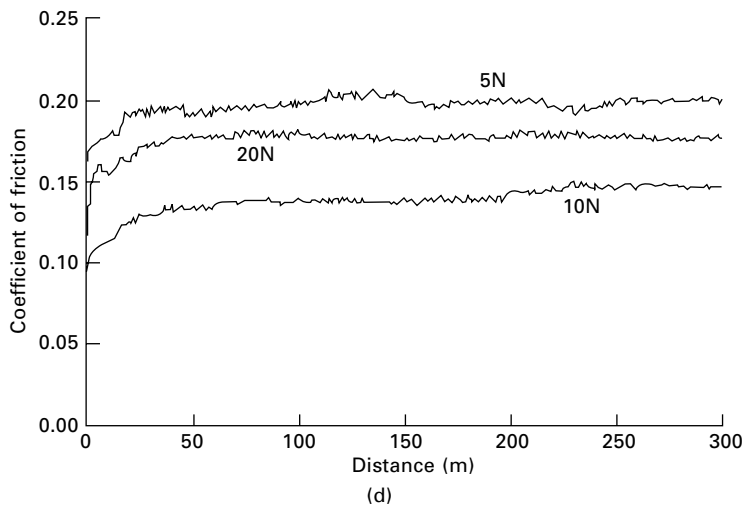
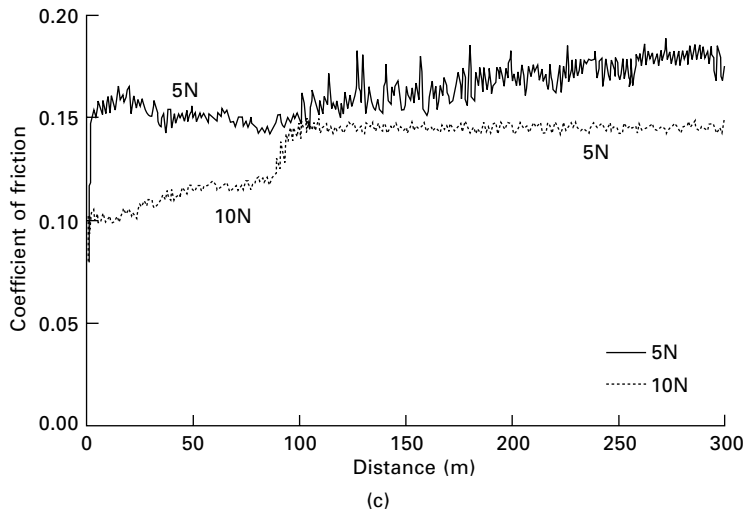
Figures 15.9a-d show comparisons of coefficients of friction under different normal loads and dry sliding condition using a pin-on-disc wear tester for different samples (Fu *et al.*, 2000f). The counterpart is an alumina ball. Under a normal load of 5 N, both the plasma nitrided specimen and duplex treated sample show a relatively low value of coefficient of friction (Fig. 15.9) compared with that of the Ti substrate. However, the coefficient of friction of the plasma nitrided specimen increased gradually during further sliding (Fig. 15.9b), whereas that of the duplex treated specimen remained low and stable (Fig. 15.9d). CN_x film deposited on Ti-6Al-4V substrate showed a low value of coefficient of friction. However, due to poor adhesion and the occurrence of spallation, the coefficient of friction varied significantly during sliding. When the normal loads were 5 N and 10 N, the coefficient of friction of the duplex treated specimen remained at a low value of about 0.15 (Fig. 15.9d). That of the plasma nitrided specimen jumped to a high level of 0.6 to 0.7 due to the spallation of the compound layer. In brief, the duplex treated system was more effective in maintaining a favourable low and stable coefficient of friction than both individual plasma nitriding and individual CN_x films.

Figures 15.10a-d show the comparison of wear rates for the three types of

specimens. Both the plasma nitriding and duplex treated coating can improve the wear resistance significantly under low normal loads of 2 N and 5 N. Clearly, the duplex treated system was more effective in terms of improving



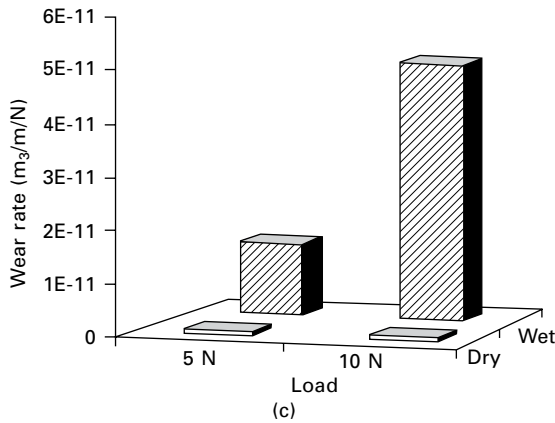
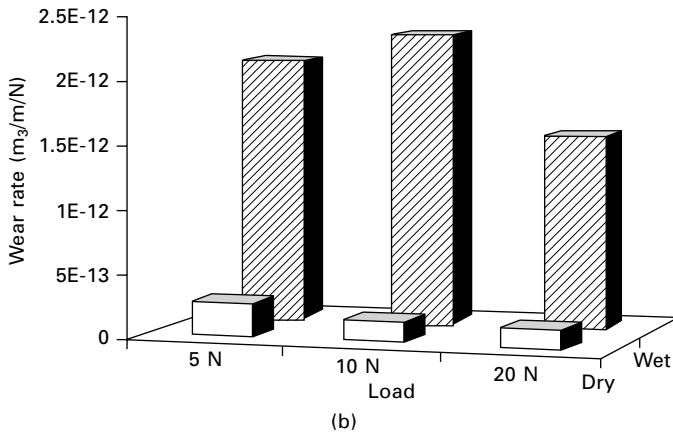
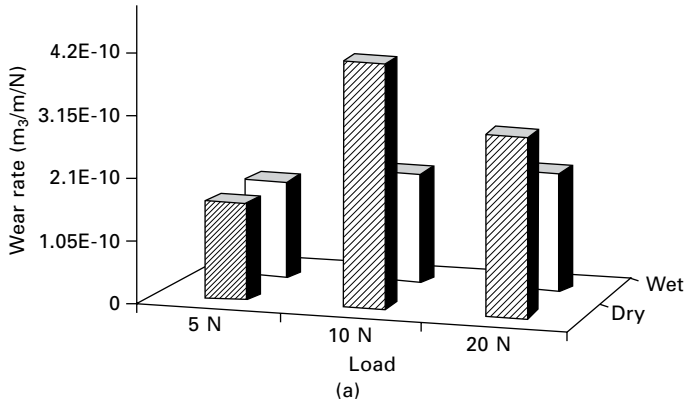
15.9 Coefficient of friction of different samples under dry sliding condition and different normal loads. (a) untreated Ti-6Al-4V; (b) plasma nitrided samples; (c) CN_x film deposited on untreated Ti-6Al-4V; (d) CN_x film deposited on plasma nitrided Ti-6Al-4V (Fu *et al.*, 2000d, with permission from Elsevier).



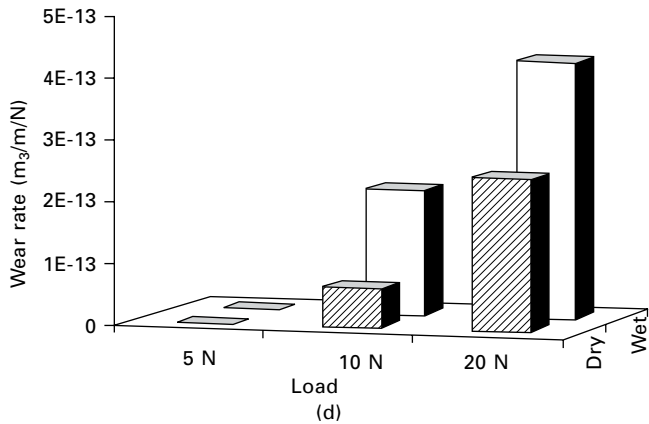
15.9 Continued

wear resistance than both individual plasma nitriding and individual CN_x film, especially at a high normal load.

The dominant wear mechanisms for untreated Ti-6Al-4V were abrasive wear, adhesive wear and delamination, with extensive ploughing and delamination (see Fig. 15.11). There were usually large quantities of wear debris on the wear tracks, which were the oxide particles according to EDX analysis results. Examination of the worn Al_2O_3 ball using EDX indicated the transfer of substrate materials onto the balls. In brief, the tribological behaviour of untreated Ti-6Al-4V was characterised by a high coefficient of friction and severe wear of materials (Molinari *et al.*, 1997).



15.10 Wear rates of different samples under both dry sliding and lubricated conditions with simulated body fluids. (a) Ti-6Al-4V; (b) plasma nitrided Ti-6Al-4V; (c) CN_x coated untreated Ti-6Al-4V; (d) film deposited on plasma nitrided Ti-6Al-4V (Fu *et al.*, 2000d, with permission from Elsevier).



15.10 Continued

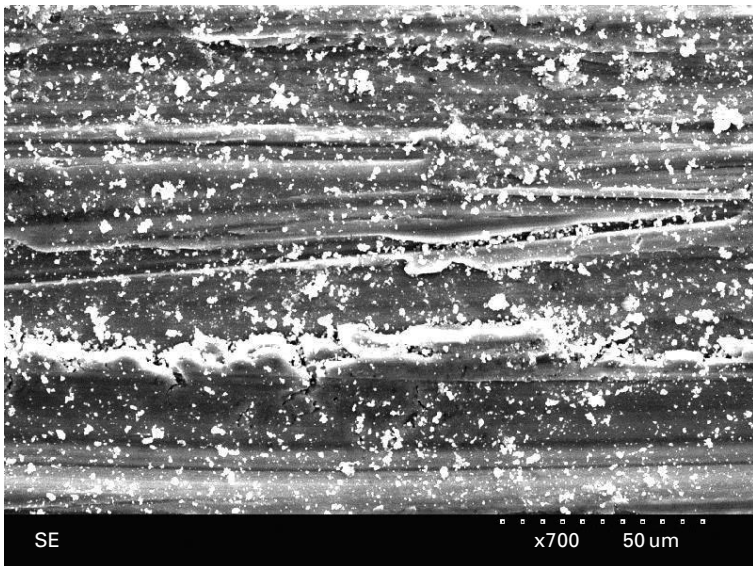
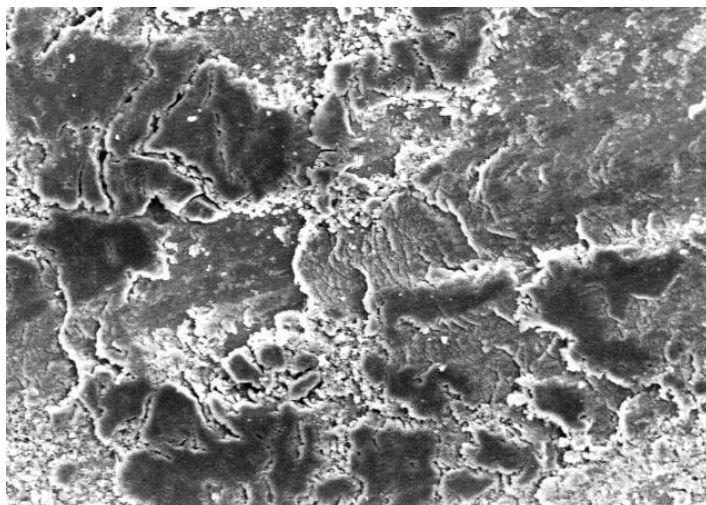
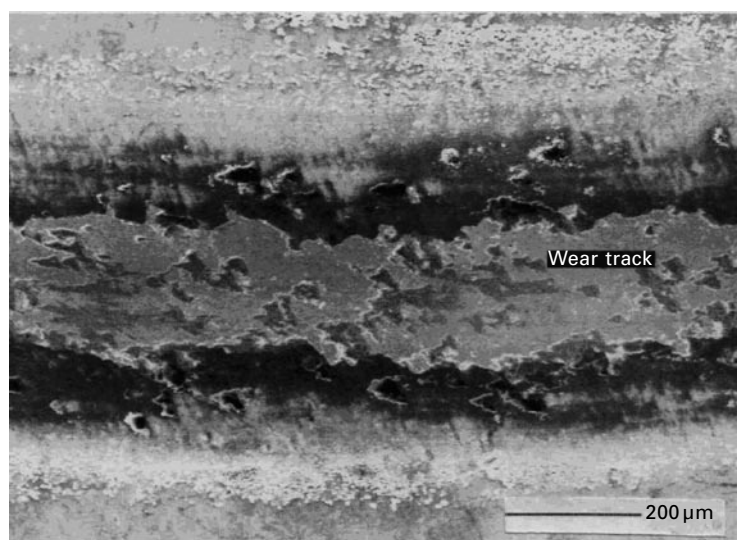

 15.11 Extensive adhesive and abrasive wear on worn Ti-6Al-4V sliding with alumina balls (Fu *et al.*, 2000d, with permission from Elsevier).

Figure 15.12 shows the worn surface morphology of the plasma nitrided sample under a normal load of 10 N. On the worn surface, crushing or spallation of the compound layer could be observed, indicating that the dominant wear mechanisms are spallation and severe abrasive wear. Figure 15.13 shows the worn surface morphology of the CN_X films on the Ti-6Al-4V substrate, indicating a large-area spallation of CN_X films. On the worn

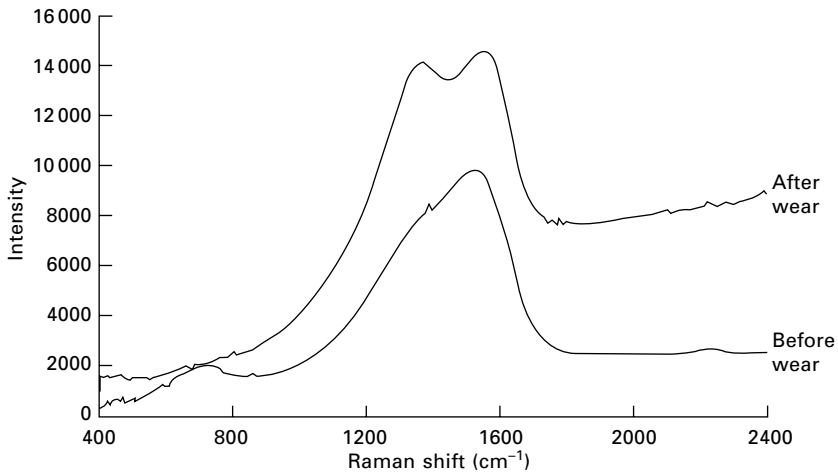


15.12 Spallation (or crushing) of a plasma nitrided layer under a normal load of 10 N and dry sliding condition (Fu *et al.*, 2000d, with permission from Elsevier).



15.13 Large-area spallation of CN_x films deposited on untreated Ti-6Al-4V substrate under dry sliding condition (Fu *et al.*, 2000d, with permission from Elsevier).

coating surface, the coating fragments were entrapped within the wear track, comminuted into fine particles, and finally mixed up with the substrate materials to form a mechanically alloyed surface. Figure 15.14 shows



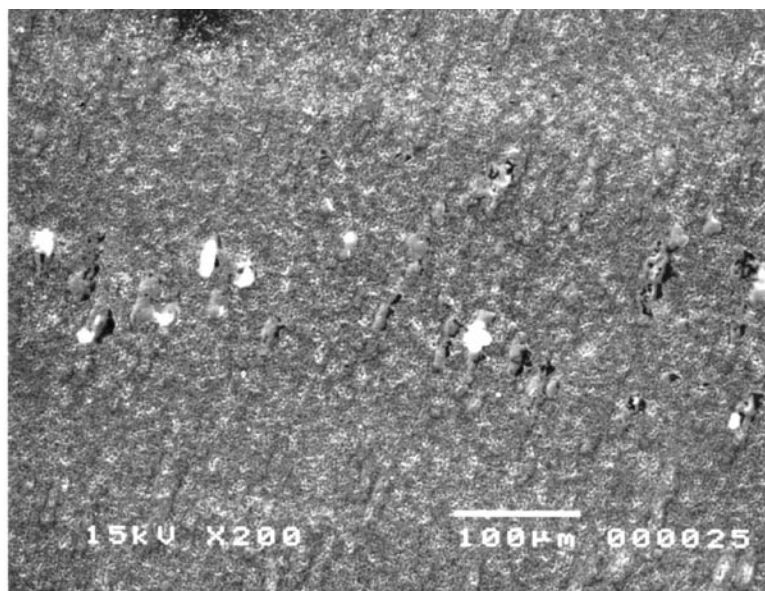
15.14 Raman analysis result on the wear tracks, showing the micrographitisation of this debris layer (Fu *et al.*, 2000d, with permission from Elsevier).

Raman analysis on these mechanically alloyed layers. Compared with those of untreated CN_x film, the D band (1335 cm^{-1}) and G band (1595 cm^{-1}) became sharp in the spectrum as a result of graphitisation (Meletis *et al.*, 1995; Liu *et al.*, 1996). These graphitised layers can act as lubrication, and probably this is the reason why, after the coating spallation, the coefficient of friction fluctuated significantly but still remained low at 0.2 to 0.3 (see Fig. 15.9c). Figure 15.15 shows the worn surface of the CN_x film on nitrided Ti alloy revealing little spallation of the films occurring on the wear track. This indicates the good wear resistance of the duplex treated coating.

15.4.2 Lubricated conditions

Figures 15.16a and 15.10a show the coefficient of friction curves and wear rates for untreated Ti-6Al-4V samples under lubricated condition and different normal loads. The liquid used was synovial fluids, which contain albumin (11.3 g/L), α -globulin (1.26 g/L), γ -globulin (3.06 g/L), hyaluronic acid (2 g/L) and distilled water (Black, 1992). The long-term coefficient of friction remained stable at about 0.25–0.35, and was much lower than that of Ti-6Al-4V under dry sliding conditions. The wear rates of untreated Ti-6Al-4V under lubricated conditions are lower than that under dry sliding conditions. Under the lubricated conditions, the dominant wear mechanism for untreated Ti-6Al-4V substrate is abrasive wear (see Fig. 15.17).

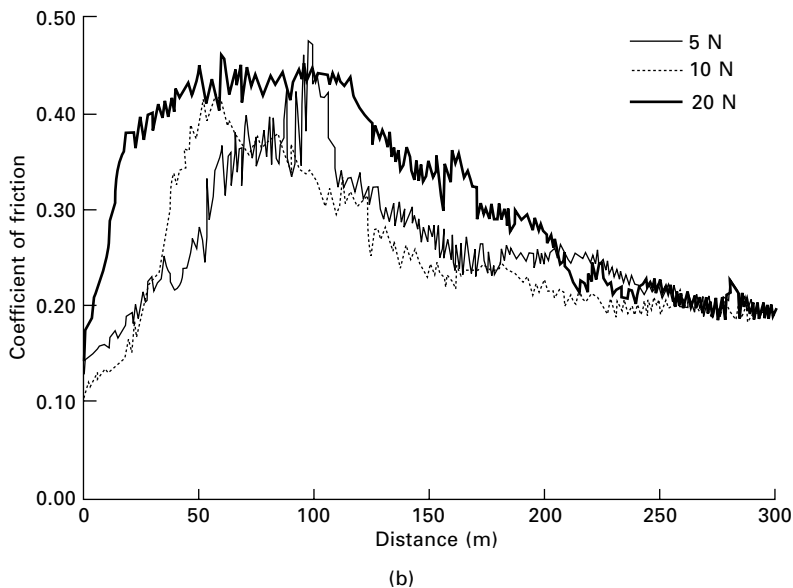
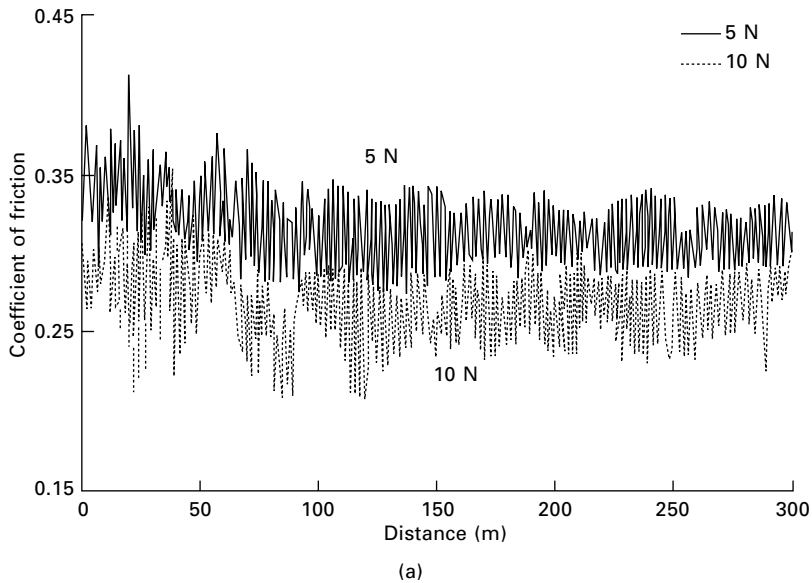
Figure 15.16b shows the coefficient of friction of plasma nitrided samples under different normal loads, lubricated with body fluids. The initial coefficient of friction was quite low, but after a short time sliding, the coefficient of



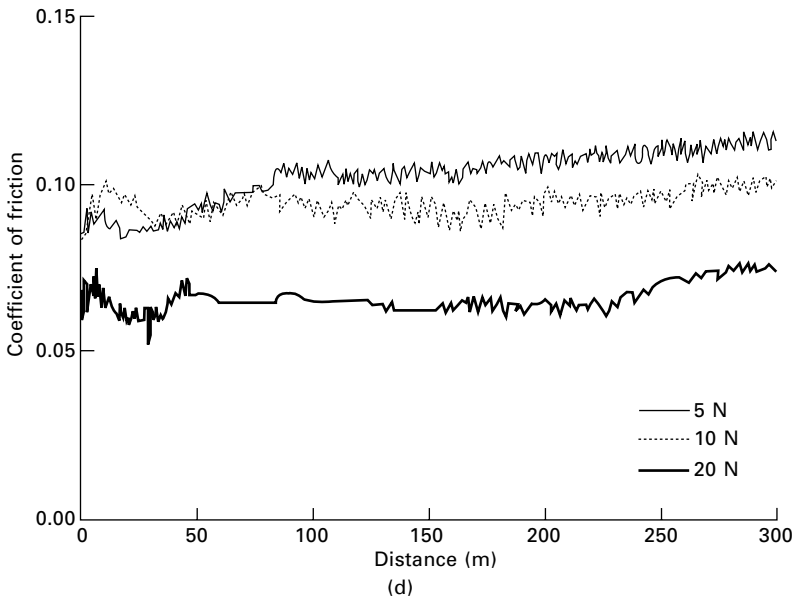
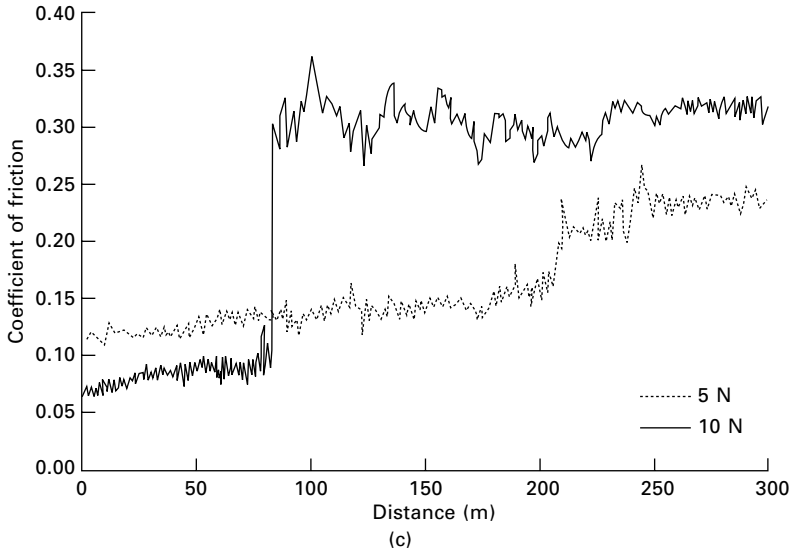
15.15 Surface morphology of wear track on a CN_x film deposited on a plasma nitrided layer, showing the small spallation of the films occurring on wear track (Fu *et al.*, 2000d, with permission from Elsevier).

friction increased rapidly to a high value, about 0.4. The higher the normal load, the earlier this sudden increase occurred. During the long term running, the coefficient of friction decreased gradually to a low value of 0.2. The significant increase in coefficient of friction was probably due to the abrasive wear caused by the rough nature of the plasma nitrided surface. The wear rates for the plasma nitrided surface under lubricated conditions were quite large compared with dry sliding conditions (see Fig. 15.10b), indicating significant abrasive wear due to the flowing away of lubricating wear debris with the body fluids (see Fig. 15.18).

Figure 15.16c shows the coefficient of friction of CN_x films deposited directly on Ti-6Al-4V substrate under lubricated condition with body fluids. The initial coefficient of friction was rather low (less than 0.1). However, after long-term sliding, the coefficient of friction suddenly jumped to a high value of 0.25–0.3, identical to that of the Ti-6Al-4V substrate under lubricated conditions. Observation of the wear tracks revealed a large-area of spallation of the CN_x films and severe wear on the Ti-6Al-4V substrate (see Fig. 15.19). The corresponding wear rates were much higher than those of the CN_x film under dry sliding conditions (see Fig. 15.10c). This is attributed to the removal of lubricated wear debris due to the flowing of fluids.

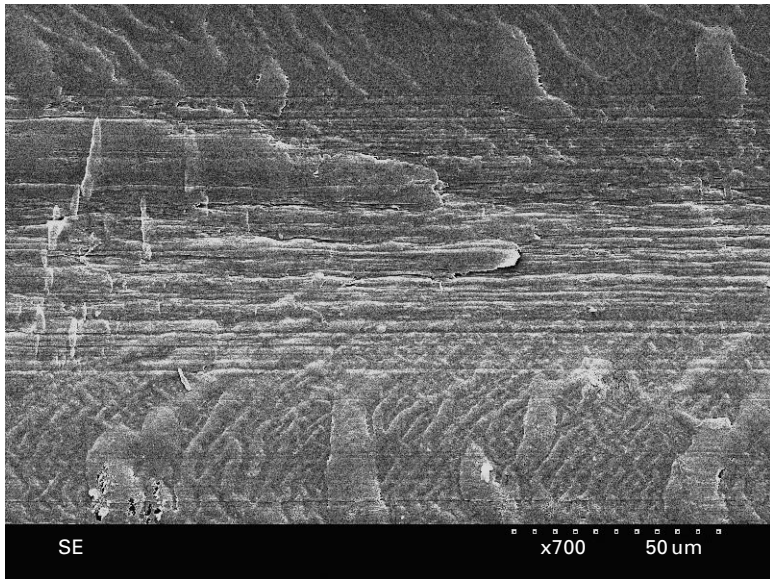


15.16 The coefficient of friction of different samples under lubricated sliding condition and different normal loads: (a) untreated Ti-6Al-4V; (b) plasma nitrided samples; (c) CN_x film deposited on untreated Ti-6Al-4V; (d) CN_x film deposited on plasma nitrided Ti-6Al-4V (Fu *et al.*, 2000d, with permission from Elsevier).

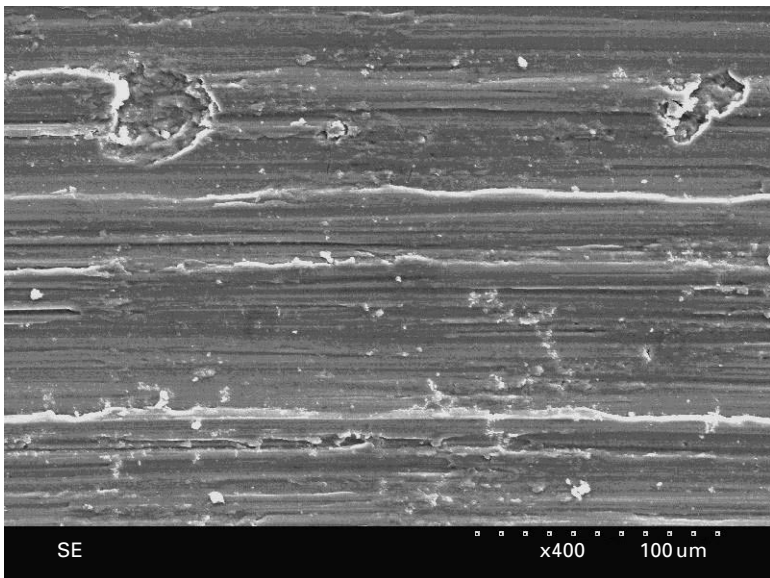


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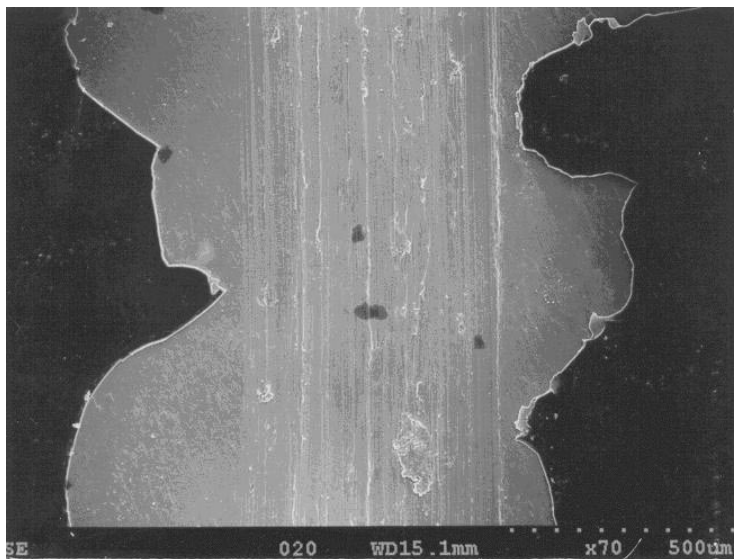
Figure 15.16d shows the variation of coefficient of friction of the duplex treated specimen under different normal loads and lubricated conditions with body fluids. The coefficient of friction of the duplex treated coatings was rather low and was stable (less than or near to 0.1). The wear rates of the duplex treated specimens under lubricated conditions were much higher



15.17 Abrasive wear on worn UHMWPE pins sliding with Ti-6Al-4V (Fu and Du, 2001, with permission from Elsevier).



15.18 Abrasive wear and adhesive wear on worn Ti-6Al-4V under lubricated sliding conditions (Fu and Du, 2001, with permission from Elsevier).

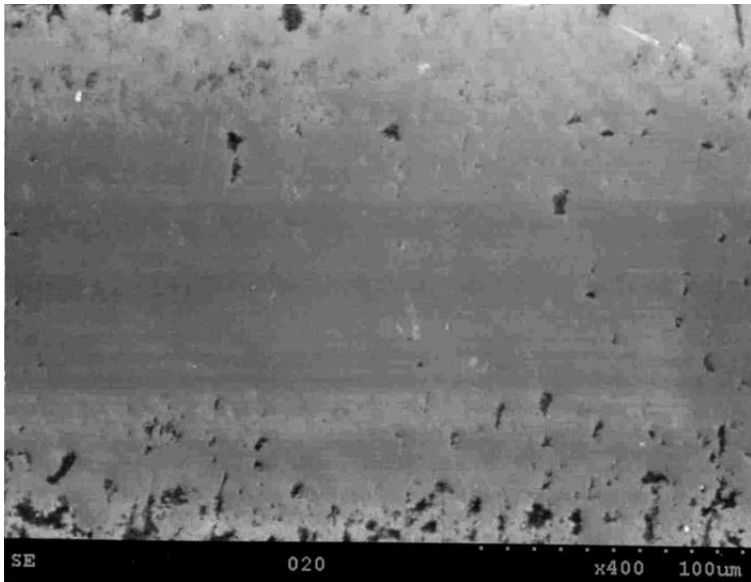


15.19 Large-area spallation of a CN_x film and severe wear on the Ti-6Al-4V substrate in the wear track deposited on an untreated Ti-6Al-4V substrate under lubricated conditions (Fu and Du, 2001, with permission from Elsevier).

than that those under dry sliding conditions (see Fig. 15.10(d)). The reason is probably due to the flowing of the lubricant, which can carry away the lubricating wear debris and cause the wear of two counterfaces. Figure 15.20 shows the surface morphology of the wear track under a normal load of 20 N revealing minor wear on duplex treated coating.

15.5 Erosion performance of duplex surface treatments

Aircraft, rockets and other aeronautical engines are often subjected to severe erosion from sands, rains or other solid particles. Erosion by solid particles or raindrop impingement can cause the rapid degradation of mechanical properties and even catastrophic failure. Examples of the failure of components include the blades and discs of aircraft engine compressors, helicopter rotor blades, and valves, piping, etc. (Sundararajan and Roy, 1997). Most of these components are made of titanium alloys, which are notorious for their poor erosion and wear resistance (Yerramareddy and Bahadur, 1991). To design and use protective coatings or surface treatments that withstand solid particle erosion is thought to be the best approach to solve this problem. The duplex treated coating (CN_x /plasma nitriding) can improve the erosion resistance of titanium substrates under a low particle impact velocity (Fu *et al.*, 2000). It

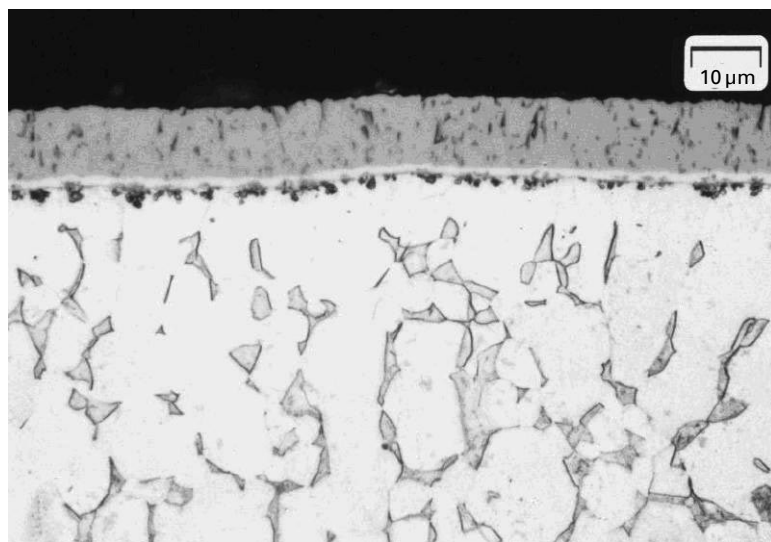


15.20 Worn surface morphology of duplex treated specimen sliding with UHMWPE pins under a normal load of 20 N, revealing mild wear on duplex treated coating (Fu and Du, 2001, with permission from Elsevier).

contains hard layers, able to resist the particle flux at low velocity. However, under a high particle velocity, the improvement of erosion resistance is not significant. For duplex treated coatings, micro-cracks propagating through the interface between the CN_x film and the plasma nitrided layers are observed (Fu *et al.*, 2000e). This crack deflection mechanism improves the impact resistance until the rupture of the coating occurs. The mechanism is only effective under low impact velocity of erodents; under high impact velocity, spallation of the CN_x layer is significant, thus the erosion resistance is not good (Sue and Troue, 1988).

15.6 Duplex surface treatment based on diamond-like carbon (DLC) or titanium nitride (TiN) films with plasma nitriding

Duplex treatments consisting of nitriding followed by TiN, TiCN, or DLC films have been frequently reported as enhancing the tribological properties of Ti6Al4V (Ma *et al.*, 2004; Kessler *et al.*, 1998, 2002). As one example, shown in Fig. 15.21, an SEM micrograph reveals a clearly visible nitrided layer, separated from the titanium alloy substrate, and a uniform and dense layer of CVD TiCN coating which is deposited on the homogeneous thick

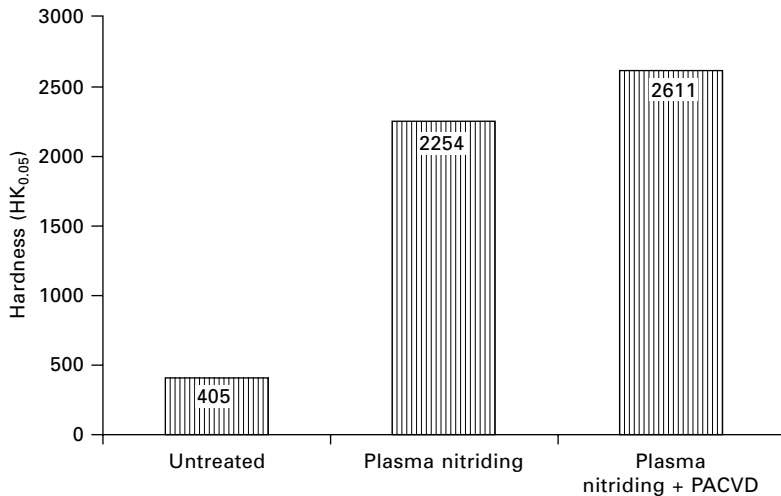


15.21 Microstructure of pressure nitrided and CVD-coated TiCN TiAl6V4 (Kessler *et al.*, 1998).

plasma nitrided layer (Kessler *et al.*, 1998). Very good bonding without delamination was confirmed at the interface between the coating and the nitrided layer.

The titanium alloy TiAl5Fe2.5, used for medical implants such as knee prostheses, has been duplex-treated by applying plasma-assisted CVD (PACVD) after plasma nitriding (Rie *et al.*, 1995; Rie, 1999). Surface hardness for plasma-nitrided and duplex-treated TiAl5Fe2.5 is shown in Fig. 15.22. The hardness of the plasma nitrided Ti alloys is more than five times higher than that of the Ti substrate, while PACVD TiN film deposition on the nitride layer can further enhance this hardening effect (Rie 1999). The hardness of the duplex-treated coating is believed to be increased by the load-bearing capacity of the TiN coating. There is a significant improvement in the wear properties of the duplex treated samples compared to those of all the other samples.

The commonly used hard coatings of DLC and TiN films are normally chemically inert and can provide good corrosion protection. When depositing the TiN coatings on the substrate surface, some defects, such as pores or cracks may occur, which leads to a pitting and delamination of the surface. Yilbas *et al.* (1995) conducted a study on the corrosion properties of TiN coated and nitrided Ti–6Al–4V alloy. They showed that TiN coating improved the corrosion properties, but nitriding made the corrosion resistance of the substrate worse. Some researchers (Khaleda *et al.*, 2001, 2006) have investigated the corrosion properties of duplex-treated



15.22 Surface hardness of TiAl₅Fe_{2.5} after plasma nitriding and duplex treatment (plasma nitriding and TiN film) (Rie, 1999, with permission from Elsevier).

(TiN/nitrided) Ti–6Al–4V in NaCl solution. The duplex treated workpiece surface was more resistant to corrosion as compared to the TiN coated and untreated Ti alloy surfaces.

Avelar-Batista *et al.* (2006) did work to improve the load bearing capacity of DLC coatings on Ti6Al4V substrates and increase the wear resistance of this coating/substrate system by means of two surface treatments: (i) plasma nitriding of the titanium alloy and (ii) plasma-assisted PVD (PAPVD) coatings (TiN, CrN and CrAlN) as intermediate layers between the top DLC coating and the Ti6Al4V substrate. Combination of these two surface treatments (plasma nitriding and PAPVD coating) was also investigated, and was proven to be more effective in improving the adhesion, load-bearing capacity and wear resistance of hard DLC coatings on Ti6Al4V alloy (Avelar-Batista *et al.*, 2006). The treatment combination provided hard and relatively deep sublayers (up to 16 μm), and increased the load support for the top DLC coating, reducing the degree of plastic deformation of the underlying material. The multilayered DLC–CrN, which had the thickest PAPVD interlayer, had the highest load-bearing capability, whilst the multilayered DLC–TiN provided the lowest wear rates in pin-on-disc wear tests against a 100Cr6 steel ball (Avelar-Batista *et al.*, 2006). It appears that a balance between the wear resistance of modified sublayers (nitrided and PAPVD layers) and load-bearing capability will provide the best wear resistance.

Plasma immersion ion implantation (PIII) has also been used to form a deep hardened nitride layer in the Ti alloys (Tendys *et al.*, 1988). It circumvents the

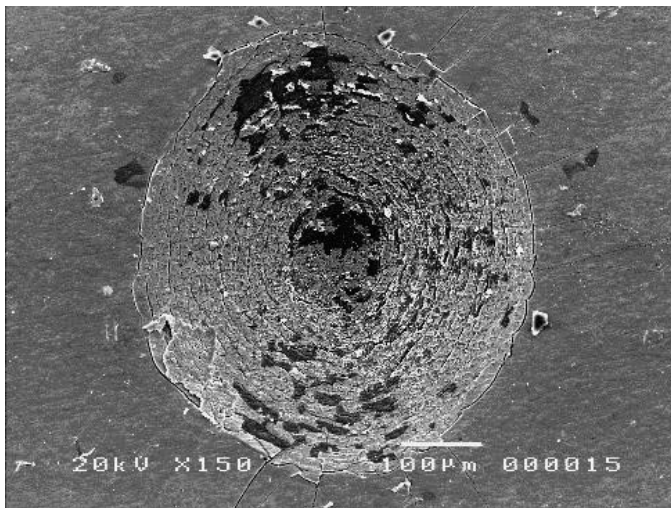
line-of-sight restriction inherent to conventional beam-line ion implantation and eliminates complicated focusing elements in the instrument. It is capable of processing complex-shaped components such as artificial organs. To improve biocompatibility and tribological properties of titanium, Ti–O/Ti–N duplex coatings were fabricated on titanium alloys by metal plasma immersion ion implantation and reactive plasma nitriding/oxidation (Tendys *et al.*, 1988). The purpose of the top Ti–O layer is to improve blood compatibility, and that of the Ti–N layer is to improve mechanical and tribological properties. The results reveal that the blood compatibility of the Ti–O/Ti–N duplex coatings is better than that of low-temperature isotropic pyrolytic carbon film. The semiconductor nature of non-stoichiometric titanium oxide is responsible for the observed improvement in blood compatibility.

In order to further improve the duplex treatment effect, a hybrid or compositionally graded intermediate layer, Ti/TiN/TiCN/TiC has been proposed to eliminate interfacial cracking by homogenising the stress distribution (Korhonen and Harju, 2000; Zhang *et al.*, 2008). A similar idea has been used to deposit an interlayer or buffer layer on the substrate for diamond film growth on the Ti alloys (Fu *et al.*, 2000a; Fan *et al.*, 1997; Wright *et al.*, 1994). During diamond growth, rapid carbon diffusion in the titanium alloy reduced significantly the diamond nucleation rate. It is well known that hydrogen easily dissolves into Ti substrate to form titanium hydrides, which have a strong influence on the coarsening of microstructure and the significant deterioration of mechanical properties (Fu *et al.*, 1999; Shih *et al.*, 1988; Heinrich *et al.*, 1996; Peng and Clyne, 1997). An interlayer on the Ti alloys is necessary: (i) to enhance the diamond nucleation rate; (ii) to minimize thermal and interfacial stresses; (iii) to provide an intermediate layer for bonding; (iv) to prevent the rapid diffusion of carbon atoms and increase the diamond nucleation and growth rate; (v) to prevent the hydrogen diffusion into the substrate and thereby prevent significant coarsening of the substrate microstructure and deterioration of mechanical properties.

Plasma nitriding can effectively achieve (v), and because it can provide a diffusion-barrier layer for hydrogen and carbon atoms, it can be used as the first step for diamond deposition. On top of the plasma nitrided layer, plasma carbonitriding can provide a carbide layer, which serves as the precursor for the nucleation and growth of diamond crystals. A gradual structure design has been proposed: plasma nitrided layer, carbonitrided layer to diamond coating (i.e. an interlayer of Ti(N)/Ti₂N/TiN/TiCN/TiC). This compositionally graded interlayer can eliminate interfacial cracking by homogenising the stress distribution, facilitating good bonding and improving the load bearing capacity (see Figures 15.23a and b), as well as promoting the diamond nucleation and growth (Sun *et al.*, 2002).



(a)



(b)

15.23 Rockwell indentation morphology of (a) diamond coatings deposited with a H_2/CH_4 gas ratio of 196:4 and a plasma power of 0.8 kW for 12 hours; (b) diamond coatings deposited on pre-plasma nitriding/carbonitriding graded layer (Fu *et al.*, 2000a, with permission from Elsevier).

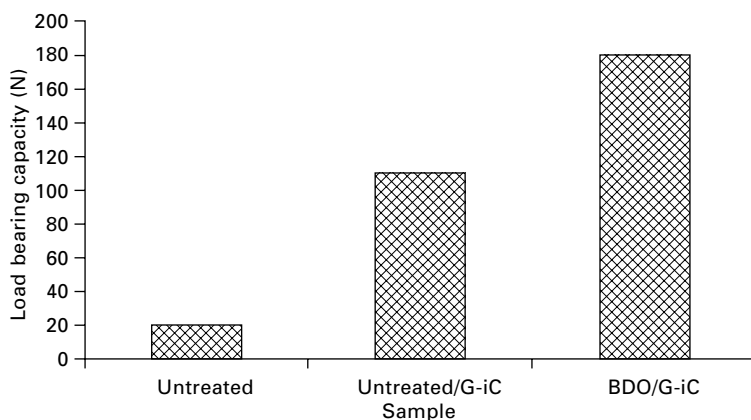
15.7 Duplex surface coating with oxygen diffusion inlayer

A dense natural oxide layer is normally found on Ti alloy surfaces. Recently, a boost diffusion oxidation (BDO) process has been used to acquire a deep

hardened case in Ti alloys (Dong and Li, 2000). The BDO process consists essentially of two steps: (i) titanium specimens are thermally oxidised in air; and (ii) the pre-oxidised specimens are further diffusion treated in vacuum. The BDO process can effectively harden a titanium surface to a depth of about 300 μm without evoking the inevitable scaling or oxide spallation associated with long-time oxidation at high temperatures.

Duplex surface treatment combining the BDO treatment with carbon-based hard coatings (BDO/Cr-DLC) has been designed that can significantly improve the tribological properties of the Ti6Al4V titanium alloy and increase its load bearing capacity (Zhang *et al.*, 2006) (see Fig. 15.24). The low friction of DLC could effectively reduce both the interface stress and the stresses near the surface. DLC coating is a unique material which has both a high hardness and an extremely low friction coefficient against most engineering materials. In the layered coating system, friction has significant effects on the stress distribution. The maximum Von Mises stress not only decreases in value but also moves inwards towards the substrate when the friction coefficient decreases; and the maximum shear stress at the interface also decreases with decreasing friction coefficient (Zhang *et al.*, 2006). The graded BDO intermediate layers successfully facilitate a high level of adhesion and bonding strength between the coating and the substrate material. The deep case-hardened layer formed from BDO treatment provides a strong support to the carbon-based coating by suppressing plastic deformation.

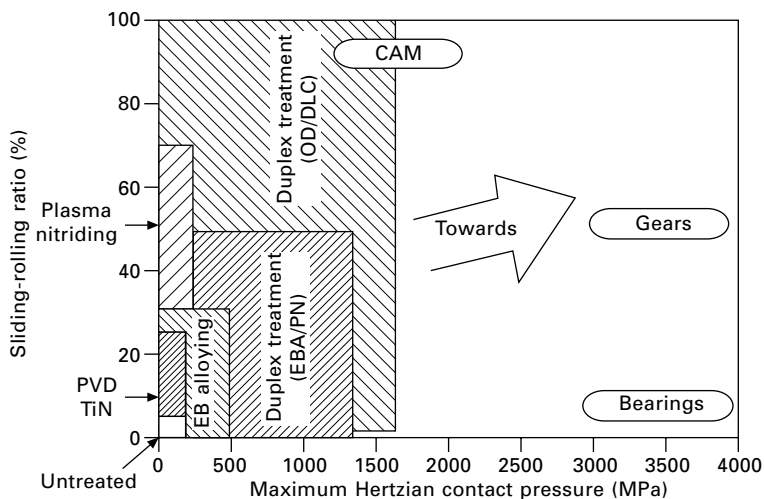
This novel duplex system, combining oxygen diffusion treatment with the DLC coating, possesses excellent load bearing capacity and good tribological properties. It has effectively extended the window of the design service conditions for titanium components, in terms of both high sliding/rolling



15.24 Load-bearing capacities of untreated and surface-treated Ti6Al4V (G-iC is a name of Cr-DLC film) (Zhang *et al.*, 2006, with permission from Elsevier).

ratio and/or higher loads (Fig. 15.25), and it is thus seen as an important step towards titanium designer surfaces (Bell *et al.*, 1998). This outstanding performance can be attributed to the optimised design of the duplex system. DLC is usually characterised by high levels of residual stress and poor adhesion when coated directly onto most engineering materials. These problems have been successfully addressed by adapting a graded intermediate layer between the DLC and the BDO treated sublayer. The compositionally graded intermediate layer eliminates interfacial cracking by homogenising the stress distribution. A significant improvement in load bearing capacity can be achieved only when the DLC coating is deposited on a deep hardened sublayer (about 300 μm) produced by the BDO treatment, thus mitigating against plastic deformation.

In order to fully realise the potential of advanced duplex treatment, a contact mechanics model has been developed, based on modern theories of multi-layered surface contact, taking into account the multi-layered structure, real surface roughness and friction effects (Luo *et al.*, 2006). Contact mechanics is concerned with the stresses and deformations that arise when the surfaces of two solid bodies are brought into contact (Johnson, 1987). Contact parameters such as pressure, stress and deformation are of great importance in the study of the mechanisms of friction, wear, mixed lubrication, load bearing capacity and fatigue. In view of the difference in the elastic and plastic properties between the surface layers and substrate materials, traditional contact mechanics approaches based on homogeneous



15.25 The effect of duplex surface engineering extending the areas of application of Ti6Al4V (Bell *et al.*, 1998, with permission from Elsevier).

materials cannot be directly applied to the design of layered surfaces. The finite/boundary method is the most popular traditional method due to its flexibility in treating complicated three dimensional (3D) component geometries and the ready availability of commercial finite/boundary analysis packages (Luo *et al.*, 2006). However, for rough surface contact problems with many asperities of arbitrary shape, the requirement for a large number of mesh elements makes this approach unfeasible. The Fourier integral transform method is most suitable for modelling the line contact problem, such as surface-treated Ti alloy gears (Luo *et al.*, 2006).

Design of multi-layered surface systems refers to the design activities that are carried out to choose the optimal layered surface structures for a given service condition and environment through the application of contact mechanics and material strength theories in the context of technical availability of surface treatment processes and their cost effectiveness (Luo *et al.*, 2006). An automatic search algorithm for the load bearing capacity of a surface engineering system has been incorporated into the existing Birmingham numerical model for the two-dimensional sliding contact of a cylinder. The model is then used in the design of surface engineered Ti gears against contact fatigue (Luo *et al.*, 2006). For the three target racing car engine gears (alternator, pump and cam gears), it has been shown that the thermal oxidation (TO) treatment (which creates a relatively shallow surface hardened case) can provide sufficient load bearing capacity for the alternator and pump gears, while the relatively heavily loaded cam gear can be supported only by the duplex treatment of oxygen diffusion (OD) plus TO (which creates a much deeper surface hardened case). The evaluation cam rig tests showed good agreement with the model prediction, thus demonstrating the power of the predictive design methodology employed. These results prove the importance of the design of duplex surface engineering systems that involve the sequential application of two (or more) established surface technologies to produce a surface composite with combined properties which are unobtainable through any individual surface technology (Luo *et al.*, 2006).

15.8 Other duplex surface treatments for titanium alloys

Surface treatment technologies with high energy beams (electron beam (EB) or laser beam (LB)) offer alternatives to the mostly used bulk heat-diffusion treatment. The energy deposition is precisely focused, so it is possible to exactly limit the heat treatment to highly-loaded areas and up to the depth where a transformation (hardening) is necessary. Therefore, the bulk materials are not heated up to critical temperatures, the thermal load of the overall component is minimized and thus distortion can also be avoided. The combination of

PVD hard protective coatings (based on Ti(C)N, TiAlN, Cr_xN_y and DLC) with electron beam surface hardening has been studied (Zenkera *et al.*, 2007). It is not only the sequence of treatments (beam hardening before or after coating) which has a considerable influence on treatment results, but also the parameters of EB surface treatment (energy density distribution, speed of treatment, vacuum).

A duplex method has been proposed in which Ti6Al4V alloy is first coated with aluminium and then subjected to a glow discharge treatment, producing a multi-component intermetallic TiAl layer with Al₂O₃ on the outer surface (Garbacz *et al.*, 2008). Significant increase in wear resistance of the material after duplex treatment is caused by the presence of the Al₂O₃ on the surface. The presence of the intermetallic phases from the TiAl system is very important, because they ensure continuous changes in the mechanical properties when passing from the surface (Al₂O₃) to the substrate (Ti6Al4V). The final surface layer has a diffusion layer which contains the Ti₃Al + TiAl + TiAl₃ + Al₂O₃ phases. The intermetallic layers obtained substantially increase the surface hardness and improve the wear resistance of the Ti6Al4V titanium alloy in both the dry wear test and the wear test performed in a fluid (Garbacz *et al.*, 2008).

Chromium nitride films have high hardness and good corrosion resistance (Berg *et al.*, 1996; Navinsek *et al.*, 1995; Gautier *et al.*, 1996; Zili and Patu, 1992; Sugiyama *et al.*, 1994). The thermal stability and corrosion resistance of CrN films are better than those of titanium nitride (TiN) films (Jensen *et al.*, 1995). CrN films are usually in a low compressive stress state, whereas TiN films are generally in a high compressive stress state (Navinsek *et al.*, 1995) which limits the deposition of thick TiN films (Demaree *et al.*, 1996). CrN film usually has a good surface finish; however, for fretting wear, the smoother the surface, the poorer the fretting wear resistance. The hard and relatively brittle CrN film may have low fracture toughness, thus increasing the rate of wear particle formation. The wear debris becomes trapped between the contact area and will act as hard abrasive particles to promote fretting wear (Was *et al.*, 1994). However, during fretting fatigue, the smooth surface will reduce the stress concentration and therefore reduce the possibility of the initiation of a fatigue crack. The residual compressive stresses in the CrN films enhance the fretting fatigue strength. The high hardness can prevent the formation of surface damage and thus can also reduce the occurrence of the surface cracks.

A duplex treatment combining shot peening followed with a CrN film has been reported to prevent fretting wear and fretting fatigue of Ti alloys (Fu *et al.*, 1998b). Shot peening can improve fretting wear and fretting fatigue resistance significantly. The reasons for the significant improvement in fretting wear resistance by using shot peening can be attributed to: (i) hardening of the surface; (ii) inducing a compressive residual stress; (iii) roughening

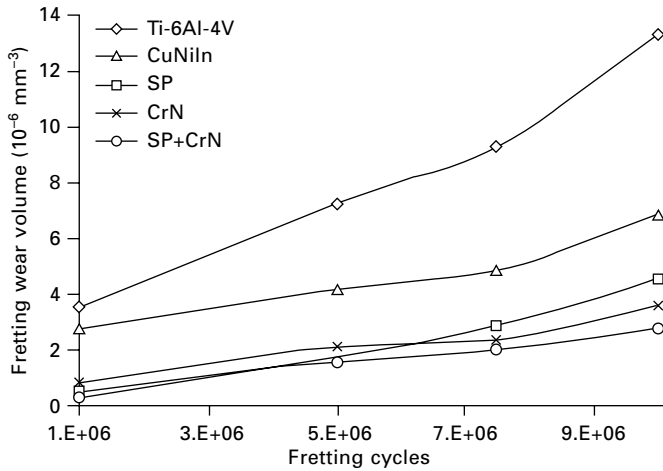
of the surface (Fair *et al.*, 1984). The first two effects are better for the prolongation of the fatigue life, but a rough surface containing potential stress raisers is very dangerous in fatigue conditions (Fair *et al.*, 1984). In the shot-peened specimen, the initiation of the cracks is often accelerated, and this can be attributed to: (i) surface damage, such as folds caused by shot-peening, leading to the initiation of fretting fatigue cracks (Leadbeater *et al.*, 1988); (ii) working-hardening of the surface and the resultant reduction in the fracture toughness of surface material. The subsurface damage, which probably takes place at the sites of surface folding in as-peened specimens, provides sites for the initiation of fretting fatigue cracks and the paths for easy crack growth.

A duplex treatment of Ti alloys has been applied: a shot peening process and an ion beam enhanced deposition (IBED) CrN film. For the specimens with IBED CrN film deposited on the shot-peened substrate, the fretting wear resistance can be increased and the coefficient of friction can be reduced. A much harder surface can improve the abrasive wear resistance and the CrN phase can improve the anti-corrosive and anti-oxidative resistance of the as-peened specimen. This kind of duplex treatment combines the benefits of the two surface engineering methods and shows the best performance in fretting wear and fatigue resistance (see Figures 15.26a and b) (Fu *et al.*, 1998b; Liu *et al.*, 1999).

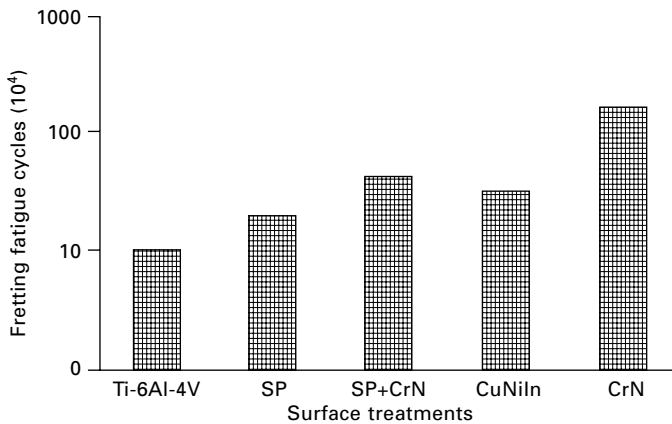
15.9 Duplex surface treatment of aluminium (Al) alloys

Aluminium alloys are the most widely used non-ferrous metals in engineering owing to their attractive properties, such as high strength-to-weight ratio, good ductility, good corrosion resistance, availability and low cost (King, 1987). However, as has been discussed in Chapter 2, their applications have often been restricted because conventional Al alloys are soft and notorious for their poor wear resistance, such as high friction coefficient, serious wear and a tendency for cold-welding when sliding with other metals, especially steel (Subramanian, 1992). Aluminium alloys do not exhibit allotropic transformation as in iron and cobalt alloys, so there is little possibility of a martensitic transformation, and the hardening effects by conventional solid state treatments are very limited. In many cases, surface treatments and coatings are necessary to ensure optimum performance in service (Wernick and Sheasby, 1987).

Previous coatings applied to aluminium alloys in traditional processes, such as hard anodising and thermal spraying, have suffered from low load support from the underlying material and/or insufficient adhesion, which reduces their durability (Wernick and Sheasby, 1987). Recently, many new methods have been proposed; for example, laser alloying, ion implantation,



(a)



(b)

15.26 Fretting resistance comparison of duplex treatment, shot peening and IBED CrN film with other types of surface treatment on Ti alloy substrate: (a) Fretting wear volume loss for different surface treatments under a normal load of 20 N and a slip amplitude of 50 mm; (b) Improvement in fretting fatigue strength with the application of different surface treatments and thin films (Fu *et al.*, 1998b, with permission from Elsevier).

PVD coatings, etc. (Fu and Batchelor, 1998a,b; Fu *et al.*, 1998a; Gadow and Scherer, 2002; Katipelli *et al.*, 2000; Liao *et al.*, 2004b; Nayak and Dahotre, 2004). Duplex treatment by using two types of surface modification techniques has proved to be one of the best ways to prevent the wear and corrosion of Al alloys.

15.9.1 PEO based duplex treatment

Anodic oxidation is an effective method of enhancing the wear resistance of aluminium alloy, e.g. an aluminium oxide coating of a few to several hundred micrometres thick can be formed to increase the hardness of the surface and improve the wear-resistant properties (Yerokhin *et al.*, 1999). Recently, plasma electrolytic oxidation (PEO) has been developed as a cost-effective surface engineering process to provide thick and hard ceramic coatings with excellent surface load-bearing capacity on aluminium alloys (Yerokhin *et al.*, 1999). PEO, also called micro-arc oxidation (MAO) (Sundararajan and Rama, 2003) is an unconventional plasma–electrochemical treatment. It operates at potentials above the breakdown voltage (typically 400–600 V) of an original oxide film growing on the surface of a passivated metal anode dipped in an aqueous solution containing modifying elements (e.g. SiO_2) to be incorporated in the resulting coating (Yerokhin *et al.*, 1998) (more details can be found in Chapters 5, 6 and 18). The relatively high conductivity of the Al_2O_3 coatings and the high frequency DC pulse power supply used to bias the target avoids charging-up and associated arcing damage of the substrates during deposition.

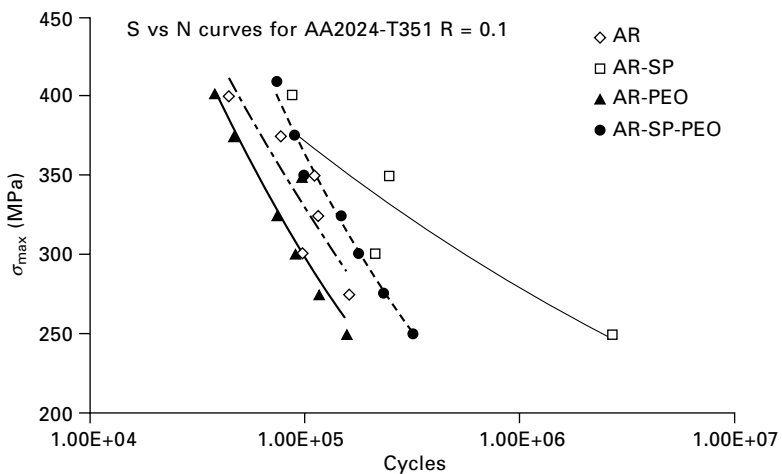
However, for sliding wear applications, such ceramic oxide coatings often exhibit relatively high friction coefficients against many counterface materials. Coatings such as TiN are well known for providing surfaces with a high hardness. In practice they often exhibit poor performance under mechanical loading, since the coatings are usually too thin to protect the substrate from the contact conditions. These challenges can be overcome by a duplex process of PEO and arc ion plating (AIP) TiN film. The alumina layer Al_2O_3 is deposited on an Al alloy substrate (using PEO as a pre-treatment process) for load support, and on top of it a TiN hard coating is deposited (using AIP) for a low friction coefficient (Awad and Qian, 2006). The Al_2O_3 intermediate layer is obviously beneficial in providing the load support essential for withstanding sliding wear at high contact loads. A hard and uniform TiN coating, with good adhesion and a low coefficient of friction, can successfully be deposited on top of the alumina intermediate layer to provide excellent load support. A duplex combination of PEO coating and TiN PVD coating represents a promising technique for surface modification of Al alloys for heavy surface load bearing application.

As discussed above, PEO treatment can produce a layer of alumina film on the surface of the aluminium alloy. A hard and uniform tetrahedral amorphous carbon film (diamond-like carbon, DLC) was deposited on the top of the alumina layer of the 2024 aluminium alloy by a pulsed filtered cathodic vacuum arc (FCVA) deposition system with a metal vapour vacuum arc source (Wu *et al.*, 2007). The test results suggested that the duplex DLC/ Al_2O_3 coating had good adhesion and a low friction coefficient,

which improved significantly the wear resistance of the aluminium alloy. An intermediate layer to provide improved load support is essential for practical applications of hard coatings such as DLC on Al-alloys. This benefit can be achieved by PEO prior to DLC coating, which can cost-effectively provide Al-alloys with a load-supporting oxide layer giving excellent mechanical properties and corrosion resistance. A low friction coefficient is usually required for sliding wear applications, and DLC coatings are a good choice for this purpose.

Aluminium alloys are widely used in the aerospace and automotive industries in structural applications. Exploiting such environments often has inherent problems associated with corrosion. Frequently, because of environmental difficulties, aluminium components are treated with an anodising or similar process. PEO has benefits over conventional anodising in that it creates a thicker and harder oxide layer to act as a barrier to corrosion. However, PEO can have a detrimental effect on the fatigue behaviour of aluminium. The loss in fatigue life can be recovered, to a certain extent, by the application of a suitable surface cold-work process such as shot-peening, prior to PEO treatment. However, shot-peening is known in some cases to be detrimental to corrosion resistance, particularly if a ferrous peening media is used (Asquith *et al.*, 2005, 2006). This is generally attributed to the transfer of iron between shot and work-piece during the peening process. A combination of shot-peening and PEO seems a good method for obtaining both corrosion and fatigue resistance.

Figure 15.27 shows stress vs. life curves for four different specimen types. The as-received sample curve is shown as a benchmark and falls



15.27 Stress-life curves for four different surface conditions (AR: as-received, SP: shot-peened, PEO: plasma electrolyte deposition) (Asquith *et al.*, 2006, with permission from Elsevier).

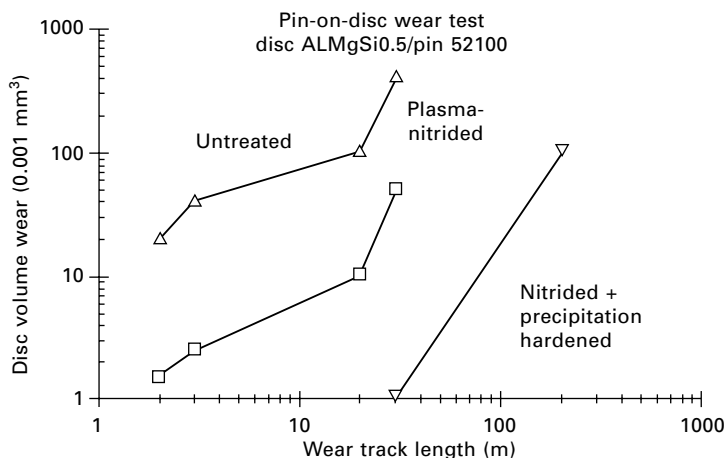
approximately between the coated and peened-coated curves, but consistently below the shot-peened curve (Asquith *et al.*, 2006). The curve for PEO-treated specimens is lowest; ~32% on average below the curve for as-received material. This can be explained by the tensile residual stress state at the coating/substrate interface. It has been suggested that this is the most likely region for crack initiation, and therefore a tensile residual stress field will help drive cracks and accelerate failure (Asquith *et al.*, 2006). The shot-peened and coated specimens were consistently above the as-received baseline and were comparable to shot-peened only material in low cycle performance. The in-plane compressive residual stress field will assist crack tip closure and slow crack growth rates, thereby increasing fatigue life. Shot-peened specimens were significantly better under high cycle loading conditions. It is of significant interest that shot-peening increased the fatigue life of PEO-treated specimens by an average of 85% (Asquith *et al.*, 2006).

In Sun *et al.* (2001), the 2024 Al alloys was anodically oxidised and then coated with Rare Earth Metal Fluorinated Compound (REMF)–MoS₂–Au nanocomposite film and Ti/Ag dual layer film, by rf-sputtering and multi-arc ion-plating, respectively. It is shown that duplex treatment, especially sputtered REMF–MoS₂–Au nanocomposite film, can decrease the friction coefficient and improve the endurance life of 2024 Al in vacuum. The lubrication failure mechanism of the duplex treated 2024 Al is attributed to the generation of cracks in the anodic oxide coating induced by the normal load combined with friction force (shearing force) and the crack propagation mainly caused by friction force. However, since the friction of duplex treated films is much lower than that of PEO treated Al alloys, the crack propagation rate in the duplex films is much lower (Sun *et al.*, 2001).

15.9.2 Plasma nitriding-based duplex treatment

The age hardening Al-alloy AlMgSi0.5 (AA 6060) was plasma nitrided and then precipitation hardened (Kessler *et al.*, 1998). Plasma nitriding produces an AlN-layer, which is 4 mm thick, homogeneous and shows some cracks. This AlN-layer withstands post-solution annealing, quenching and ageing without any problems. The wear behaviour of the plasma nitrided and precipitation hardened Al-alloy tested against pins of steel (AISI 52100) is shown in Fig. 15.28. Plasma nitriding alone already enhances the wear resistance, but the highest wear resistance is found for the plasma nitrided and precipitation hardened state. This is due to the higher hardness of the precipitation hardened AlMgSi0.5, which causes a better load support for the AlN-layer.

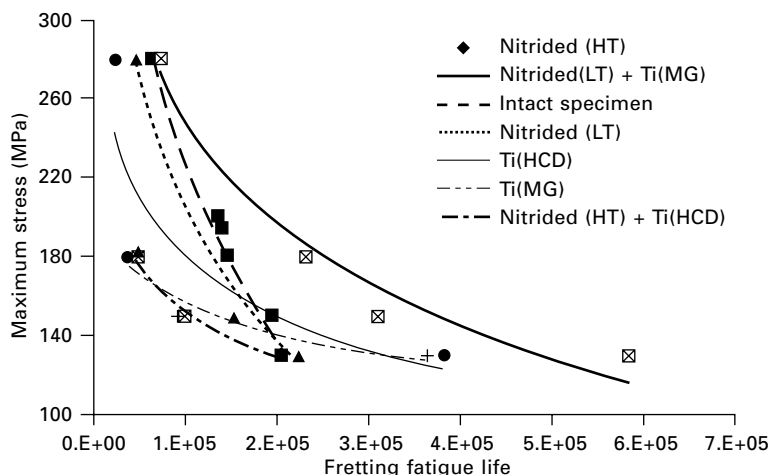
Improvement of fretting fatigue resistance of Al-7075 was studied using surface treatments including nitriding and titanium coating by hollow cathode discharge (HCD) and magnetron sputtering techniques (Majzoobi and Jaleh,



15.28 Wear of plasma nitrided and precipitation hardened Al-alloy AlMgSi0.5 (Kessler *et al.*, 1998, with permission from Elsevier).

2007). The surface nitriding reduces the fretting fatigue resistance of the Al alloys. Titanium coating, using HCD technique, may increase the fatigue life up to 85% at low working stresses, while at higher stresses the increase is not considerable. Titanium coating, using a magnetron sputtering technique, may increase the fatigue life up to 77% at low working stresses, while at higher stresses it gives rise to a reduction in fretting fatigue life. Duplex treatment including nitriding titanium coating by DC magnetron sputtering technique increases the fatigue life by up to 185% at low stresses and up to almost 60% at higher stresses (Majzoobi and Jaleh, 2007). Neither nitriding nor titanium coating could yield satisfactory improvement in the fretting fatigue response of AL7075-T6. Figure 15.29 shows the $S-N$ curves for the duplex treatment of nitriding plus titanium ion coating and the single treatment, nitriding. From a comparison between the $S-N$ curves for various surface modifications, it can be deduced that the duplex surface treatment of nitriding at low temperature plus titanium coating using magneto sputtering technique yields the best performance of AL7075-T6 against fretting fatigue damage.

For aluminium alloys, the compact oxide layer on the surface is a strong barrier to the diffusion of nitrogen into the bulk material. It is impossible to produce aluminium nitride layers thicker than 1–3 μm by conventional nitriding. To overcome these shortcomings, plasma-immersion ion implantation (PIII) can be used, since it allows implantation of nitrogen ions behind the surface oxide barrier. In the PIII processes, components to be treated are immersed in plasma. When high negative voltage (10–50 kV) pulses are repetitively applied to the target, ions from the plasma are accelerated



15.29 Comparison between the S-N curves for various surface modifications including: nitrided Al 7076-T6 alloy (at different temperatures); hollow cathode discharge gun (HCD) and magnetron sputtered (MG) Ti films (Majzoubi and Jaleh, 2007, with permission from Elsevier).

towards the target and are implanted from all sides simultaneously. One of the main reasons for interest in PIII is the fact that it can be used as a hybrid treatment together with a diffusion process (Blawert and Mordike, 1997). Due to the high-energy ion bombardment and sputtering of the Al alloy surface during the PIII process, appropriate conditions for an efficient subsequent nitrogen nitriding process can be created. Substantially thicker modified layers exhibiting superior wear resistance could be obtained by a combination of beam ion implantation and subsequent surface nitriding treatment for aluminium alloy 5052 (Kanno *et al.*, 1991). The results have shown that PIII can provide effective surface property improvements for some materials, especially when used in combination with plasma nitriding at low pressure. This kind of hybrid treatment is achievable by using a high voltage pulser capable of feeding an offset negative DC bias together with the high voltage pulses. For Al alloys in which the formation of nitrides is not so straightforward, it should be highly efficient.

15.9.3 Duplex treatment with other methods

Energy beam surface treatment of Al alloys has been widely studied. The combination of a primary treatment of surface alloying with Si or Ni, followed by PVD ion plating has been studied on Al-Si alloys (Bell *et al.*, 1990). An electron beam with a maximum power of 3 KW was used for surface alloying of Si and Ni. The resulting microstructures contained

primary silicon particles or nickel aluminide particles. The surface hardness was dramatically improved. Prior to the PVD ion plating, the electron beam alloyed Al alloys were ground flat, and then different types of films, Cr, Ni and Cu were deposited on the substrate. Hardness measurement results proved that the electron beam surface alloying increases the load bearing capacity of the subsequent PVD metallic layers. Wear tests showed that the duplex treatment outperformed the Ni-alloyed materials, and PVD coated materials. Therefore, laser and electron beam surface alloying can be used in duplex treatment to have good friction/wear resistant surface layers. The reasons for this improvement include (Bell *et al.*, 1990):

- (i) Support of PVD coating; removing the effects of plastic deformation of the substrate from the wear process, plays a major role in the enhanced performance over the single PVD process. For the same load, the duplex treatment will therefore allow the PVD layer to wear more before collapse occurs, and provide effective protection at a higher load.
- (ii) The presence of the PVD layer at the surface provides protection for the beam alloyed substrate, and after the PVD layer has been removed, a more wear resistant surface exists, allowing a higher extended lifetime of the component.
- (iii) A change in the nature of the PVD coating/substrate interface will result. Enhanced adhesion between the surface coating and the substrate may be provided by a suitable chemical couple.

Majzoobi and Jaleh (2007) investigated the improvement in fretting fatigue life of AL 7075-T6 by titanium surface coating using a magnetron sputtering technique and shot peening. They found that: (i) shot peening can increase the fatigue life up to 400%, (ii) the duplex treatment including titanium coating, using the magnetron sputtering technique plus shot peening, may increase the fatigue life of material up to 1000% for low working stresses, while this increase is not significant for higher working stresses. Majzoobi and Jaleh (2007) also studied the improvement of fretting fatigue life of AL 7075-T6 by titanium surface coating using an ion beam enhanced deposition (IBED) technique and shot peening. From their experiments, they found that the duplex treatment including titanium coating, using IBED technique plus shot peening, may increase the fatigue life of the material by up to 45% for low working stresses, while it can reduce the fatigue life significantly at higher working stresses.

15.10 Summary

The development of the novel duplex system is a big step towards designing dynamically loaded titanium and aluminium engineering components under high loading and scratch conditions. The last twenty years have seen

the emergence of many new surface engineering technologies and many incremental improvements in traditional techniques for surface treatment, which have stimulated the emergence of the new multi-disciplinary subject of surface engineering. Although integrated duplex processes have the advantages of possibly better process control, simple logistics and better delivery time, they have an economic disadvantage. This potential, technically, economically, and environmentally, will be increasingly realised through the further development and widespread industrial acceptance of duplex surface engineering in the component design process.

15.11 References

- Asquith D T, Yerokhin A L, Yates J R, Matthews A (2005), 'The effect of combined shot-peening and PEO treatment on the corrosion performance of 2024 Al alloy', *Thin Solid Films*, 516, 417–421.
- Asquith D T, Yerokhin A L, Yates J R, Matthews A (2006), 'Effect of combined shot-peening and PEO treatment on fatigue life of 2024 Al alloy', *Thin Solid Films* 515, 1187–1191.
- Avelar-Batista J C, Spain E, Fuentes G G, Sola A, Rodriguez R, Housden J (2006), 'Triode plasma nitriding and PVD coating: A successful pre-treatment combination to improve the wear resistance of DLC coatings on Ti6Al4V alloy', *Surface and Coatings Technology*, 201, 4335–4340.
- Awad S H, Qian H C (2006), 'Deposition of duplex $\text{Al}_2\text{O}_3/\text{TiN}$ coatings on aluminum alloys for tribological applications using a combined microplasma oxidation (MPO) and arc ion plating (AIP)', *Wear*, 260, 215–222.
- Bailey D M, Sayles R S (1991), 'Effect of roughness and sliding friction on contact stresses', *J. Tribol. Trans. ASME*, 113, 133–139.
- Bell, T (1987), 'Surface engineering: A rapidly developing discipline', *Europ. J. Engng. Edu.*, 12, 27–32.
- Bell T, Bergmann H W, Lanagan J, Morton P H, Staines A M (1986), 'Surface engineering of metallic alloys', *Surf. Engng.*, 2, 133–143.
- Bell T, Dong H, Sun Y (1998), 'Realising the potential of duplex surface engineering', *Tribol. Inter.*, 31, 127–137.
- Bell T, Morton P H, Bloyce A (1994), 'Towards the design of dynamically loaded titanium engineering components', *Mater. Sci. Engng.*, A, 184, 73–86.
- Bell T, Sohi M H, Betz J R, Bloyce A (1990), 'Energy beam in second generation surface engineering of Al and Ti alloys', *Scandinavian Journal of Metallurgy*, 19, 218–226.
- Bell T, Sun Y (1990), 'Load bearing capacity of plasma nitrided steel under rolling–sliding contact', *Surf. Engng.*, 6, 133–139.
- Berg G, Friedrich C, Broszeit E, Berger C (1996), 'Development of chromium nitride coatings substituting titanium nitride', *Surf. Coat. Technol.*, 86–87, 181–191.
- Black J (1992), *Biological Performance of Materials, Fundamentals of Biocompatibility*, Marcel Dekker Inc., 2nd, USA.
- Blawert C, Mordike B L (1997), Industrial applications of plasma immersion ion implantation, *Surf. Coat. Technol.*, 93, 274–279.
- Budinski K G (1991), 'Tribological properties of titanium alloys', *Wear*, 151, 203–217.

- Chandra L, Chhowalla M, Amaratunga G A J, Clyne T W (1996), 'Residual stresses and debonding of diamond films on titanium alloy substrates', *Diam. Relat. Mater.*, 5, 674.
- Demaree J D, Fountzoulas C G, Hirvonen J K (1996), 'Chromium nitride coatings produced by ion-beam assisted deposition', *Surf. Coat. Technol.*, 86–87, 309–315.
- Dong H, Bell T (1998), 'Designer surfaces for titanium components', *Industrial Lubrication and Tribology*, 50, Issue 6, 282–289.
- Dong H, Bloyce A, Bell T (1998), 'Realising the potential of duplex surface engineering', *Surf. Engng.*, 14, 505–512.
- Dong H, Sun Y, Bell T (1997), 'Enhanced corrosion resistance of duplex coatings', *Surf. Coat. Technol.*, 90, 91–101.
- Dong H, Li X Y (2000), 'Oxygen boost diffusion for the deep case hardening of titanium and its alloys', *Mater. Sci. Eng.*, A280, 303–310.
- Evans A G, Hutchinson J W (1995), 'The thermomechanical integrity of thin films and multi-layers', *Acta Metall. Mater.*, 43, 2507.
- Fair G, Noble B, Waterhouse R B (1984), 'The stability of stresses induced by shot-peening under conditions of fatigue and fretting fatigue', *Advances in Surface Treatments*, 1, Pergamon Press, Oxford, UK, 3–8.
- Fan W D, Jagannadham K, Narayan J (1997), 'Adhesion of diamond films on Ti-6Al-4V alloys', *Surf. Coat. Technol.*, 91, 32–36.
- Fu Y Q, Batchelor A W (1998a), 'Laser nitriding of pure titanium with Ni, Cr for improved wear performance', *Wear*, 214, 82–90.
- Fu Y Q, Batchelor A W, Gu Y W, Khor K A (1998a), 'Investigation on laser alloying of aluminum alloy AA6061 with Ni, Cr. Part I. Effect of laser parameters on the morphology, microstructure and hardness distribution', *Surf. Coat. Technol.*, 99, 287–294.
- Fu Y Q, Batchelor A W (1998b), 'Investigation on laser alloying of aluminum alloy AA6061 with Ni, Cr. Part II. Effects of laser alloying on fretting wear resistance', *Surf. Coat. Technol.*, 102, 119–126.
- Fu Y Q, Du H J (2001), 'Effects of counterface materials on the wear and friction properties of duplex treated coating on titanium substrate', *Mater. Sci. Engng. A*, 298, 16–25.
- Fu Y Q, Yan B B, Loh N L, Sun C Q, Hing P (1999), 'Deposition of diamond coating on pure titanium using micro-wave plasma assisted chemical vapor deposition', *J. Mater. Sci.*, 34, 2269–2283.
- Fu Y Q, Yan B B, Loh N L (2000a), 'Effects of pretreatment and interlayer on the nucleation and growth of diamond coatings on titanium substrate', *Surf. Coat. Technol.*, 130, 173–185.
- Fu Y Q, Loh N L, Batchelor A W, *et al.* (1998b), 'Comparison of different surface engineering methods on improvement of fretting wear and fretting fatigue resistance of Ti-6Al-4V', *Surf. Coat. Technol.*, 106, 193–197.
- Fu Y Q, Loh N L, Wei J, Yan B B (2000b), 'Indentation and scratch tests on amorphous CN_x films deposited on plasma nitride Ti-6Al-4V', *J. Mater. Engng. Perform.*, 9, 499–505.
- Fu Y Q, Wei J, Batchelor A W (2000c), 'Some considerations on the mitigation of fretting damage by application of surface modification technologies', *J. Mater. Proc. Technol.*, 99, 231–245.
- Fu Y Q, Wei J, Loh N L, Yan B B, Hing P (2000d), 'Characterization and tribological evaluation of duplex treatment by depositing carbon nitride films on plasma nitrided Ti-6Al-4V under dry and lubricated conditions', *J. Mater. Sci.*, 35, 2215–2227.

- Fu Y Q, Du H J, Gu Y W (2000e), 'Effects of surface treatments on the improvement of erosion resistance of titanium alloys', *J. Mater. Engng. Perform.*, 9, 571–579.
- Fu Y Q, Loh N L, Wei J, Yan B B, Hing P (2000f), 'Friction and wear behaviour of carbon nitride films deposited on plasma nitrided Ti-6Al-4V', *Wear*, 237, 12–19.
- Fu Y Q, Loh N L, Yan B B, Sun C Q, Hing P (2000g), 'Characterization and tribological evaluation of MW-PACVD diamond coatings deposited on pure titanium', *Mater. Sci. Engng. A*, 282, 38–48.
- Gadow R, Scherer D (2002), 'Composite coatings with dry lubrication ability on light metal substrates', *Surf. Coat. Technol.*, 151–152, 471–477.
- Garbacz H, Wicinski P, Ossowski M, *et al.* (2008), 'Surface engineering techniques used for improving the mechanical and tribological properties of the Ti6Al4V alloy', *Surf. Coat. Technol.*, 202, 2453–2457.
- Gautier C, Moussaoui H, Elstner F, Machet J (1996), 'Comparative study of mechanical and structural properties of CrN films deposited by d.c. magnetron sputtering and vacuum arc evaporation', *Surf. Coat. Technol.*, 86, 254–262.
- Grill A (1997), 'Wear resistant fluorinated diamondlike carbon films', *Surf. Coat. Technol.*, 94–95, 507–513.
- Grill A, Patel V (1993), 'Tribological properties of diamond like carbon and related materials', *Diam. Relat. Mater.*, 2, 1519–1524.
- Heinrich G, Grogler T, Rosiwal S M, Singer R F, Stockel R, Ley L (1996), 'The influence of diamond chemical vapour deposition coating parameters on the microstructure and properties of titanium substrates', *Diam. Relat. Mater.*, 5, 304–307.
- Heinrich G, Grogler T, Rosiwal S M, Singer R F (1997), 'Diamond growth on titanium alloys', *Surf. Coat. Technol.*, 94–95, 514–520.
- Huang H H, He J L, Hon M H (1994), 'Hydrogen adsorption on sulfur and nitrogen covered surfaces', *Surf. Coat. Technol.*, 64, 41–46.
- Jensen H, Jensen U M, Sorensen G (1995), 'Reactively sputtered Cr nitride coatings studied using the acoustic emission scratch test technique', *Surf. Coat. Technol.*, 74–75, 297–305.
- Johnson K L (1987), *Contact Mechanics*, Cambridge University Press, Cambridge, UK.
- Kaestner P, Olfe J, He J W, Riea K T (2001), 'Improvement in the load-bearing capacity and adhesion of TiC coatings on TiAl6V4 by duplex treatment', *Surf. Coat. Technol.*, 142–144, 928–933.
- Kanno I, Nomoto K, Nishijima S, Nishiura T, Okada T (1991), 'Tribological properties of aluminum modified with nitrogen ion implantation and plasma treatment', *Nucl. Instrum. Methods*, B59/60, 920–924.
- Katipelli L R, Agarwal A, Dahotre N B (2000), 'Laser surface engineered TiC coating on 6061 Al alloy: microstructure and wear', *Appl. Surf. Sci.*, 153, 65–78.
- Kessler O H, Hoffmann F T, Mayr P (1998), 'Combination of coating and heat treating processes: establishing a system for combined processes and examples', *Surf. Coat. Technol.*, 18, 299–304.
- Kessler O H, Surm H, Hoffmann F T, Mayr P (2002), 'Enhancing surface hardness of titanium alloy Ti-6Al-4V by combined nitriding and CVD coating', *Surf. Engng.*, 18, 299–304.
- Khaled M, Yilbas B S, Shirokoff J (2001), 'Electrochemical study of laser nitrided and PVD TiN coated Ti-6Al-4V alloy: The observation of selective dissolution', *Surf. Coat. Technol.*, 148, 46–54.
- Khaled M M, Yilbas B S, Al-Qaradawi I Y, Coleman P G, Abdulmalik D, *et al.* (2006),

- 'Corrosion properties of duplex treated Ti-6Al-4V alloy in chloride media using electrochemical and positron annihilation spectroscopy techniques', *Surf. Coat. Technol.*, 201, 932-937.
- Khurshudov A, Kato K, Sawada D (1996), 'Comparison of tribological properties of carbon and carbon nitride protective coatings over magnetic media', *Tribol. Lett.*, 2, 13-21.
- King F (1987), *Aluminum and its Alloys*. 1st Edition, Ellis Horwood, Chichester.
- Korhonen A S, Harju E (2000), 'Surface engineering with light alloy – Hard coatings, thin films, and plasma nitriding', *J. Mater. Engng. Perfor.*, 9, 302-305.
- Koskinen J, Hirvonen J P, Levoska L, Torri P (1996), 'Tribological characterization of carbon-nitrogen coatings deposited by using vacuum arc discharge', *Diam. Relat. Mater.*, 5, 669-673.
- Kwietniewski C, Dong H, Strohaecker T, Li X Y, Bell T (2001), 'Duplex surface treatment of high strength Timetal 550 alloy towards high load-bearing capacity', *Surf. Coat. Technol.*, 139, 284-292.
- Lai F D, Wu J K (1996), 'Effect of substrate surface roughness on the characteristics of CrN hard film', *Surf. Coat. Technol.*, 88, 183-189.
- Leadbeater G, Noble B, Waterhouse R B (1988), 'Metallurgical observation on the fretting of shot-peened aluminum surfaces', *Metal Treatments against Wear, Corrosion, Fretting and Fatigue*, Eds. By R.B. Waterhouse and A. Nikulari, Pergamon, 67-86.
- Li D, Chu X, Cheng S C, Lin X W, Dravid V P, Chung Y W (1995), 'Synthesis of superhard carbon nitride composite coatings', *Appl Phys Lett*, 67, 203-205.
- Liao J X, Xia L F, Sun M R, *et al.* (2004a), 'The tribological properties of a gradient layer prepared by plasma-based ion implantation on 2024 aluminum alloy', *Surf. Coat. Technol.*, 183, 157-164.
- Liao J X, Xia L F, Sun M R, *et al.* (2004b), 'Tribological behavior of gradient modified layer on 2024 aluminum alloy modified by plasma-based ion implantation', *Wear*, 256, 840-845.
- Liu D X, Tang B, Zhu X D, *et al.* (1999), 'Improvement of the fretting fatigue and fretting wear of Ti6Al4V by duplex surface modification', *Surf. Coat. Technol.*, 116, 234-238.
- Liu Y, Erdemir A, Meletis E I (1996), 'A study of the wear mechanism of diamond-like carbon films', *Surf. Coat. Technol.*, 82, 48-56.
- Luo L, Dong H, Bell T (2006), 'Model-based contact fatigue design of surface engineered titanium gears', *Comp. Mater. Sci.* 35, 447-457.
- Ma S L, Xu K W, Jie W Q (2004), 'Wear behavior of the surface of Ti-6Al-4V alloy modified by treating with a pulsed d.c. plasma-duplex process', *Surf. Coat. Technol.*, 185, 205-209.
- Majzoobi G H, Jaleh M (2007), 'Duplex surface treatments on AL7075-T6 alloy against fretting fatigue behavior by application of titanium coating plus nitriding', *Mater. Sci. Engng.*, A, 452-453, 673-681.
- Man H C, Zhang S, Cheng F T, Yue T M (2001), 'Microstructure and formation mechanism of *in situ* synthesized TiC/Ti surface MMC on Ti-6Al-4V by laser cladding', *Script. Mater.* 44, 2801-2807.
- Marumo Y, Yang Z, Chung Y W (1996), 'Structure and hardness studies of CN_x/TiN nanocomposite coatings', *Surf. Coat. Technol.*, 86-87, 586-591.
- Meletis E I, Erdemir A, Fenske G R (1995), 'Tribological characteristics of DLC films and duplex plasma nitriding/DLC coating treatment', *Surf. Coat. Technol.*, 73, 39-45.
- Michler T, Grischke M, Bewilogua K, Hieke A (1999), 'Continuously deposited duplex

- coatings consisting of plasma nitriding and a-C : H : Si deposition', *Surf. Coat. Technol.*, 111, 41–45.
- Molinari A, Straffellini G, Tesi B, Bacci T (1997), 'Dry sliding wear mechanisms of the Ti6Al4V alloy', *Wear*, 208, 105–112.
- Narayan J, Fan W D, Narayan R J, Tiwari P, Stadelmaier H H (1994), 'Diamond, diamond-like carbon and titanium nitride biocompatible coatings for human body parts', *Mater. Sci. Engng.*, B, 25, 5–10.
- Navinsek B, Panjan P, Cevclbar A (1995), 'Characterization of low temperature CrN and TiN (PVD) hard coatings', *Surf. Coat. Technol.*, 74–75, 155–161.
- Nayak S, Dahotre N B (2004), 'Surface engineering of aluminum alloys for automotive engine applications', *JOM*, 56, 46–48.
- Park J B (1984), *Biomaterials Science and Engineering*, Plenum, New York, 193–233.
- Peng X L, Clyne T W (1997), 'Formation and adhesion of hot filament CVD diamond films on titanium substrates', *Thin Solid Films*, 293, 261–269.
- Polmear I J (1989), *Light Alloys, The Metallurgy of the Light Metals* (2nd edition) Edward Arnold, 265–268.
- Rahman M, Duggan P, Dowling D P, Hashmi M S J (2007), 'Continuously deposited duplex biomedical coatings', *Surf. Coat. Technol.*, 201, 5310–5317.
- Rie K T, Stucky T, Silva RA, *et al.*, (1995), 'Plasma surface treatment and PACVD on Ti alloys for surgical implants', *Surf. Coat. Technol.*, 74–75, 973–980.
- Rie K T (1999), 'Recent advances in plasma diffusion processes', *Surf. Coat. Technol.*, 112, 56–62.
- Ronkainen H, Koskinen J, Varjus S, Holmberg K (1999), 'Load-carrying capacity evaluation of coating/substrate systems for hydrogen-free and hydrogenated diamond-like carbon films', *Tribol. Lett.*, 6, 63–73.
- Shih D S, Robertson I M, Birnbaum H K (1988), 'Hydrogen embrittlement of alpha titanium *in-situ* TEM studies', *Acta Metall.*, 36, 111–124.
- Staines A M (1991), 'Trends in plasma-assisted surface engineering processes', *Heat Treatment of Metals*, 4, 85–92.
- Stappen M V, Kerhofs M (1993), 'Introduction in industry of a duplex treatment consisting of plasma nitriding and PVD deposition of TiN', *Surf. Coating Technol.*, 62, 655–661.
- Subramanian C S (1992), 'Some considerations towards the design of a wear resistant aluminum alloy', *Wear*, 155, 193–205.
- Sue J A, Troue H H (1988), 'Effect of crystallographic orientation on erosion characteristics of arc evaporated titanium nitride coatings', *Surf. Coat. Technol.*, 36, 695–705.
- Sugiyama K, Hayashi K, Sasaki J, Ichiko O, Hashiguchi Y (1994), 'Microstructure and wear behavior of chromium nitride films formed by ion-beam-enhanced deposition', *Surf. Coat. Technol.*, 66, 505–508.
- Sun C Q, Fu Y Q, Yan B B, Hsieh J H, Lau S P, Sun X W, Tay B K (2002), 'Improving diamond-metal adhesion with graded TiCN interlayers', *J. Appl. Phys.* 91, 2051–2054.
- Sun J Y, Weng L J, Xue Q J (2001), 'Duplex treatment for surface improvement of 2024 Al', *Vacuum*, 62, 337–343.
- Sun Y, Bell T (1992), 'Combined plasma nitriding and PVD treatments', *Trans. Instit. Metal Finishing*, 70, 38–44.
- Sundararajan G, Rama A (2003), 'Mechanism underlying the formation of thick alumina coatings through the MAO coating technology', *Surf. Coat. Technol.* 167, 269–277.
- Sundararajan G, Roy M (1997), 'Solid particle erosion behaviour of metallic materials at room and elevated temperatures', *Tribol. Inter.*, 30, 339–359.

- Tendys J, Donnelly I J, Kenny M J, Pollock J T A (1988), 'Plasma immersion ion implantation using plasmas generated by radio frequency techniques', *Appl. Phys. Lett.*, 53, 2143.
- Wanstrand O, Larsson M, Kassman-Rudolphi A *et al.* (2000), 'An experimental method for evaluation of the load-carrying capacity of coated aluminum: The influence of coating stiffness, hardness and thickness', *Surf. Coat. Technol.* 127, 107–113.
- Was G S, Demaree J D, Rotberg V and Kim K (1994), 'Corrosion and mechanical behavior of ion implanted bearing steels for improved fretting behavior', *Surf. Coat. Technol.*, 66, 446–452.
- Wei R, Wibur P J, Kustas F M (1992), 'A rolling contact fatigue study of hard carbon coated M-50 steel', *J. Tribol. Trans. ASME*, 114, 298.
- Wernick S, Sheasby P G (1987), *The Surface Treatment and Finishing of Aluminum and its Alloys*. Metals Park, ASM International, 5th edition.
- Wierzchon T (2003), 'Surface engineering of titanium alloys: New prospective applications', *Mater. Sci. Forum*, 426, 2563–2568.
- Wright J K, Williamson R L, Maggs K J (1994), 'Finite element analysis of the effectiveness of interlayers in reducing thermal residual stresses in diamond films', *Mater. Sci. Engng.*, A187, 87–96.
- Wu X L, Li X J, Zhang X, Xue W B, Cheng G A, Liu A D (2007), Tribological behaviors of duplex DLC/ Al_2O_3 coatings fabricated using micro-arc oxidation and filtered cathodic vacuum arc system, *Surf. Rev. Lett.*, 14, 193–197.
- Yan B B, Loh N L, Fu Y Q (1999), 'Tribological evaluation of diamond coatings on pure titanium in comparison with plasma nitrided titanium and uncoated titanium', *J. Mater. Engng. Perform.*, 8, 660.
- Yerokhin A L, Lyubimov V V, Ashitkov R V (1998), 'Phase formation in ceramic coatings during plasma electrolytic oxidation of aluminum alloys', *Ceram. Int.*, 24, 1–6.
- Yerokhin A L, Nie X, Leyland A, *et al.* (1999), 'Plasma electrolysis for surface engineering', *Surf. Coat. Technol.* 122, 73–93.
- Yerramareddy S, Bahadur S (1991), 'Effect of operational variable microstructure and mechanical properties on the erosion of Ti-6Al-4V', *Wear*, 142, 253–263.
- Yilbas B S, Sahin A Z, Ahmad Z, Abdul Aleem B J (1995), 'Study into corrosion properties of TiN coated and nitrided Ti-6Al-4V material', *Corros. Sci.*, 37, 1627–1636.
- Zenkera R, Sachera G, Buchwaldera A, Liebich J, Reiterd A, Häßlere R (2007), 'Hybrid technology hard coating – Electron beam surface hardening', *Surf. Coat. Technol.*, 202, 804–808.
- Zhang S, Sun D, Fu Y Q, Du H J (2005a), 'Toughness measurement of thin films: A critical review', *Surf. Coat. Technol.*, 198, 74–84.
- Zhang S, Sun D, Fu Y Q, Du H J (2005b), 'Toughening of hard nanostructural thin films: A critical review', *Surf. Coat. Technol.*, 198, 2–8.
- Zhang Z X, Dong H, Bell T (2006), 'The load bearing capacity of hydrogen-free Cr-DLC coatings on deep-case oxygen hardened Ti6Al4V', *Surf. Coat. Technol.*, 200, 5237–5244.
- Zhang Z X, Dong H, Bell T, Xu B S (2008), 'The effect of deep-case oxygen hardening on the tribological behaviour of a-C:H DLC coatings on Ti6Al4V alloy', *J. Alloy. Compound*. 464, 519–525.
- Zili C, Patu S (1992), 'Microstructure and corrosion behavior of chromium nitride grown by dynamical ion beam mixing', *Surf. Coat. Technol.*, 51, 222.

Surface engineered light alloys for sports equipment

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Abstract: The popularity of sports activities boosts the ever-increasing demands for improving sports equipment to meet various needs. There are two major methods of making advanced sports equipment – the application of advanced design and use of advanced materials. Light metals, aluminum, titanium and magnesium have been widely adopted in many sports activities because of their low density. However, these bulk light materials cannot possess all the combined desired attributes, especially their surface attributes, such as mechanical properties, wear resistance, corrosion resistance and aesthetic appearance. Therefore, surface engineering technologies have been used to satisfy the specific needs of advanced sports equipment. In this chapter, the application of surface engineered light alloys, aluminum, titanium and magnesium alloys, in various sports activities are introduced and discussed.

Key words: light alloys, sports equipment, surface engineering.

16.1 Introduction

Sports activities not only improve our health but also increase the enjoyment and quality of our life. Obviously it has become a necessary part of our life. In the Beijing 2008 Olympic Games, a total of 11 028 athletes from 204 National Olympic Committees attended 302 different competitions in 28 sports, for example, football, triple jumping, 100 meter sprint, and cycling. The popularity of sports activities boosts the ever-increasing demands for improving sports equipment to meet different needs. Athletes desire advanced equipment that can improve their performance; beginners may wish to use their equipment more comfortably and easily; disabled people may hope to use assisted sports equipment to improve the quality of their life.

The applications of new design and new materials are two major ways to make better sports equipment. In particular, the adoption of new materials and processing technologies plays an important role in the development of sports equipment. It may be because the use of advanced materials could bring a subsequent revolutionary change. Vaulting poles, as an example, were originally made from natural materials such as wood and bamboo, due to their light weight. The length of poles, however, was limited. The development of glass fiber composite poles in the 1960s enabled an appreciable improvement

in properties, such as strength, stiffness and density, corresponding to a step change in the world record (Jenkins, 2003).

Light metals, aluminum, titanium and magnesium have been widely adopted for the production of sports equipments (Jenkins, 2003; Hanson, 1986; Lütjering and Williams, 2007; Friedrich and Mordike, 2006; Kleiner *et al.*, 2003; Foxall and Johnston, 1991). The property of lightness translates directly to material property enhancement for many products, since by far the greatest weight reduction is achieved by a decrease in density. Moreover, titanium and aluminum alloys show good corrosion resistance. These advantages are the main reasons why light metals are favored in many sporting fields, such as cycling, golfing, tennis, mountaineering, and motor racing.

Besides these new materials, sports equipment manufacturers are also using more and more complex technologies to satisfy the needs of continuously developing diverse and professional sports activities. In most situations, bulk materials cannot possess all the combined desired properties, especially the surface properties. Surface engineering technologies have been successfully used in many engineering sectors. Thus, these technologies attract more and more attention. For example, the most general application of surface engineering technologies is conventional painting, which can provide not only aesthetic appearance but also various functional properties.

Bicycle manufacturers started to use magnesium alloys to produce advanced bicycles owing to their low density and relative high strength-to-weight ratio. However, magnesium has a very high electro-negative potential, which results in the poor corrosion resistance (Friedrich and Mordike, 2006). Surface engineering technologies such as anodizing, ceramic conversion, vapor deposition, laser treatment, have been used to protect the surface.

To clarify the importance of surface engineered light alloys, aluminum, titanium and magnesium alloys, in advanced sports equipments, this chapter introduces the status of the application of light alloys in sports products. Successful applications of advanced surface engineering technologies in improving the quality of sport products and enhancing sport performance are given in three major case studies; the first is concerned with the friction control of golf clubs, the second with surface engineered bicycles, and the last with ceramic conversional titanium components for motor sports. Finally, the prospects for the further application of surface engineering in sport are briefly discussed.

16.2 Light alloys in sports equipment

The term ‘light metals’ has traditionally been given to aluminum, titanium and magnesium because they are frequently used to reduce the weight of products. These three metals possess relative low densities, 1.7 g/cm^3 (magnesium), 2.7 g/cm^3 (aluminum) and 4.5 g/cm^3 (titanium) when compared with

7.9 g/cm³ and 8.9 g/cm³ for the heavy structural materials, iron and copper (Rooy, 1990; Friedrich and Mordike, 2006; Lütjering and Williams, 2007). This is an obvious reason why light metals have been associated with transportation, notably aerospace, which has provided great stimulus to the development of light alloys during the last fifty years.

In general, the strength of these light metals, especially, aluminum and magnesium, is less than that of steels as shown in Table 16.1. Therefore, the major objective in the design of alloys is to increase strength, hardness, and resistance to wear, creep, stress relaxation, and fatigue. Different combinations of alloying elements have been added to improve these properties. Their processing history, including solidification, thermomechanical history, heat treatment and cold working, can also be optimized to significantly improved their mechanical properties (Rooy, 1990; Friedrich and Mordike, 2006; Lütjering and Williams, 2007).

Strength-to-weight ratios have been a dominant consideration and these are particularly important in engineering design when parameters such as stiffness or resistance to buckling are involved. As shown in Table 16.1, higher strength-to-weight ratios can be achieved with these light alloys than with steels. Thus, light alloys are favored by racing car manufacturers because the weight of the car may be significantly reduced without losing

Table 16.1 Tensile strength and strength-to-weight ratios of light metals and their alloys

Materials		Tensile strength (MPa)	Strength-weight
Aluminum	99.99% sheet, fully soft annealed	55 (Brandes and Brook, 1992)	~20
Magnesium,	99.9% sheet, annealed	185 (Brandes and Brook, 1992)	~110
Titanium	Commercially pure (grade 2), casting,	552 (Destefani, 1990)	~120
Steel	0.1 carbon, BS 055M15, rolled	310 (Brandes and Brook, 1992)	~40
	0.38 carbon, BS MOM36, hardened and tempered	790 (Brandes and Brook, 1992)	~100
Al alloy	A02010, solution heat treated and artificially aged (T6)	485 (Kearney, 1990)	~180
	A07005, solution heat treated and artificially aged (T6)	317 (Kearney, 1990)	~117
Ti alloy	Ti-6Al-4V, annealed	930 (Eylon <i>et al.</i> , 1990)	~200
Mg alloy	Mg-Zn AZ63A solution heat treated and artificially aged	275 (Housh and Mikucki, 1990)	~160

mechanical properties. In the following sections, the applications of light alloys in various sports fields will be introduced.

16.2.1 Cycling

Interest in reducing the weight of competition bicycles originated in the thought that the weight of the bicycles can influence the performance of racing cyclists. Generally, it is believed that the less weight, the better the performance (Buchanan, 2003; Brown, 2008; Jenkins, 2003). In practice, bicycle manufacturers even consider that parts that give reliable service might be 'overbuilt', and redesign these to save a few grams.

The major part of a bicycle is the frame, which is usually made from one of five different materials: steel, aluminum, titanium, carbon composite or magnesium (Brown, 2008; Jenkins, 2003). High-strength steel is the most traditional frame material. Steel frames generally are heavier than those made from the other four materials. To reduce their weight, large diameter thin-wall tubing design has been adopted to build the frames (Jenkins, 2003). In theory, by significantly increasing the tube size and reducing the wall thickness, a much lighter frame can be obtained. However, this is not practical because of two reasons. Firstly, the thinner the walls of the tubing, the more difficult it is to make a good joint. This is the reason for butting tubes; the walls get thicker near the ends, where the tubes come together with other tubes. In addition, if the walls get too thin, the tubes become too easy to bend, and connection points for bottle cages, cable stops, shifter bosses and the like have inadequate support. Therefore, light materials such as aluminum alloys, titanium alloys, carbon fiber and magnesium alloys are used in their production. In this section this application is briefly introduced.

Aluminum alloys

In pure form, aluminum is so soft that it cannot be used as a structural part. To increase its strength and other mechanical properties, it is normal to add various alloying elements and apply sequential heat treatments. Aluminum alloy 6061 and alloys of the 7000 series are most commonly used in the production of bicycle frames (Easton Sports). The 6061 aluminum alloy (Al-Mg-Si) contains 0.8–1.2Mg, 0.4–0.8Si and 0.15–0.4Cu (wt%). It shows good corrosion resistance, strength and weldability (Kearney, 1990). The 7000 series alloys (Al-Zn-Mg-(Cu)) have the highest strength of all aluminum alloys. The 7005 Al-4.0-5.0Zn-1.0-1.8Mg and 7075 (Al-5.1-6.1Zn-2.1-2.9Mg-(1.2-2.0Cu)) alloys are used to produce frames. 7075 aluminum alloy is also widely used in the aero industry.

Normally, these aluminum alloys need proper heat treatment after welding to achieve good mechanical properties. Age hardening is used to form hard

precipitates to increase their strength. For example, the strength of the 6061 aluminum alloy can be increased by two to five times using T6 heat treatment (solution plus artificial aging) (Kearney, 1990). As mentioned earlier, another benefit arising from aluminum frames is good corrosion resistance. Once exposed to air, aluminum is readily oxidized to form a dense and thin aluminum oxide surface film. Such a film is a barrier to further oxidation.

In order to reduce the stiffness of aluminum frames, new designs have also been explored, such as increasing the tube wall thickness or changing the shape of the cross-over tube.

Titanium alloys

In the 1960s, titanium alloys were firstly used to make bicycle frames in the United States. The most commonly used titanium alloy is Ti-6Al-4V, which possesses low density and good strength, which can reach 1160 MPa after aging treatment (Eylon *et al.*, 1990), good fatigue strength and excellent corrosion resistance. Wheelchairs using titanium tubing can also be found in the market for people with disability. This is attributed not only to its light weight but also good shock absorbing ability. However, titanium alloys are expensive due to the difficulty in extracting titanium from its ore. Moreover, titanium welding requires an inert atmosphere because of its strong affinity to oxygen. Thus, the cost of titanium products is significantly higher than that of aluminum alloys, magnesium alloys and steels (Eylon *et al.*, 1990).

It is believed by many cyclists that bicycle frames made from aluminum and titanium alloys are not rigid enough because of their lower stiffness than steel. However, Ian Buchanan has tested the torsion stiffness of the rear triangle and vertical frame compliance of various common frame designs (Buchanan, 2003) and found that these properties are decided by the size, shape and wall thickness of the tubing used, and the manufacturing technique, rather than the materials themselves.

Magnesium alloys

The density of magnesium is as low as 1.74 g/cm^3 , about 1/5 that of iron, 2/3 that of aluminum and 2/5 that of titanium. The strength-to-weight ratios of magnesium alloys are normally higher than those of aluminum alloys. Therefore, it is possible to produce lightweight frames using magnesium alloys. Moreover, their excellent anti-shock property is better than those of aluminum alloys and titanium alloys. From the environmental angle, magnesium alloys are easy to be recycled and are so called 'green materials'.

The main concerns using magnesium alloys are their low stiffness and poor corrosion resistance. To address the first concern, new designs and alloys are used; for example, the wall thickness of the tubes is increased

so as to improve stiffness. Regarding the corrosion resistance, magnesium is very active, reacting with oxygen in the air. Magnesium cannot be used in its pure form. However, by adding aluminum, zinc, manganese, etc., its corrosion resistance can be greatly improved. At the same time, its strength and mechanical properties can also be enhanced.

As described above, the frame is the largest part of a bicycle. Light materials are successfully used to produce frames that reduce the weight of bicycles. There are also other parts made from light materials, for example, gears, steering bars, seat posts, wheels, chains, bearings and cranks. The successful adoption of light materials has boosted cycling as a sport.

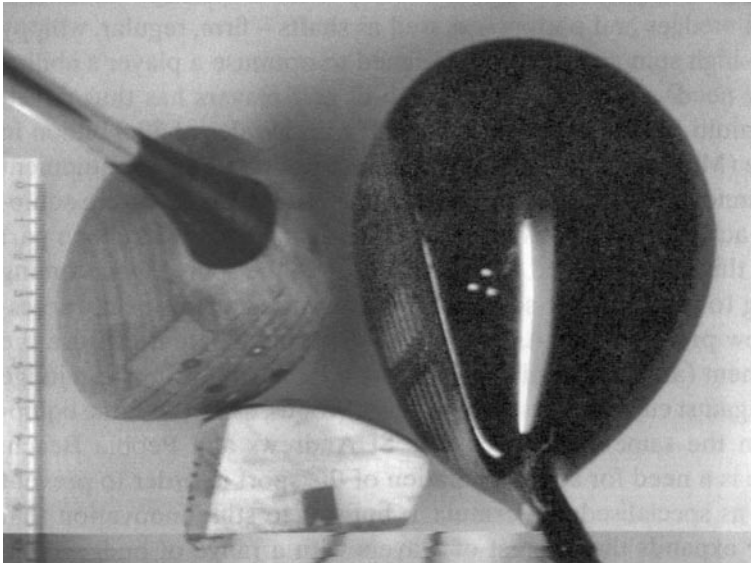
16.2.2 Golf

Despite the apparent ‘simple’ goal of hitting the golf ball into the hole using as few strokes as possible, much work has been carried out to improve golf clubs to realize this objective. Golf clubs are expected to be able to carry out many different functions, depending on the circumstances, ranging from driving the ball as far as possible from the tee to much more controlled shots on the putting green. According to its function, the golf club head can be briefly divided into five categories:

- (i) drivers (very long shots from the tee)
- (ii) fairway woods (controlled long-distance shots)
- (iii) irons (for medium distance and accuracy)
- (iv) wedges (short-distance shots from sand and/or deep rough)
- (v) putters (getting the ball into the hole from the green)

Although there are many kinds of golf clubs, they are basically composed of a shaft, a lance (grip) and a club head, which is the part hitting the ball. Due to the limitations of materials and processing technologies, the traditional club head was made from persimmon wood. In order to keep a good balance, the weight of club head is normally limited to 185 ~ 205 gram (Cochran and Stobbs, 2005). For a solid club head, the size has to be limited resulting in the difficulty in hitting the small sweet spot. With the development of materials and processing methods, high strength steels, aluminum alloys, titanium alloys, zirconium alloys and composites are successfully used in producing golf clubs (Jenkins, 2003). Especially, the introduction of light alloys with a hollow design allows manufacturers to produce lightweight club heads with larger sizes, as shown in Fig. 16.1. These over-sized metallic club heads can allow less skillful players to make a greater swing.

Commercially, pure titanium cannot be used for golf club heads because of its lower strength necessitating a thicker (hitting) face. The major titanium alloy ‘woods’ are made from Ti-6Al-4V, using casting approaches such as



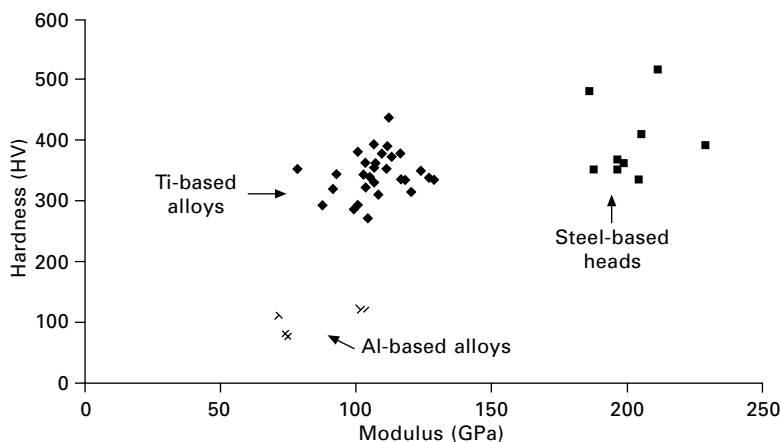
16.1 Traditional wooden driver (top left); 2001 titanium-based alloy driver (top right) and section through traditional wooden driver (bottom) showing plastic insert in face (Jenkins, 2003).

centrifugal- and static-casting techniques. There are a few other alloys being used, including Ti-3Al-2.5V and the beta alloy Ti-15V-3Cr-3Sn-3Al (Froes, 1999).

With respect to the kinetics, the energy of the ball is transferred from the surface of the club heads, thus the strength, elasticity and friction of the surface can significantly affect the speed and spin of the ball. In theory, the interactive surface should be as thin as possible to limit the deformation of the ball, which can cause loss of kinetic energy. For Ti-6Al-4V, a 3.8 mm face thickness is needed for drivers and fairway woods, because of the level of the impact force on the club face (Froes, 1999). Although club designers would like to go even thinner, the yield stress (σ_y) is required to be high to minimize the risk of plastic deformation during use. The elastic modulus (E) should be low to maximize elastic deformation energy. Thus, from a materials point of view, club head materials can be evaluated by the performance index, σ_y/E (Jenkins, 2003). As shown in Fig. 16.2, Ti alloys have the highest σ_y/E followed by steels and finally age-hardening Al-based alloys.

16.2.3 Motor sports

As is well known, light weight is one of the key factors in deciding the performance of racing cars. For example, the acceleration of cars is



16.2 Plot of hardness vs. E for head materials (Jenkins, 2003).

proportional to the ratio of power-to-weight. Thus, light and strong materials are preferred for producing various parts of racing cars. Titanium and its alloys possess a high strength-to-weight ratio and thus are increasingly used in the construction of motor engines. Currently, titanium alloys have replaced steel for many components, including wheel hubs, roll-over hoops, suspension assemblies, engine mounting brackets, drive shafts, pedals, and fasteners (Yamada, 1996; Hanson, 1986). Aluminum alloys are also popular in construction of the racing engine. For Formula 1 racing car engines, the crankcase and cylinder block are regulated to be made of cast or wrought aluminum alloys (l'Automobile, 2005).

From another angle, the reduction of reciprocating or rotating parts in the engine can improve the performance of racing cars and reduce lap times due to better efficiency (Taylor, 1998). Research work shows that lower valve spring loads can be used with lighter weight TiAl valve train components, thus reducing noise and friction, enhancing fuel economy and increasing the upper limit of the engine speed (Badami and Marino, 2006; Jenkins, 2003). Besides the valve trains, titanium alloys are also used for such components as connection rods, crank shafts and springs.

16.2.4 Other sports

Tennis rackets were initially made from wood. To increase the shear and fatigue strength and the ability to produce complex profiled frames, metal was gradually introduced. Aluminum alloy 6061 has been successfully accepted by players because the desired characteristics can be produced after specific heat treatments (Jenkins, 2003). Though the current market, especially the high quality market, is dominated by composite rackets, aluminum 6061

is still used for low-cost rackets that fill and hold an important position in the market.

Mountaineering amateurs have also benefited from the adoption of light alloys. Lightweight equipment can be produced using a combination of low-density materials and design. Karabiners are metal loops with a sprung or screwed gate which is extensively used in linking components of mountaineering systems. The majority of karabiners are made from T6 tempered (solution treated and then artificially aged) 7075 aluminum alloy. Aluminum alloys are also widely used in belays, camming devices and ice tools (Jenkins, 2003).

Light alloys, e.g. titanium alloys, began to be used in self-contained underwater breathing apparatus (SCUBA) owing to its light weight, high strength, good corrosion resistance against sea water and bio-compatibility (Maberry, 2000). Aerodynamic javelins use aluminum alloy for their construction to modify shape and weight distribution. In archery, the manner in which an arrow is constructed is one factor affecting the accuracy to which it can be shot. Aluminum arrows are considered to be the best for accuracy (Reilly and Lees, 1984).

In summary, light alloys have been widely used in sports equipment to improve performance, enjoyment, durability and safety. With the popularity of sporting activities in human society, more and more can benefit by adopting light alloys and innovative designs. However, as discussed in other chapters of this book, the surface properties, in terms of corrosion and wear resistance, need to be significantly enhanced to meet ever-increasing performance requirements.

16.3 Surface engineering in sports equipment

As described, sports equipment has been improved by the adoption of new design innovations. Meanwhile, efforts have also been devoted to enhancing the performance and the equipment life by adopting advanced surface engineering technologies. Surface engineering, a term originally coined by Bell, *circa* 1983 (Tytkiel and Dearnley, 1995), involves the application of traditional and innovative surface technologies to engineer components and materials in order to produce a combined material with properties unattainable in either the base or surface materials. Widely speaking, surface engineering can be applied to all kinds of sports materials to enhance the surface physical, chemical and mechanical properties, or bring other desired functions such as bio-compatibility, or magnetic and electrical properties.

Currently, surface engineering involves a wide-range of technologies, which can be grouped into two broad categories: surface coatings and surface modifications. The desired coatings can be obtained by various surface coating processes which are generally divided into electrochemical,

chemical, spraying, welding, physical vapor deposition (PVD) and chemical vapor deposition (CVD) coatings. Compared to surface coatings, surface modification methods rely on the direct transformation of the surface using thermal, mechanical, physical and chemical methods (Grube, 1991). There are four main surface modification techniques – thermal hardening, mechanical working, ion implantation and thermo-chemical treatments. It is also common to combine two or more techniques from the surface coatings and/or modifications, to obtain properties that are unattainable from the individual technique. These combined surface engineering technologies are called duplex or multiple surface treatments. Because the principles and the applications of these surface engineering technologies have been discussed in other chapters, readers can refer to the relevant chapters for more detailed information about them.

As discussed in previous chapters, the surface properties of light alloys often do not meet the requirements for sports applications. For example, the surfaces of the light alloys are normally easily scratched, and magnesium alloys corrode in many environments. Various surface engineering technologies, e.g. from conventional painting to advanced physical vapor deposited coatings, have been used in sports equipment. The adoption of advanced surface engineering technologies can provide more solutions and encourage novel designs for current sports equipment. In the following sections, three application cases, surface engineered bicycle frames, golf club heads and racing car engine valves, will be discussed.

16.3.1 The bicycle

A frame is one of the most important parts of a bicycle. As described in Section 16.2.1, five types of materials, namely steels, aluminum alloys, titanium alloys, carbon composites and magnesium alloys, are widely adopted for the manufacture of bicycle frames. Four metal materials will be discussed. Carbon composites are also widely used, but are not in the scope of this particular study.

Notwithstanding, light alloys normally have lower strength compared to steel, manufacturers have used various designs, such as big thin wall tube, to address this problem. These designs can successfully provide light bicycle frames with enough strength, and they are currently widely adopted by manufacturers. Unfortunately, abrasion wear resistance of the surface of these light alloys cannot be satisfied by manufacturers and users. For example, titanium, claimed as ‘the metal of the gods’ for bicycle application (Jenkins, 2003), is also characterized by its poor tribological behavior, in terms of high and unstable friction due to the low shear strength caused by the low c/a ratio as a hexagonal close-packed metal, abrasive wear due to the low hardness, and also severe adhesive wear and strong tendency to

scuffing (Jenkins, 2003; Bloyce *et al.*, 1994). For aluminum and magnesium alloys, the wear resistance of the surface is also not as good as expected. Once scratched and damaged on the surface, the bicycles not only lose their aesthetic appearance, but also their fatigue strength and corrosion resistance, due to the introduction of these flaws.

To protect the surface from wear, various solutions have been used, such as painting, powder coating, plating, or anodizing. Possibly, painting is the most widely used method for decorative, protective, and functional purposes. The main advantages of painting over other processes are two fold. Firstly, the cost of the painting process and investment in equipment are much lower than the others. Secondly, a wide range of paints are available to satisfy different needs. When selecting a paint system, many factors concerning the service environment must be considered, such as pre-treatment and the painting method. Most paints, also called organic coatings, are based on a film-former or binder that is dissolved or dispersed in a solvent or water. According to their specific applications, various substances can be added into the film-forming liquid to provide not only aesthetic appearance, but also specific properties, such as mechanical properties, corrosion resistance, and/or resistance to heat, cold, sunlight and weathering. Prior to painting, proper surface preparation is required to remove all contamination, which can either interfere with the adhesion of the paint film or allow corrosion to progress beneath the paint film and cause it to fail prematurely. Combined mechanical cleaning and chemical cleaning methods are normally used. Commonly used mechanical cleaning methods include power brushing, grinding, and abrasive blasting. Chemical cleaning methods include emulsion cleaning, solvent cleaning, vapor degreasing, alkaline cleaning, acid cleaning, pickling, and steam cleaning. When a clean surface is obtained, a subsequent pre-painting treatment, including phosphate coatings and organic pretreatments is generally used to improve paint adhesion and reduce corrosion.

Various painting methods are used to paint bicycle parts, such as spraying, powder coating, dip painting, flow coating, roller coating, curtain coating, tumble coating and electrocoating (Gossner and Tator, 1994). In industry, quality control is routinely undertaken to ensure that the produced coatings maintain satisfactory application properties, appearance, stability and performance characteristics. Quality control includes a number of tests including color, abrasion resistance, blistering, environmental tests, film thickness, hardness and impact tests.

Besides painting, another important surface technology is to form oxide layers using anodizing on titanium, aluminum and magnesium alloys (Stevenson, 1994). The intrinsic ceramic nature of oxides has much higher hardness and chemical inertness than the original metal, resulting in excellent abrasion resistance and corrosion resistance. It can also realize control of the color of the surface layer by controlling the thickness of the oxide layers.

Another advantage of anodizing is to provide a good substrate for subsequent painting by improving the surface adhesion.

Recently, magnesium, has attracted more and more interest from bicycle manufacturers. Compared with magnesium, titanium alloys are limited by their high costs, due to difficulties in refining, machining, welding, heat-treatment, etc. (Jenkins, 2003). Magnesium also possesses the lower density and elastic modulus, which enables the production of a lighter bicycle, with better damping behavior than aluminum. Therefore, larger tubes for bicycle frames can be produced with better resistance to non-axial loads without any increase in weight. A magnesium tube with a 60 mm diameter and a wall thickness of 2.5 mm weighs no more than an aluminum tube of only 50 mm diameter, and a wall thickness of 1.95 mm. The abundance of magnesium, a low and stable price, and security of supplies also encourage industry to adopt magnesium and its alloys in various products.

However, the major problems in using magnesium and its alloys are that they are very susceptible to corrosion and abrasion; and they are notoriously difficult to paint. Thus it is important to modify their surface to satisfy the application requirements, such as appearance and corrosion resistance. Anodizing has also proved its success in improving the surface of magnesium alloys (see Chapter 4). Especially, based on anodizing, a new technology called plasma electrolytic oxidation (PEO) has been developed (see Chapters 5 and 6).

It has been reported that a Keronite (PEO) treated surface of magnesium AZ91 alloy can obtain a hardness of over 700 HV (Keronite Ltd, 2004), which is harder than most anodized aluminum alloys. The wear resistance can be improved to twenty times more than that of untreated magnesium in a two-body abrasive wear test. Moreover, the friction coefficient can be reduced to less than 0.15 with a polishing process. This coating is corrosion resistant in various media and also has decorative attractiveness in the colors of the coatings. In the bicycle market, early adopters of this technology will benefit most from the novelty value of magnesium, whilst the more adventurous cyclists can enjoy a smooth ride on the most lightweight of materials.

In summary, the adoption of light metals in bicycles is demanded by ever-increasing needs for improving the performance and enjoyment during cycling. However, the use of these light alloys is limited by some surface problems such as poor wear and corrosion resistance, which can be addressed by advanced surface engineering technologies.

16.3.2 Golf club heads

As discussed previously, various types of golf clubs are used by players of the game. Drivers are used to drive the ball as far as possible, while putters are designed to control the ball better. It is obvious that these clubs are made

with different designs and materials. One of the most important differences is the material used for the actual club head. When choosing the materials for the club head, many properties need to be considered, such as strength, weight, elastic modulus and friction force.

In golf theory and practice, the friction between the hitting surface and the ball, play an important role because it can significantly affect the spin rate of the ball (Jenkins, 2003). Low friction force is favored for drivers in order to reduce the loss of energy due to the spin of the ball. As a result, the ball can reach a higher speed and a longer flight distance. However, a strike on the green requires better control, which can be achieved by creating the desired back-spin on the ball. In general, the higher the friction force, the better the controlling ability. Thus, a constant and high friction surface is designed for clubs such as putters.

Surface engineering is very attractive for obtaining a particular desired surface on the club head, with a suitable friction coefficient. For low-friction golf club faces, the traditional method is to apply a lubricant coating (a mixture of silicone, PTFE, waxes and water-based lubricants) to the surface of the club head prior to hitting (Jenkins, 2003). This is simple, low-cost and very flexible. However, the lubricants can pass onto the golf ball, thus causing the ball to fly unevenly through the air. It is also inconvenient to apply a liquid lubricant prior to a shot and have to remove it afterwards.

Another surface engineering technology, physical vapor deposition (PVD), can be used to coat the club heads with permanent low-friction coatings. A hard and low-friction titanium nitride coating is cast onto golf club heads made of 316 austenitic stainless steel (Buettner, 1996) using conventional PVD. The titanium nitride coating provides a very hard (1500–2000 HV), low-friction and wear resistant surface to the club head. The high wear-resistance enables the corner of the grooves in the hitting surface to remain sharp, thus maintaining driving power imparted to a golf ball during extended use. Besides ceramic nitride coatings, a diamond-like coating (DLC) can also be adopted on the surface of a club head. A US patent has been granted to Lin *et al.*, which discloses a PVD technique used to apply DLC on golf club heads (Lin *et al.*, 2002). These DLC coatings show a much lower friction coefficient (between 0.05–0.10) than TiN coatings. Moreover, the hardness of the DLC coatings can reach 3000–4000 HV, which can confer a much better scratch resistance to the coatings. After using the DLC-coated clubs, most golfers feel that their golf performance, in particular, their driving distance (due, in part, to a lesser degree of hooking or slicing) had noticeably improved.

For high-friction golf club faces, the traditionally used surface engineering technology is sand or bead blasting to increase surface roughness and thus surface friction. However, the durability of the treated surface is poor due to the wear caused by the impact and sliding of the golf ball. To address this

problem, the popular way is to use a high-friction wear-resistant insert. For example, the irons and wedges made by Carbite Golf use inserts made from fine titanium powders and diamond particles, using a powder metallurgy process. During the lifespan of the club, the insert maintains a high level of surface roughness, since a fresh playing surface is continually uncovered. In addition to irons and wedges, a series of high-friction surface ‘woods’ have been developed to achieve good spin control resulting in straighter and softer landing shots by Carbite Golf and Gyrosevon.

In summary, advanced surface engineering technologies can produce titanium club heads with optimal friction, which is required by golfers with various abilities to enhance performance.

16.3.3 Motor sport engines

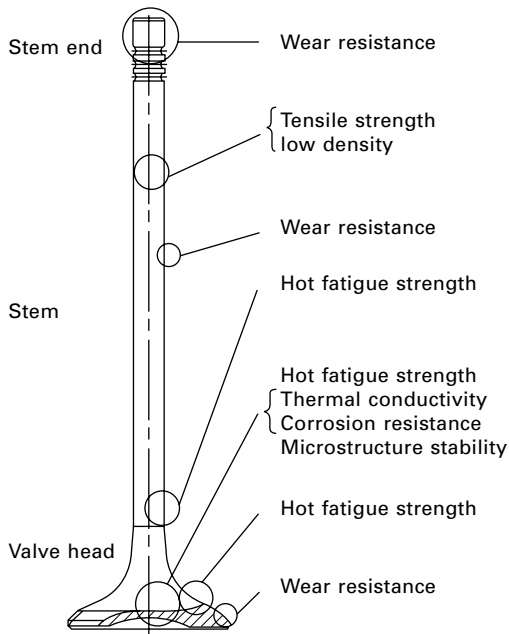
As discussed in Section 16.2.3, titanium and aluminum alloys are widely used in the construction of racing engines. However, these alloys are characterized by poor tribological properties, and require surface treatment. Two case studies are presented as follows:

Ceramic conversion of TiAl valves

In engines, valve train systems reciprocate and control the gas and fuel flow into and out of the cylinders to facilitate combustion. When lighter weight valves train components are used, the engine performance can be improved by the reduced noise and friction. Klause (Gebauer, 2006) demonstrated that the required cam torque is clearly reduced by using lightweight valves, in particular, when the cam rotation speed is less than 2000 rpm.

Titanium-based alloys are gradually replacing steel in high performance automobiles, such as racing cars and motorcycles (Badami and Marino, 2006). Gamma titanium aluminide (TiAl) based alloys have a low density ($3.8\text{--}4.0\text{ g/cm}^3$), which is about half that of steel. These alloys possess good high-temperature strength, modulus retention and excellent creep properties. They also show good oxidation resistance below 700°C . As engines for better efficiency need to run at higher temperatures and speeds, TiAl is a good candidate material for engine valves. However, the wear resistance of TiAl is a major concern for such applications.

The valves need not only precision machining, but also require different properties in different areas. Figure 16.3 (Gebauer, 2006) shows a typical valve design and the specific requirements for its properties. It is clear that the stem end, stem and seat need high wear-resistance when used in high performance engines. Considering the size of these areas, the stem end suffers the highest stresses due to its small area. When the hydrodynamics are not fully developed during operation, wear can happen in a short time. Various



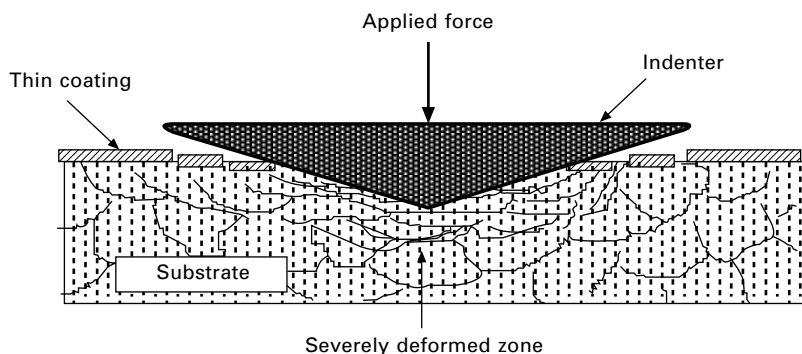
16.3 Valve design and characteristic areas (Gebauer, 2006).

surface engineering technologies, nitriding, carburizing, PVD coatings and laser treatments, have been investigated in attempts to satisfy these needs (Zhecheva *et al.*, 2005; Hauert, 2004). Although these coatings have proven to be successful in cutting-tools, they cannot protect the TiAl valves because, under the high load, catastrophically premature failure occurs to the thin, hard but brittle coatings. These phenomena can resemble the so-called ‘thin-ice effect’ (Fig. 16.4) (Jenkins, 2003), when the soft substrate plastically deforms under the applied load. To address this problem, a ceramic conversion treatment has been successfully developed (see Chapter 14). The surface layer consists of a hard rutile TiO_2 and an oxygen diffusion zone. After 600 hours testing, no significant wear could be observed at the valve tip.

Thermal spray for aluminum engine blocks

During the operation of engines, hard carbon particles form due to inefficient fuel combustion and accumulate on the piston top rings. Because of the low hardness and poor wear properties of aluminum alloys (see Chapter 2), the surface can undergo liner wear, resulting in excessive oil consumption, ring and bore scuffing and seizure.

Advanced plasma sprayed coatings (Chapter 7) have been successfully developed to address this problem. According to the specific requirements



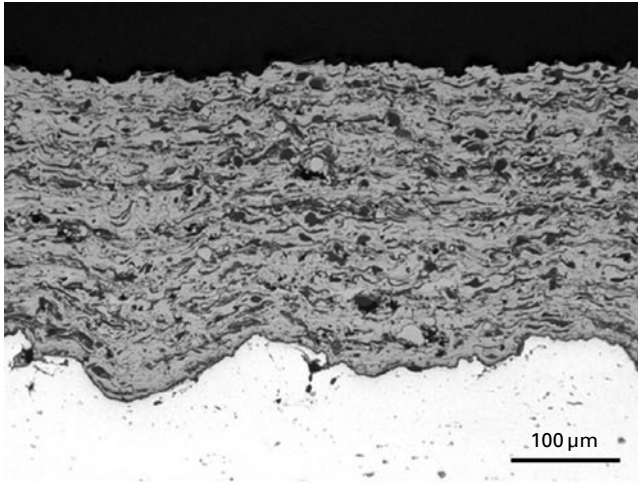
16.4 Schematic of 'ice effect' (Jenkins, 2003).

Table 16.2 Coating materials deposited by plasma spraying (Barbezat, 2005)

Coating type	Hardness/ HV0.3	Microstructure
A: Carbon steel with solid lubricant wustite and magnetite	400	Ferrite with fine iron carbides and FeO (wustite) and Fe ₃ O ₄ (magnetite)
B: Composite of carbon tool steel and molybdenum	400	Ferrite with fine iron carbides and isolate phase of molybdenum. Low level of iron oxides
C: Corrosion resistant steel (Cr and Mo alloyed)	350	Iron with fine carbides and some oxides
D: Metal matrix composite (MMC, Type 1)	450	Material A with addition of about 20% discrete particles of ceramic
E: Metal matrix composite (MMC, Type 2)	400	Material C with addition of about 20% discrete particles of ceramic

of the engines, various sprayed coatings can be applied, as shown in Table 16.2 (Barbezat, 2005). For example, the coating with discrete particles can be used for highly loaded diesel engines because these particles can increase compressive strength and wear resistance. A typical microstructure of the metal matrix composite (MMC) materials developed by Sulzer Metco is shown in Fig. 16.5 (Ernst and Barbezat, 2008). This coating has been tested at AVL Austria in a four cylinder diesel engine (50 kW/l, 150 bar). The results show the total wear loss has been significantly reduced from 9.7 nm/h for standard cast iron liners to 1.4 nm/h. The oil consumption and the blow-by have also been dramatically reduced.

Currently, these coatings have been applied not only to passenger vehicles but also in motor racing sports. For example, several qualified V10, V8 and V4 racing engines, are produced with plasma coatings (Gebauer, 2006).



16.5 Typical microstructure of the MMC plasma coating (carbon steel with 30 vol.% of non-abrasive ceramic particles) (Ernst and Barbezat, 2008).

16.4 Summary

Light alloys are favored by sports equipment manufacturers because of their high strength-to-weight ratios and are gradually being adopted in more and more professional sports fields. Limitations of this equipment are likely to be surface-related failures, caused by inadequate tribological, chemical, and related technical properties. Surface engineering, as a general term for numerous technologies, has demonstrated its ability to solve many of these technical problems. Moreover, with the development of new technologies and popularity of sports activities, it can be predicted that surface engineered light alloys will find more applications in sports.

16.5 Acknowledgements

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16.6 References

- Badami, M. and Marino, F. (2006) Fatigue tests of un-HIP'ed [gamma]-TiAl engine valves for motorcycles. *International Journal of Fatigue*, 28, 722–732.
- Barbezat, G. (2005) Advanced thermal spray technology and coating for lightweight engine blocks for the automotive industry. *Surface and Coatings Technology*, 200, 1990–1993.
- Bloyce, A., Morton, P. H. and Bell, T. (1994) Surface Engineering of Titanium and Titanium Alloys. In *ASM Handbook*. Vol. 5, ASM International.

- Brandes, E. A. and Brook, G. B. (1992) *Smithell's Metals Reference Book*, Oxford, Reed Educational and Professional Publishing Ltd.
- Brown, S. (2008) Frame Materials for the Touring Cyclist, www.sheldonbrown.com/frame-materials.html aluminium
- Buchanan, I. (2003) An Overview of Material Applications in Bicycle Frames, www.fitwerx.com/an-overview-of-material-applications-in-bicycle-frames
- Buettner, D. (1996) Coated golf club and apparatus and method for the manufacture thereof. US Patent.
- Cochran, A. J. and Stobbs, J. (2005) *Search for the Perfect Swing*, Chicago, Triumph Books.
- Destefani, J. D. (1990) Introduction to Titanium and Titanium Alloys. In *ASM Handbook*, ASM International.
- Easton Sports, *Materials: Aluminium alloys*, Technical Report. www.eastonbike.com
- Ernst, P. and Barbezat, G. (2008) Thermal spray applications in powertrain contribute to the saving of energy and material resources. *Surface and Coatings Technology*, 202, 4428–4431.
- Eylon, D., Newman, J. R. and Thorne, J. K. (1990) Titanium and Titanium Alloy Castings. In ASM (Ed.) *ASM Handbook*. Vol 2, ASM International.
- Foxall, G. R. and Johnston, B. R. (1991) Innovation in Grand Prix motor racing: The evolution of technology, organization and strategy. *Technovation*, 11, 387–402.
- Friedrich, H. E. and Mordike, B. (2006) *Magnesium – Technology, Metallurgy, Design, Data, Applications*, Springer, Berlin, Heidelberg, New York.
- Froes, F. H. (1999) Will the titanium golf club be tomorrow's mashy niblick? *Journal of the Minerals, Metals & Materials Society*, June.
- Gebauer, K. (2006) Performance, tolerance and cost of TiAl passenger car valves. *Intermetallics*, 14, 355–360.
- Gossner, J. P. and Tator, K. B. (1994) Painting. In ASM (Ed.) *ASM Handbook*. Vol 5, ASM International.
- Grube, W. L. (1991) *Plasma (Ion) Carburizing*, Vol 4, ASM International.
- Hanson, B. H. (1986) Present and future uses of titanium in engineering. *Materials & Design*, 7, 301–307.
- Hauert, R. (2004) An overview on the tribological behavior of diamond-like carbon in technical and medical applications. *Tribology International*, 37, 991–1003.
- Housh, S. and Micucki, B. (1990) Selection and Application of Magnesium and Magnesium Alloys. In *ASM Handbook*, ASM International.
- Jenkins, M. (2003) *Materials in Sports Equipment*, CRC Boca Raton, Woodhead Publishing Limited, Cambridge, UK.
- Kearney, A. L. (1990) Properties of Cast Aluminum Alloys. In *ASM Handbook*. Vol 2, ASM International.
- Keronite, Ltd (2004) Keronite technology enables production of super lightweight magnesium bicycle frames, www.keronite.com/press_releases.asp
- Kleiner, M., Geiger, M. and Klaus, A. (2003) Manufacturing of Lightweight Components by Metal Forming. *CIRP Annals – Manufacturing Technology*, 52, 521–542.
- L'automobile, F. I. D. (2005) *2008 Formula One Technical Regulations*.
- Lin, F. S., Pai, Y. L. and Sung, C.-M. (2002) Diamond-like carbon coated golf club head United States. Pat. 2002004426 www.freepatentsonline.com/553144.html
- Lütjering, G. and Williams, J. C. (2007) *Titanium*, Springer, Berlin, Heidelberg, New York.
- Maberry, S. (2000) Commercial diving operations in construction. *Journal of Construction Engineering and Management*, 126, 433–439.

- Reilly, T. and Lees, A. (1984) Exercise and sports equipment: Some ergonomic aspects. *Applied Ergonomics*, 15, 259–279.
- Rooy, E. L. (1990) Introduction to Aluminum and Aluminum Alloys. In ASM (Ed.) *ASM Handbook*. Vol 2, ASM International.
- Stevenson, M. F. (1994) Anodizing. In ASM (Ed.) *ASM Handbook*. Vol 5, ASM International.
- Taylor, C. M. (1998) Automobile engine tribology—design considerations for efficiency and durability. *Wear*, 221, 1–8.
- Tyrkiel, E. and Dearnley, P. A. (1995) *A Guide to Surface Engineering Terminology*, London, The Institute of Materials.
- Yamada, M. (1996) An overview on the development of titanium alloys for non-aerospace applications in Japan. *Materials Science and Engineering: A*, 213, 8–15.
- Zhecheva, A., Sha, W., Malinov, S. and Long, A. (2005) Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods. *Surface and Coatings Technology*, 200, 2192–2207.

Surface engineered titanium alloys for biomedical devices

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Abstract: Titanium and its alloys are the most important metallic biomaterials due to their good biocompatibility and mechanical properties. However, they are still not ideal materials to meet the needs of clinical application. In order to develop advanced medical devices, many efforts have been made to modify their surface properties. In this chapter, the state of the art of surface modification of titanium-based biomaterials for cardiovascular, orthopedic and dental implants is reviewed.

Key words: titanium-based biomaterials, surface engineering, biocompatibility, cardiovascular implants, orthopedic implants, dental implants.

17.1 Introduction

Implantable biomedical devices and prostheses have become very widely used in clinical application for replacing human organs or tissues that have suffered from disease, so as to recover some of their functionality. These devices have become a very important means for patient life preservation and have led to a new industry, comparable to the medical drug industry.

Among materials that are used for biomedical devices or prostheses, metallic biomaterials constitute one important category for prostheses bearing mechanical loads, such as hip joints, bone substitutes, dental implants, artificial hearts and ventricular pumps and stents. Metallic materials currently used for surgical implants include 316L stainless steel (316L SS), cobalt chromium (Co-Cr) alloys, titanium and its alloys, and some noble metals. Table 17.1

Table 17.1 Mechanical properties of metallic biomaterials and cortical bone (Shi, 2006)

Material	Density (g/cm ³)	Young's modulus (GPa)	Yield strength (MPa)	Fatigue strength (MPa)
Cortical bone	~2.0	7–30	70–150	
Cobalt-chrome alloy	~8.5	230	655–1896	207–950
316L stainless steel	8.0	200	586–1351	241–820
Ti and its alloys	4.51	55–110	485–1107	300–620
TiNi	6.7	60		

(Shi, 2005) shows the properties of several metals used for biomedical implants, as well as cortical bone for comparison.

Table 17.1 shows that 316L SS and Cr-Co alloys have a much higher modulus than bone, which can lead to stress shielding (i.e. insufficient stress transfer to the bone), bone resorption and premature loosening of the implant. In addition, although stainless steel and Cr-Co alloys have been successfully applied clinically for many years and, in most cases, these alloys possess adequate corrosion resistance, nevertheless there have been some cases reported in which toxic effects occur due to the release from the prosthetic implants of Ni, Co and Cr, present in 316L SS and Cr-Co alloys (Wapner, 1991). Skin-related diseases, such as dermatitis due to Ni toxicity, have been reported and numerous animal studies have shown carcinogenicity due to the presence of Co (McGregor *et al.*, 2000). Crevice corrosion is encountered beneath the heads of fixing screws made of 316L stainless steel, and mechanically-assisted crevice corrosion of modular total hip arthroplasty components has been associated with elevated levels in serum of cobalt and urine chromium (Jones *et al.*, 2000). Pitting corrosion of cobalt-based alloys leads to the release of carcinogens into the body (Clerc *et al.*, 1997; Blackwood, 2003).

Compared to 316L SS and Cr-Co alloys, titanium-based materials possess outstanding mechanical and chemical characteristics, such as high specific strength, low Young's modulus and good corrosion resistance. The lower modulus of Ti alloys varies from 110 GPa to 55 GPa compared to 210 GPa for 316 L stainless steel and 230 GPa for chromium cobalt alloys. The strength of titanium alloys is very close to that of 316 L SS, and its density is 55% less than that of steel, hence, when compared by specific strength (strength-to-density ratio), the titanium alloys outperform any other implant materials. The corrosion resistance of titanium-based biomaterials is better than that of stainless steel and Cr-Co alloys; Ti and its alloys show good corrosion resistance, complete inertness to the body environment, enhanced biocompatibility, and a high capacity to join with bone and other tissues (Niinomi, 2001) in long-term implant application such as hip joints and dental implants. Based on these advantages, Ti and its alloys have become the most widely applied biomaterials among all metals.

However, titanium alloys tend to undergo severe wear when in motion against themselves or with other metals (Miller and Holladay, 1958). These alloys, which have a high coefficient of friction, can lead to the formation of wear debris that results in inflammatory reaction, causing pain and loosening of implants due to osteolysis (Liang *et al.*, 1967). Furthermore, although the Ti alloys (mainly Ti-6Al-4V(Ti64)) have an excellent reputation for corrosion resistance and biocompatibility, long-term performance of these alloys has raised some concerns due to the release of aluminum and vanadium from Ti64 alloy. Both Al and V ions are found to be associated with long-term health problems, such as Alzheimer's disease, neuropathy and osteomalacia

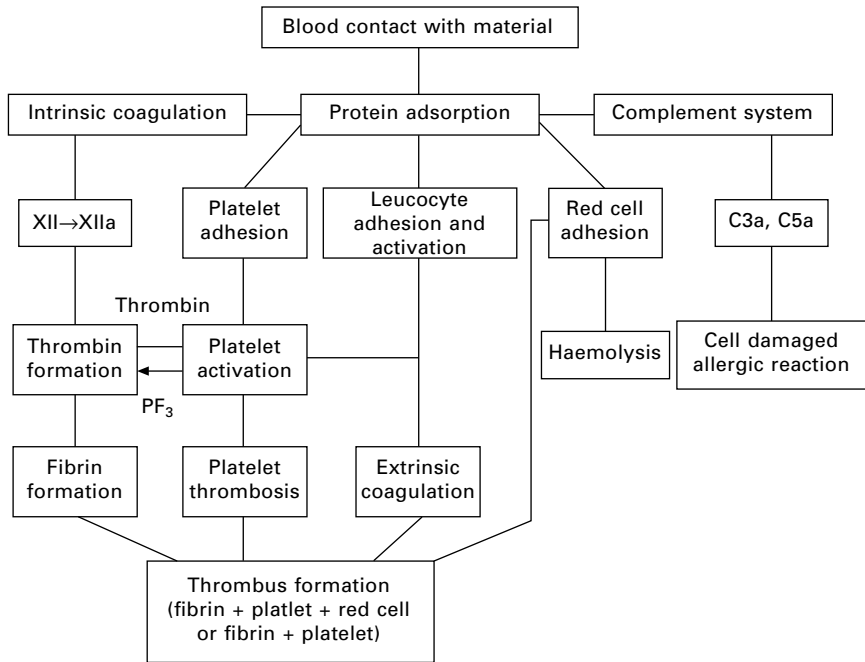
(Nag *et al.*, 2005). In addition, vanadium is toxic both in the elemental state and in the oxide form, V_2O_5 , which are present at the surface (Wapner, 1991; Eisenbarth *et al.*, 2004). Newly developed Ti alloys such as Ti-7Al-6Nb and Ti-13Nb-13Zr without Al and V and with decreased Young's modulus, show more advantages for biomedical applications (Shi, 2005).

The biocompatibility of titanium and its alloys is thought to come from the nature of the inert surface of the TiO_2 layer which exists on Ti and Ti alloys, with a thickness of 5–20 nm, which prevents metal ion release from the matrix into the human body and thus improve their biocompatibility to tissues and blood. However, this surface layer is too thin to be adequate under biological conditions. Therefore, huge efforts have been made in improving their biocompatibility and the surface mechanical properties by improving their surface characteristics. In this chapter, the surface modification of Ti based biomaterials is reviewed.

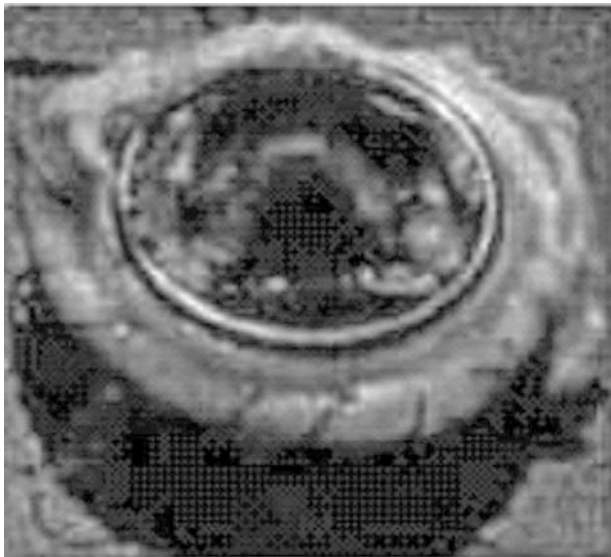
17.2 Surface engineering of titanium (Ti) and its alloys for cardiovascular devices

Titanium and Ti alloys have been used to fabricate artificial heart valves, ventricular pumps, artificial hearts, peripheral vascular stents, and more, for implants for long-term application. Because these devices come into contact with blood, blood-compatibility is the key property for these implants. The interaction of blood with a material surface is a complicated process. When an artificial device is implanted into an acceptant body and contacts the blood environment, there is an immediate interaction between the material and blood. It is general agreed that the first step of the interaction is protein adsorption on the material surface, followed by activation of platelets, coagulation factors, complement and leukocytes, and consequent thrombus formation or haemolysis, which leads to failure of the implant. Among the consequences of failure, that with the highest frequency is thrombus formation on the implant surface, as shown in Fig. 17.1. Figure 17.2 shows an image of a failed artificial heart valve on which thrombus has formed and has led to loss of leaflet opening and closing function.

The kind, quantity, and conformation of proteins adsorbed on the surface are thought to be critical factors affecting the interaction between blood and biomaterial. If fibrinogen or globulin is adsorbed on the surface and denatured, it will further activate clotting factors and/or platelets, and initiate clotting cascade processes to form thrombus. If albumin is adsorbed on the material and if the adsorbed protein can maintain conformation, the coagulation process can be stopped. Therefore, many different kinds of surface modification techniques have been aimed at modifying the surface characteristics of the material so as to modulate the adsorption behavior of proteins on the surface.



17.1 Schematic showing material-induced blood reaction processes (Khor *et al.*, 1999).



17.2 A failed artificial heart valve with thrombus formed on the valve surface.

17.2.1 Surface coating with inorganic thin films

Titanium oxide films

It has been reported that the blood compatibility of titanium surfaces is not yet sufficient to fully prevent the tendency to thrombogenicity (Hong *et al.*, 1999). Thus many different kinds of thin films have been considered as coating materials to modify the surface of titanium-based alloys. Among these, titanium oxide films and carbon-based films have been most widely investigated.

Some early investigations of the interaction of a titanium oxide surface with blood proteins were carried out by Sunny and Sharma (1991). By means of anodic oxidation processes, titanium oxide surface layers were prepared with different layer thicknesses, from several nanometers (the natural surface state of titanium) up to about 200 nm, and the relationship between the thickness of the titanium oxide layer and the adsorption rate of plasma proteins albumin/fibrinogen on the oxide layer surface was investigated. It was found that when increasing the thickness of the titanium oxide layer, the adsorption rate of albumin/fibrinogen increased by up to seven times compared with untreated titanium.

Huang *et al.* (1994) studied the relationship between clotting time and the thickness of an oxide layer prepared by heat treatment. It was found that increasing the thickness of the oxide layer led to a clotting time increase, for example by a factor of 1.5 when the thickness of the titanium oxide film was increased from 10 to 250 nm.

Takemoto *et al.* (2004) investigated the correlation between titanium oxide layers on oxidized titanium substrates and platelet adhesion. They prepared oxide layers on Ti substrates using three different oxidation methods: treatment in hydrogen peroxide solution (H_2O_2), heating in air at moderate temperatures, and processing with both H_2O_2 and heating in air. They found that the composition and thickness of the oxide layer influenced platelet adhesion. Thick titanium oxide layers, formed on Ti substrates by heating, displayed less platelet adhesion than thin oxide layers on untreated Ti substrates. The largest number of adhesive platelets was found on H_2O_2 -oxidized substrates. They concluded that Ti substrates with H_2O_2 and heat treatment above 300°C are the most inhibitory for platelet adhesion.

Huang *et al.* (2004) have investigated the relationship between the structural characteristics of titanium oxide films and blood compatibility behavior. It was shown that crystallization, doping, and non-stoichiometry of Ti-O films can improve the blood compatibility of Ti-O films significantly. They synthesized their films by plasma immersion ion implantation and deposition process (PIID). Table 17.2 shows the structure and composition of the films, the behavior of platelet adhesion, and the electrical resistivity of the films.

Table 17.2 PIIID parameters, film structure, behavior of platelet adhesion, and electrical resistivity of the films

Sample	Pressure of O ₂ (Pa)	Structure	Composition	Platelet adhesion		Resistivity ρ ($\Omega \cdot \text{cm}$)
				Number/ 2500 μm^2	Deformed (pseudopodium/ aggregation) %	
A	4.5E-3	Amorphous	TiO _{1.3}	110 $\pm$ 22	98/95	2.96×10^{-4}
B	2.6E-2	Amorphous + crystalline	TiO _{1.7}	44 $\pm$ 14	68/25	9.62×10^{-3}
C	4.0E-2	Rutile	TiO _{1.9}	15 $\pm$ 11	12/20	6.76×10^{-1}
D	10E-2	Rutile	TiO ₂	36 $\pm$ 10	47/21	$>10^4$

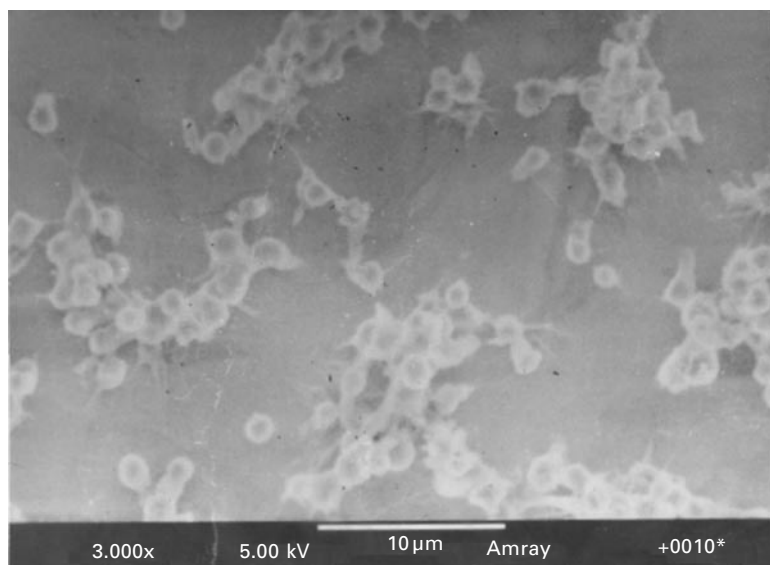
Figure 17.3 shows the platelet adhesion state on titanium oxide films with different compositions as given in Table 17.2.

As demonstrated in Fig. 17.3, the adhesion state of platelets is improved with increasing oxygen content in the film. However, as the Ti–O film becomes stoichiometric TiO₂, platelet adhesion worsens (Fig. 17.3c). Other work investigating the effect of film structure on blood compatibility also revealed that platelet adhesion on a rutile Ti–O film surface is superior to that on amorphous Ti–O films which have about the same composition as rutile (Huang *et al.*, 2003). N-type semiconducting non-stoichiometric TiO_{2–x} with a rutile structure was the most effective in the suppression of platelet adhesion.

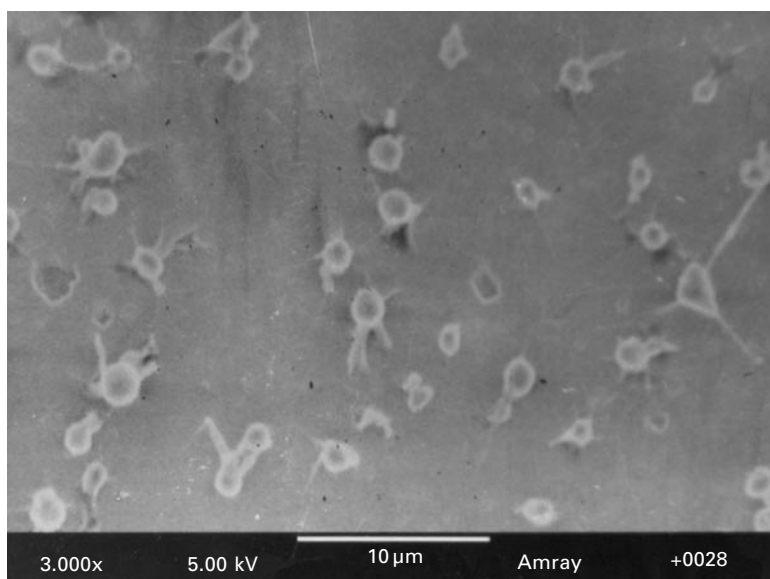
In vivo test results have further shown the excellent blood compatibility of n-type Ti–O films (Huang *et al.*, 2003). *In vivo* tests after 17 to 90 days display almost no coagulation on Ti samples with a Ti–O film surface, while thrombus formation is found on LTIC samples, as shown in Figures 17.4 to 17.6.

Twenty weeks *in vivo* test results on coronary stents showed that with untreated stents, thrombi form and lead to a constriction at the stent position. A thin layer of endothelial cells is formed on the surface of Ti–O film coated stents, but no thrombus is found. These results confirm further that Ti–O films have excellent blood compatibility, which should have good potential for clinical applications (Huang *et al.*, 2006).

A titanium oxide surface layer has also been applied for ventricular pumps. Davidson *et al.* (1996) used titanium-niobium-zirconium (Ti–Nb–Zr) alloys as ventricular pump material. The Ti alloy was fabricated in complex shapes as required for the pump components, and the surfaces were oxidized to form a hard, wear-resistant, low-friction ceramic surface layer. The combined benefits of this stable, wear-resistant, low-friction ceramic surface layer together with the toughness, strength, formability, and thermal conductivity of the metal provided improvements in the design and performance of blood pumps and peripheral grafts and percutaneous (power) components of the pump.

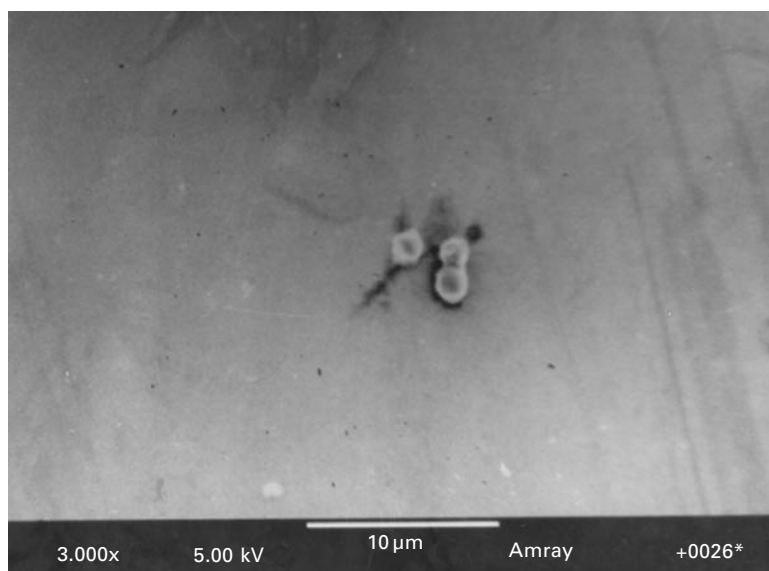


(a)

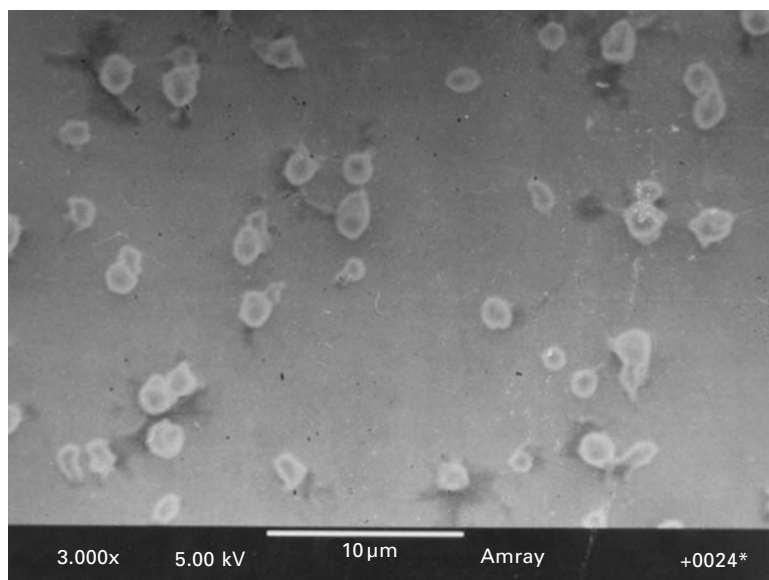


(b)

17.3 Morphology of platelets on Ti-O films: (a) amorphous Ti-O film, with composition $\text{TiO}_{1.3}$; (b) Amorphous + crystalline Ti-O films with composition $\text{TiO}_{1.7}$; (c) Rutile Ti-O films with composition $\text{TiO}_{1.9}$; (d) Rutile TiO_2 films. Incubation time: 90 min.



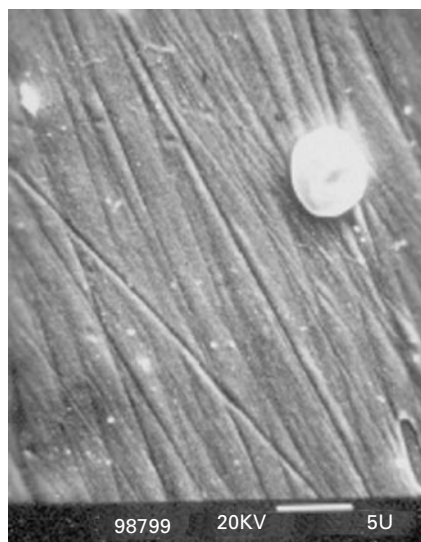
(c)



(d)

17.3 Continued

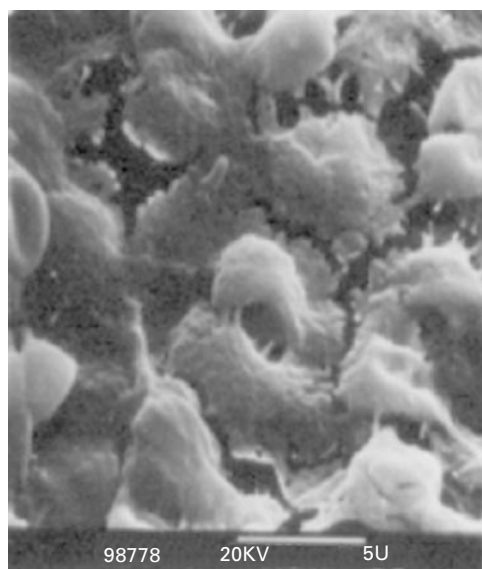
NiTi shape memory alloy is a very important Ti alloy that is used for biomedical devices because of its memory effect and superelasticity properties. This alloy has been applied for peripheral vascular stents. However, release of the toxic element Ni into the body has raised concerns for some



(a)



(b)



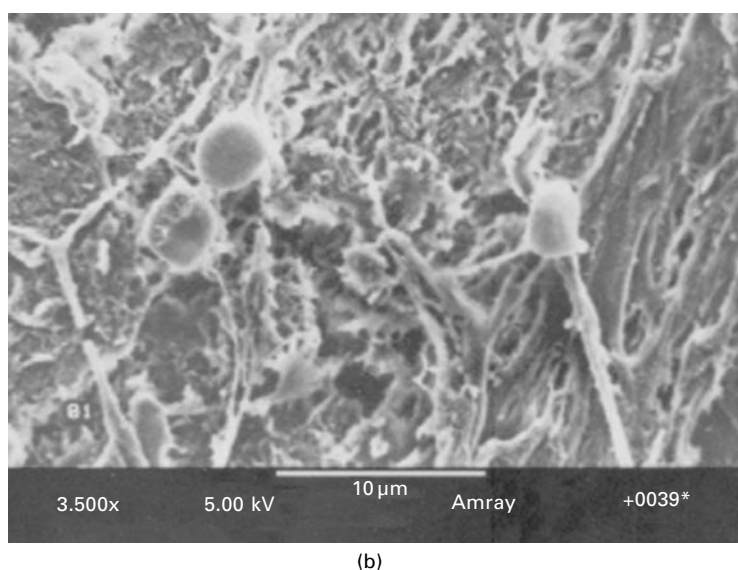
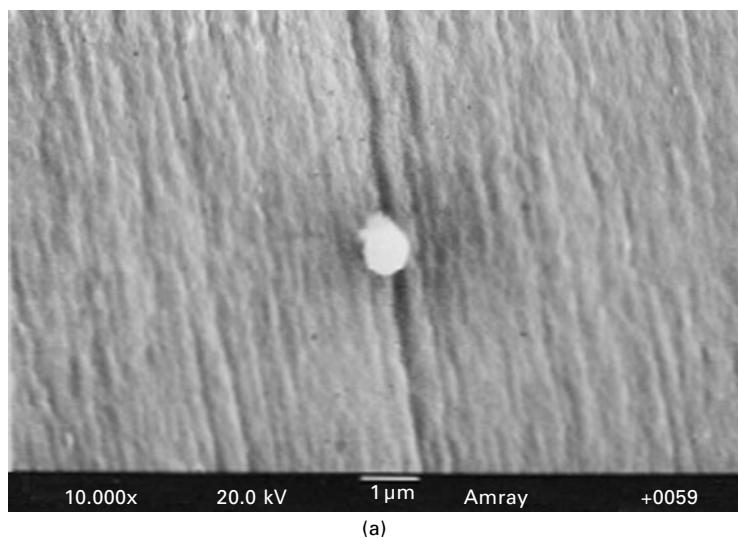
(c)

17.4 SEM micrographs of materials after 17 days' implantation:
(a) Ti-O film; (b) and (c) LTIC.

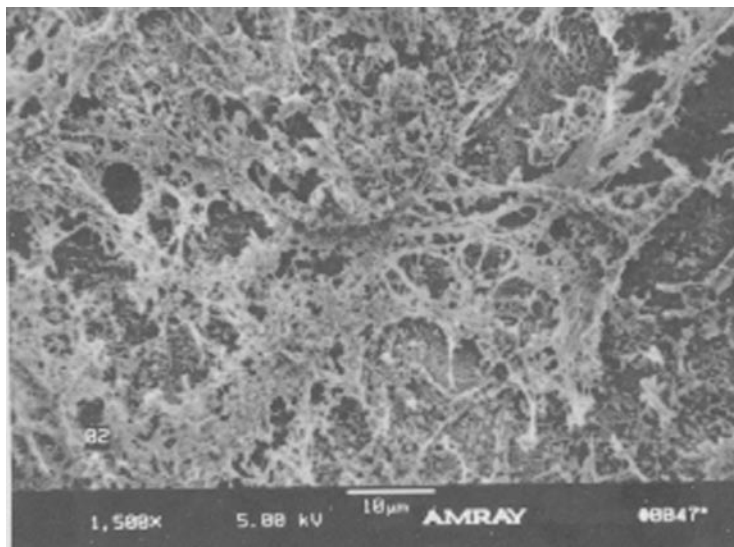
researchers. Firstov *et al.* (2002) treated NiTi alloy in air in the temperature range 300–800°C. They found that NiTi alloy exhibited different oxidation behavior at temperatures below and above 500°C. A Ni-free zone was found in the oxide layer formed at 500°C and 600°C. Oxidation at 500°C produced

a smooth protective nickel-free oxide layer with a relatively small amount of Ni at the air/oxide interface, which is favorable for good biocompatibility of NiTi implants.

Chu *et al.* (2007) used Fenton's oxidation, in which H_2O_2 is catalytically decomposed by ferrous irons into hydroxyl radicals ($\cdot\text{OH}$), to modify the



17.5 SEM micrographs of materials after 30 days' implantation: (a) Ti-O film; (b) and (c) LTIC.



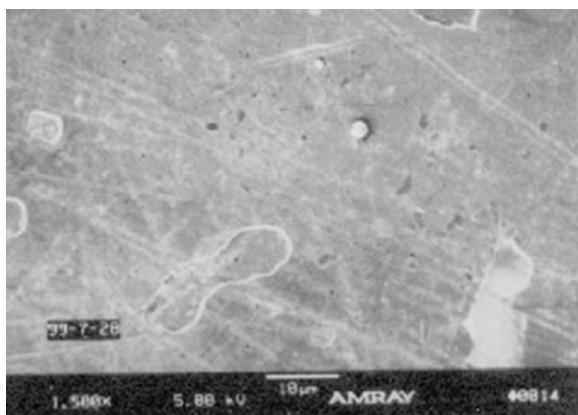
(c)

17.5 Continued

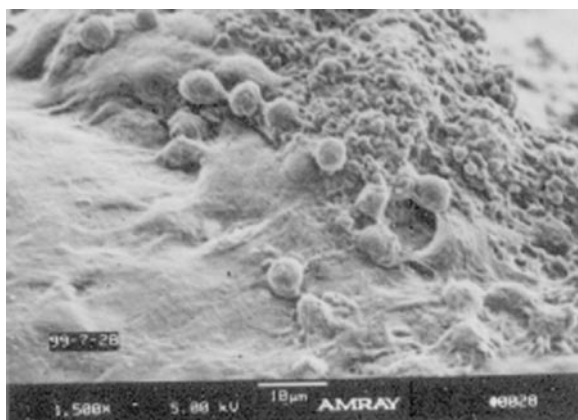
surface of biomedical NiTi shape memory alloy (SMA). They showed that Fenton's oxidation produces a novel nanostructured titania gel film with a graded structure on the NiTi substrate, without an intermediate Ni-rich layer that is typical for high-temperature oxidation. Moreover, there is a clear Ni-free zone near the top surface of the titania film. The treatment improved the electrochemical corrosion resistance and mitigated Ni release. Blood platelet adhesion was remarkably reduced after Fenton's oxidation.

Plant *et al.* (2005) investigated the effect of oxide treatment temperature on the surface Ni ion content and the toxicity to human umbilical vein endothelial cells (HUVEC). They found that when oxidation occurred after mechanical polishing or post polishing heat treatments at 300°C and 400°C in air, a significant amount of metallic nickel or nickel oxide (10.5 and 18.5 at%) remained on the surface. Exposure of HUVECs to these surfaces resulted in increased oxidative stress within the cells, loss of VE-cadherin and F-actin, and significantly increased paracellular permeability. However, if the TiNi alloy was heat treated at 600°C, these pathological phenomena were not found. At this temperature, thickening of the TiO₂ layer occurs due to diffusion of titanium ions from the bulk of the alloy, displacing nickel ions to sub-surface regions, resulting in a significant reduction in nickel ions detectable on the sample surface (4.8 at%).

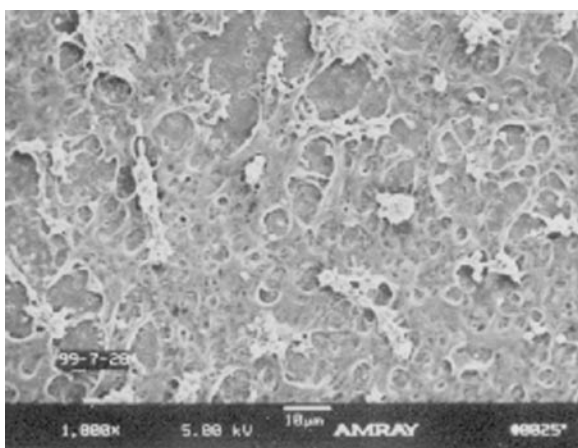
Maitz and Shevchenko *et al.* (2006), by means of PIII, used oxygen and helium to form a titanium oxide layer in a NiTi surface, and investigated the effect on blood compatibility of this surface and its suitability for vascular



(a)



(b)



(c)

17.6 SEM micrographs of materials after 90 days' implantation:
(a) Ti-O film; (b) and (c) LTIC.

stents. It was found that a nickel-lean titanium-oxide surface with a nanoporous structure was formed after helium PIII treatment. The oxygen-ion-implanted NiTi surface adsorbed less fibrinogen on its surface and activated the contact system less than the untreated NiTi surface, but conformation changes of fibrinogen were higher for the oxygen-implanted NiTi. No difference between initial and oxygen-implanted NiTi was found for platelet adherence, endothelial cell activity, or cytokine release. The nanoporous, helium-implanted NiTi behaved worse than the initial unimplanted surface in most aspects. This suggests that oxygen-ion implantation is a useful method for decreasing the nickel concentration in the surface of NiTi for cardiovascular applications.

Carbon-based films

Carbon-based films include diamond films, diamond-like carbon films (DLC, further divided as hydrogenated DLC films (a-C:H) and non-hydrogenated DLC films (a-C)), pyrolytic carbon films, and graphite films. Their differences originate from the structure and carbon bonding state. Diamond films have a face-centered cubic (FCC) lattice crystal structure and contain 100% sp^3 bonds; diamond is the hardest material known to man. Diamond-like carbon films have an amorphous structure and contain hybrid bonds, both sp^3 and sp^2 ; its hardness can vary from near that of diamond to near that of graphite. Pyrolytic carbon has a nano-amorphous structure and is sp^2 bonded. Graphite has a hexagonal crystal structure with sp^2 bonding. Among the four kinds of carbon films, diamond, diamond-like carbon and pyrolytic carbon films have been used in the biomaterial field, while graphite is too soft and brittle to be used for implants.

The most significant property of all carbon-based films for cardiovascular biomaterials is high chemical inertness, with an associated low level of interaction between material surfaces and blood. The high hardness and excellent wear resistance are also beneficial for the blood contacting devices, which may experience mechanical loads in applications such as artificial heart valves and ventricular pumps. However, the advanced mechanical characteristics of carbon-based films are more important benefits for orthopedic implants that experience the heavy load of the human body, such as for hip joints, which will be discussed in Section 17.3.1.

Artificial heart valves have been widely applied clinically for about a half century. The most commonly used kind of valve is a bileaflet valve made of pyrolytic carbon. In another design, the valve housing is made of Ti-6Al-4V titanium alloy coated with a pyrolytic carbon (made by the Italian company Sorin Biomedica). The pyrolytic carbon film enhances the blood compatibility of the valve housing and the titanium alloy matrix brings the advantage of enhanced stiffness (Arru *et al.*, 1996). Recently Jozwik and Karczemska (2007) coated an artificial heart valve ring made of Ti6Al4V titanium alloy

with a nanocrystalline diamond (NCD) film using a radio-frequency plasma-activated chemical vapor deposition (RF PACVD) technique. This heart valve, with a NCD coating and a Derlin disk, was tested for long-term mechanical fatigue. The surface morphology of the local contact and movement area of the ring were investigated by scanning electron microscopy (SEM) and Raman spectroscopy before and after fatigue testing to about 7×10^8 cycles, which can be estimated as about 17.5 years of valve operation in the human body. The results revealed that the surface after the experiments remained in good condition, still tight, and the NCD layer thickness was the same as before testing. The Raman spectra indicated that the NCD coating still covered the entire surface of the ring.

Among carbon-based thin films, diamond-like carbon (DLC) has been widely investigated for biomaterial applications. An early study of the blood compatibility of DLC films was performed by Dion *et al.* (1993). The haemocompatibility was studied in terms of protein adsorption and platelet retention on DLC-coated Ti-6Al-4V titanium alloy. These researchers reported that the static protein adsorption of albumin was 237% compared to the results obtained with a silicone elastomer; while the quantity of fibrinogen adsorbed on the DLC surface was slightly greater than that adsorbed on the silicone surface. Platelets adhered about twice as much as they did on the reference surface. They concluded that DLC possesses good haemocompatibility.

Up to now, many attempts have been made to understand the effects of material factors of DLC films on blood compatibility. Huang *et al.* (2004) found that the relationship between DLC film characteristics and blood compatibility is very complicated. Their work, and that of many other researchers, shows that it is possible to modify the blood compatibility of DLC films by changing the DLC bonding state, elemental doping of the film, and other factors. Huang synthesized hydrogenated DLC films using acetylene gas PIID. In his investigation, a DLC film prepared at a low bias voltage, such as -75 V, showed low platelet adhesion and activation, similar to low temperature isotropic pyrolytic carbon (LTIC) and better than stainless steel. When prepared at a high bias, such as -900 V, the platelet adhesion and activation properties of the DLC film are not good. It seems that a higher sp^3/sp^2 bonding ratio may contribute to the blood compatibility of DLC. They suggested that the suppression of the contact activation path of the clotting process and reduction of the activation of platelets accounted for the better haemocompatibility of the a-C:H films.

Some attempts were made to investigate the influence on haemocompatibility of the sp^3 and sp^2 hybrid bond fraction in the films. It was observed that for magnetron sputtered a-C films, the haemocompatibility improved with increasing sp^3 fraction (Logothetidis *et al.*, 2005). However for a-C:H films deposited by PIID, the blood compatibility was enhanced at higher sp^2/sp^3 ratios (Chen *et al.*, 2002), and on investigating the haemocompatibility

of pulsed vacuum arc deposited ta-C films, it was also found that the haemocompatibility tended to improve with increasing sp^2/sp^3 (Leng *et al.*, 2003).

Logothetidis *et al.* (2005) compared the haemocompatibility of magnetron sputtered a-C, a-C:H, and tetrahedral amorphous carbon (ta-C) films. Spectroscopic ellipsometric studies were done in the energy range from 1.5 to 6.5 eV and albumin/fibrinogen ratios were derived from the analysis of ellipsometric data. For the a-C:H films, the albumin/fibrinogen ratio was higher for films deposited at higher hydrogen atomic percent in the plasma and positive substrate bias. It has also been observed that the albumin/fibrinogen ratio was higher for lower refractive index of the carbon films. These results imply that films with greater polymeric component exhibit better haemocompatibility.

Elemental doping is also a hot point for researchers as a possible route to the improvement of the blood compatibility of DLC coatings. Kwok *et al.* (2005) investigated the blood compatibility of P-doped a-C:H films deposited by PIII. They obtained a water contact angle of 16.98° for their films and observed that the coatings minimized the interaction with plasma proteins. This gives rise to preferential adsorption of albumin, which is a prerequisite for good haemocompatibility.

Si doping of either a-C or a-C:H films seems to have a positive effect on blood compatibility. Ong *et al.* (2007) synthesized unhydrogenated a-C films with different silicon concentrations by magnetron sputtering, and analyzed the corresponding evolution of the surface energy and compatibility with blood. They pointed out that the incorporation of silicon not only decreased the sp^2 -hybridized carbon bonding fraction, but the static evaluation of films incubated in human platelet-rich plasma also showed a decrease in platelet adhesion. They conclude that bonding structure and surface energy of Si doping are factors contributing to the improved haemocompatibility.

Hasebe *et al.* (2006) synthesized fluorinated DLC (F-DLC) coatings for creating a more hydrophobic surface with improved antithrombogenicity. The *in vitro* whole blood model confirmed that platelet loss was lower in a F-DLC group than in the noncoated group (316L), which suggests adhesion of a smaller number of platelets to F-DLC-coated materials. Furthermore, the biomarkers of mechanically induced platelet activation (beta-thromboglobulin) and activated coagulation (thrombin-antithrombin-three complex) were markedly reduced in the F-DLC-coated group. *In vivo* rat implant model studies revealed no excessive local or systemic inflammatory responses in the F-DLC group. The thickness of the fibrous tissue capsule surrounding the F-DLC-coated disk was almost equal to that of the noncoated 316L disk.

Some negative effects of elemental doping of DLC on blood compatibility have also been reported. Andara *et al.* (2006) investigated the haemocompatibility of DLC–silver composite and DLC–titanium composite thin films prepared

using a pulsed laser deposition process with multicomponent target. They observed that dense fibrin networks with densely aggregated platelets were formed on the surfaces of DLC–silver and DLC–titanium films after being exposed to platelet–rich plasma. However no fibrin networks were found on unalloyed DLC films. This implies that silver and titanium doping of DLC decreases the anticoagulation ability of the film. However, all the results about the relationship of material factors and blood compatibility are not completely consistent. It appears that these parameters are not the only factors in governing haemocompatibility.

DLC films have been applied to cardiovascular devices. Jones *et al.* (2000) prepared TiN/TiC/DLC multilayer films on titanium substrates for use as coatings for heart valve prostheses, using Ti/TiN/TiC with gradually changing compositions to enhance the adhesion strength of DLC to the Ti matrix. These coatings proved to have good blood compatibility.

DLC-coated heart valves and stents are already commercially available or at a commercial development stage. The Cardio Carbon Company offers DLC coated titanium implants (‘Angelini Laminaflo’ mechanical heart valves and ‘Angelini Valvuloplasty’ rings) (Roy and Lee, 2007).

Salahas *et al.* (2007) evaluated the safety and clinically defined efficacy of the implantation of DLC coated stents in a group of patients who underwent percutaneous transluminal coronary revascularization procedures in two haemodynamic centers. Into 196 patients they implanted 245 stents. Implantation of intracoronary bare metal stents coated with DLC was associated with a high success rate, safety, and efficacy, both in the hospital and at the six-month follow-up after the interventional procedure.

However, Meireles *et al.* (2007) compared re-stenosis and major cardiac event rates for 180 patients at one and six months after DLC-coated stent implantation with those for uncoated stents. They concluded that DLC coated stents did not yield better outcomes in relation to uncoated stents.

This inconsistency may be due to the state of the DLC films on the stent surface. If the film does not remain stable during stent expansion, the film will delaminate from local regions where plastic deformation occurs, and the exposed matrix may be worse for stimulating the coagulation reaction and release of toxic elements from the matrix such as Ni and Cr. Attention to minimizing cracking, spallation and fracture of the DLC coating during stent expansion has been paid. Some attempts were made to incorporate certain elements in DLC and to use an interlayer to prevent spallation and cracking of the coating by the high tensile forces of stent expansion (Choi *et al.*, 2006; Maguire *et al.*, 2005).

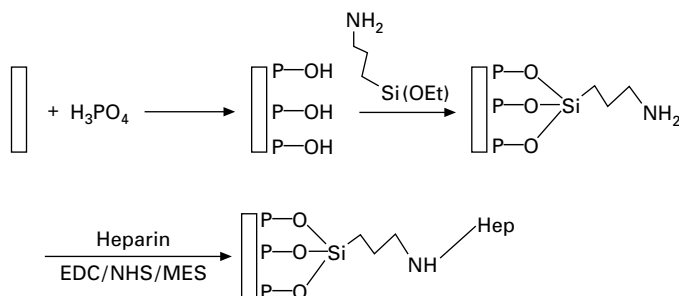
The use of DLC films for improving the properties of ventricular pumps is also of research interest. Yamazaki *et al.* (1998, 2002) developed a compact centrifugal blood pump system called ‘EVAHEART’ as an implantable left ventricular assist device for long-term circulatory support. The pump

is made from pure titanium, and the entire blood-contacting surface is covered with DLC or 2-methacryloyloxyethyl phosphorylcholine (MPC) to improve blood compatibility. They evaluated the pump in long-term *in vivo* experiments using seven calves. They concluded that no thrombi formed on blood contacting surfaces, for both DLC and MPC coatings. In all calves, the pumps demonstrated trouble-free continuous function for over six months (200 days and 222 days).

Other kinds of films have been investigated for application to blood contacting material surfaces, such as TiN (Karagkiozaki *et al.*, 2009), Al_2O_3 (Fischer *et al.*, 2007), ZrO_2 (Filiaggi *et al.*, 1996), TaO (Yang *et al.*, 2007), Si-N (Wan *et al.*, 2007), but much less work has been done compared with titanium oxide films and carbon-based films. Up to now, few of the publications in the field of hard coatings for blood contacting biomaterials have dealt with the mechanism of the film–blood compatibility. Due to lack of knowledge of the interaction process between the films and blood, it is not clear how to adjust the characteristics of the films so as to modify the blood compatibility. This is the critical problem that limits the use of hard coatings for cardiovascular materials.

17.2.2 Surface immobilization of functional molecules

Some functional molecules have been used widely for polymer surface modification to improve blood compatibility, such as poly(ethylene glycol) (PEG), heparin, hirudin, and albumin, because it is easier to form functional groups such as hydroxyls, carboxyls, and aminos on a polymer surface for functional molecular immobilization, whereas few such groups form on metal surfaces. Surface activation treatments have been developed; Weng *et al.* (2007) have studied the use of phosphoric acid chemisorption on TiO_2 films to increase hydroxyl groups and found that phosphoric acid is facile for anchoring on anatase TiO_2 films. As can be seen in Fig. 17.7, the immobilization was accomplished first by chemical adsorption of phosphoric acid and second



17.7 Schematic of the biomolecular immobilization process.

by bonding with APTES (3-aminopropyl triethoxysilane) by increased hydroxyl groups. APTES amino groups allow further chemical bonding of heparin with carboxyl groups. Usually, N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) is used as a catalyzer in the reaction of amino groups and carboxyl groups since it has a less negative effect on biocompatibility compared with glutaraldehyde. In order to minimize the hydrolysis of EDC, heparin was immobilized using EDC, N-hydroxysuccinimide (NHS) in a 2-morpholinoethane sulfonic acid (MES) systems. Figure 17.8 shows the platelet adhesion state on (a) anatase TiO₂ film, (b) heparinylated anatase Ti-O film via directly silanization; and (c) heparinylated anatase Ti-O film via chemisorption of H₃PO₄ and then silanization. It is clear that immobilized heparin inhibits platelet adhesion and aggregation.

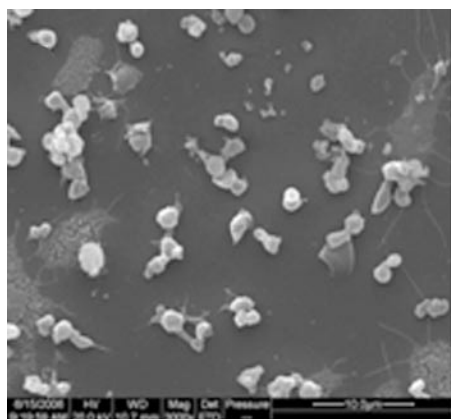
Weng *et al.* (2008) carried out further work using photochemistry to immobilize bovine serum albumin (BSA) on a titanium oxide surface. They first modified Ti-O thin films by 3-aminopropylphosphonic acid (APP) assembling, and simultaneously azido groups were introduced into BSA to act as photo-reactive points. Covalent coupling of BSA was realized by UV irradiation. Platelet experiments with both qualitative and quantitative analysis revealed that BSA immobilized surface was effective in inhibiting platelet adhesion *in vitro*. *In vivo* studies also confirmed good haemocompatibility of a BSA immobilized surface after 90 days implantation.

Grafting of PEG is another effective method to modify the polymer surface, and polyethylene glycol (PEG) is usually grafted onto polymer surfaces to resist protein and platelet adhesion (Amiji and Park, 1993). Recently Tanaka *et al.* (2009) have investigated electrodeposition of PEG on titanium to enhance blood compatibility. They found that the U-shaped PEG molecule immobilized with electrodeposition inhibited platelet adhesion and aggregation. The immobilization of PEG on the Ti surface was strongly associated with a biofunction such as platelet adhesion.

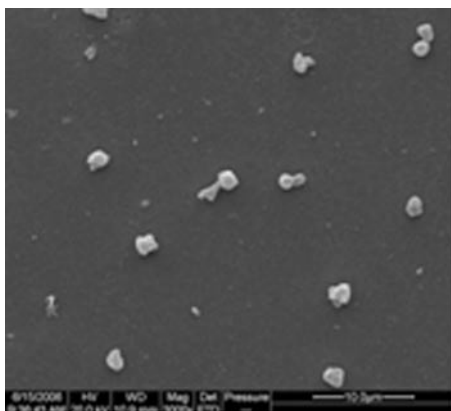
17.3 Surface engineering of Ti alloys for orthopedics and dental implants

As mentioned in Section 17.1, titanium and its alloys are widely used for orthopedics and other implants due to their high specific strength, low Young's modulus and good corrosion resistance and biocompatibility. For example, hip and knee prostheses, bone screws and plates, maxillofacial implants, intramedullary nailing systems, spinal surgery implants, external fixators, dental implants, and others have all been used. Generally, the biocompatibility of Ti and some of its alloys is quite good. In many applications as hard tissue substitutes they present very good bone conductivity and osseointegration.

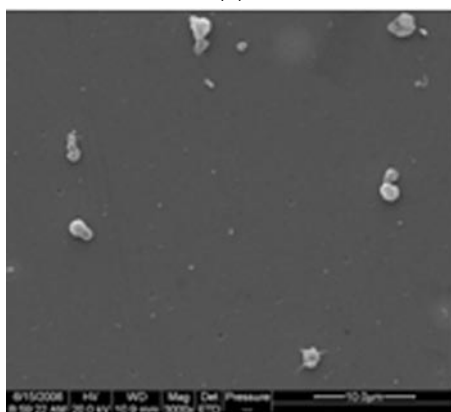
However, as hard tissue substitutes, in many cases they must bear heavy



(a)



(b)



(c)

17.8 SEM images of samples after being in contact with PRP for 4 h (a) anatase Ti-O film; (b) heparinylated anatase Ti-O film via direct silanization; (c) heparinylated anatase Ti-O film via chemisorption of H_3PO_4 and then silanization. Magnification $\times 3000$.

loads and may undergo wear; particulate wear debris in total hip replacements causes adverse local host reactions. The extreme form of such a reaction, aggressive granulomatosis, has been found to be a distinct condition and different from simple aseptic loosening. Reactive and adaptive tissue around the replaced hip was formed of fibroblast-like cells and activated macrophages. Thus improvement in the anti-wear properties of the surface is needed. In addition, further improvement of biocompatibility is needed to realize better integration of the tissue/material interface.

17.3.1 improving surface properties of Ti-based biomaterials by surface coatings

Many hard coatings have been investigated as anti-wear coatings for Ti-based biomaterials. Among them, DLC films have attracted most attention, especially for improving the tribological properties of artificial joints.

Kim *et al.* (2008) reported their work on Si-incorporated diamond-like carbon (Si-DLC) coatings with Si content up to 2 at%, deposited on Ti-alloy substrates by means of a radio-frequency plasma assisted chemical vapor deposition (r.f. PACVD) technique. The synergy in wear and corrosion of the Si-DLC coatings was investigated by tribological and electrochemical techniques. The investigation showed that these films improved wear–corrosion resistance in the simulated body fluid environment because of a lower friction coefficient and lower corrosion rate.

Brizuela *et al.* (2002) prepared functionally graded, titanium alloyed, DLC coatings using a magnetron sputtering PVD technique and studied the tribological performance of the coating during metal-on-metal contact (cobalt chromium or titanium alloys) under dry and lubricated test conditions. During mechanical testing, the DLC coatings exhibited a high elastic recovery (65%) compared with Co-Cr-Mo (15%) and Ti-6Al-4V (23%). The coatings exhibited excellent tribological performance against Ti-6Al-4V and Co-Cr-Mo alloys, especially under dry conditions, presenting a friction coefficient value of 0.12 and almost negligible wear. This coating has passed biocompatibility tests for implant devices on tissue/bone contact according to international standards.

Allen *et al.* (2001) investigated the effects of DLC coatings on the musculoskeletal system. They deposited DLC coatings on polystyrene 24-well tissue culture plates by fast-atom bombardment from a hexane precursor. Two osteoblast-like cell lines were cultured on uncoated and DLC-coated plates for periods of up to 72 h. The effects of DLC coatings on cellular metabolism were investigated by measuring the production of three osteoblast-specific marker proteins: alkaline phosphatase, osteocalcin, and Type I collagen. They proved that there was no evidence that the presence of the DLC coating had any adverse effect on any of the parameters measured in the study. They

further implanted DLC-coated metal cylinders in intramuscular locations in rats and in transcortical sites in sheep. Histological analysis of specimens retrieved 90 days after surgery showed that the DLC-coated specimens were well tolerated in both sites. They concluded that DLC coatings are biocompatible *in vitro* and *in vivo*.

Even if some studies revealed that DLC film was a promising material to reduce the wear rates of artificial hip joints, the effect of the DLC coating on such joints is still in argument. Roy and Lee (2007) discussed various factors affecting the wear behavior of DLC films. In the case of hydrogenated films, positive results were obtained when tested by pin-on-disk (POD) or ball-on-disk (BOD) type wearing. However, the positive effect of the coating was not significant in the tests using a hip or knee joint simulator. In contrast, POD or BOD type wear tests of nonhydrogenated film showed both positive and negative results. Only in case of ta-C/ta-C pairs on the simulator, was there a significant reduction in wear as compared to conventional polyethylene-metal or metal-metal pairs. Some of these conflicting results may be due to the fact that the lubricant also plays a role in determining the wear of the prosthetic joint material. Onate *et al.* (2001) did a wear test on an artificial knee couple of DLC coating-UHMWPE by means of a knee-wear simulator, using distilled water as lubricant. DLC was deposited using CC800-8 CemeCon PVD equipment involving initial deposition by magnetron sputtering. The thickness of the coatings was in the range 3–4 μm . The coating of DLC significantly decreased the generation of UHMWPE debris. However, when Saikko *et al.* (2001) did a wear test of a hip joint couple with DLC film coated heads, with the film thickness 3 μm , against UHMWPE counterface in a hip wear simulator using HyClone Alpha Calf Fraction serum (catalogue number SH30076.03) diluted 1:1 with Millipore distilled water, the wear resistance of DLC head did not markedly differ from the alumina head and CoCr alloy head.

There are also reports of failure of DLC coatings in orthopedic implants. As an example, a Swiss company, 'Implant Design AG', tried to introduce a diamond-like nanocomposite (DLN) coated knee joint implant against UHMWPE, but was forced to stop it due to excessive wear and spallation of the joint materials (Roy and Lee, 2007). Furthermore, a clinical test reported that the failure rate of DLC-coated Ti-6Al-4V femoral heads is much higher than that of alumina femoral heads (Taeger *et al.*, 2003). To understand the failures in the clinical tests, one should also consider the instability of DLC coatings in aqueous environments, which results in delamination or spallation of the coatings. Numerous surface pits that must follow the spallation of the DLC coating were observed on the coated surface of the failed femoral head (Taeger *et al.*, 2003).

Therefore a number of the factors should be take into consideration to affect the wear behavior of the DLC coated hip or knee joint wear couples,

such as the materials factors of the DLC films, including the content of sp^2 and sp^3 bonds in the DLC film, composition, adhesion strength of the film to the substrate, film thickness, surface roughness, internal stress in the film, pits state, as well as counterpart materials, lubrication conditions, loading state, contact state of the counterparts, fabrication accuracy of the wear couple, and so on. More *in vitro* and *in vivo* research with clinical tests, including failure analysis, is required to confirm the DLC film as a coating material for prosthetic joints.

Ti, being bio-inert, shows poor bone cell adhesion with an intervening fibrous capsule. Natural bone consists mainly of the inorganic substance hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ (HA) and collagen, which is a nano-scale assembled composite. Thus, hydroxyapatite is highly biocompatible and has been popularly applied for surface coatings on titanium alloys for orthopedic and dental implants. A plasma spray process for fabricating HA coatings has been applied for orthopedic and dental implants in recent decades. In this process, HA powders are injected into high temperature heat sources where they are melted and propelled at high velocity towards the titanium alloy implant. Although this process has been widely applied, the absorption behavior of the HA coating, the bond strength, and the fatigue behavior of the coating are still of some concern. Some investigations about the long-term clinical results of plasma spray coated HA implants have been reported.

Restrepo *et al.* (2008) have reviewed the results of 35 consecutive total hip arthroplasties performed in 25 patients between 1993 and 2003. All patients received a hydroxyapatite (HA) plasma sprayed titanium acetabular component and a tapered femoral stem coated with HA. Follow-up averaged 6.6 years (range: 4.2 to 10). There was a significant improvement in function and relief of pain. All uncemented components were found to be stable and osteointegrated at the most recent follow-up. There were no complications or revision operations.

Landor *et al.* (2007) evaluated the efficacy of plasma sprayed porous titanium alloy/HA coatings in promoting bony ingrowth and mechanical stabilization of total hip implants compared with total hip implants without a porous titanium alloy/HA coating. The coating consisted of a plasma-deposited first layer of porous titanium alloy (Ti-6Al-4V), similar in composition to the forged substrate, and a plasma deposited second layer of hydroxyapatite. The porous titanium alloy/hydroxyapatite (HA) coated femoral stems were implanted in 50 patients. The results were compared with a control group of 50 patients with the same type of endoprosthesis, but without the porous titanium alloy/HA coating. Both groups of patients were operated on and evaluated by the same orthopedic surgeons with a mean follow up of 11.4 years in the HA group and 10.6 years in the control group. They found a substantially higher degree and quality of osteointegration in the porous titanium alloy/HA type implants.

Chang *et al.* (2006), on the other hand, pointed out that hip arthroplasties with HA coatings on the smooth surface of the titanium cup are not reliable, according to their investigation of 90 hips in 82 patients using Omnifit hydroxyapatite (HA)-coated prostheses followed for at least seven years.

Reikerås and Gunderson (2002) reported the outcome of 191 acetabular gritblasted titanium cups with hemispherical design for press-fit insertion and coated with hydroxyapatite. The prosthesis was made of gritblasted titanium entirely coated with hydroxyapatite, and 155 patients aged 15–78 years were operated on during the years 1991–1993. The follow-up period was 7–10 years. During this period, 39 cups were revised because of mechanical loosening, a further nine had radiolucent lines and two focal osteolysis. None of these 11 patients had clinical symptoms. Failure was associated with age, wear and radiolucency/osteolysis. At revision, the soft tissues were discolored, and most of the coating had disappeared. This design of hydroxyapatite-coated cups therefore has a high rate of debonding and failure.

However, when HA coatings are applied on dental implants, the results seem better than with those on hip joint implants. Binahmed *et al.* (2007) reported the long-term (8 to 10 year) results of hydroxyapatite (HA)-coated dental implants and compared them to the 5-year results as well as to long-term results of both HA and titanium dental implants reported in the literature. A total of 302 implants were placed in 90 patients whose average age was 54.3 years (SD 13.2 years). The 10-year success rate of HA-coated dental implants was 82%. The success rate was higher in the mandible as compared to the maxilla. The 10-year results were inferior to the five-year results.

The success rate for clinical application of plasma spray HA coated implants depends on many factors such as design of the implant, surface state (porous, rough or smooth), application location, as well as plasma spray parameters. In some cases the failure rate of the HA coated implants is high (Sun *et al.*, 2001). The brittleness, low strength and low adhesion strength of these coatings to the implant restrict their use. To overcome these disadvantages of the plasma spray HA process, many new processes have been developed.

Wang *et al.* (2006) compared three different implants, bare Ti-6Al-4V alloy, Ti-6Al-4V alloy coated with plasma-sprayed hydroxyapatite (PSHA), and Ti-6Al-4V alloy coated with electrochemically deposited hydroxyapatite (EDHA), implanted into canine trabecular bone for 6 h, 7 days, and 14 days. They found that a finely textured microstructure of EDHA coatings appears to provide significant advantage for the integration of mineralized bone tissue into the coatings, and conclude that the adhesion of EDHA coatings to Ti-6Al-4V substrate needs to be improved through appropriate manipulation of the electrodeposition parameters.

To improve the adhesion strength of HA coatings to the titanium substrate, some novel coating and surface modification processes have been developed

in recent years. Current research on sputtered HA and CaP coatings has shown promise for elimination of some of the problems associated with the plasma-spraying process.

Ozeki *et al.* (2002) fabricated a functionally graded film of titanium/hydroxyapatite (HA) on a titanium substrate, using radio frequency magnetron sputtering. The ratio of titanium to HA was controlled by moving a target shutter. The film thickness was 1 micron and the HA was concentrated close to the surface while the titanium concentration increased with proximity to the substrate. They compared the bonding strength of this graded-composition film with a plasma sprayed HA coating and a pure HA sputtered film, and found that the bonding strength between the functionally graded film and the substrate was 15.2 MPa in a pull-off test and the critical load in a scratch test was 58.85 mN. The corresponding values for a pure HA sputtered film were 8.0 MPa and 38.47 mN, respectively. The bonding strength of a pure HA plasma sprayed coating was 10.4 MPa in the pull-off test. Further, they sputter-coated a graded film and a pure HA film to a thickness of 1 micron on titanium columns (10 mm in length and 4 mm in diameter) and implanted them in diaphyses of the femora of six adult dogs. After 2, 4, and 12 weeks they found that the push-out strength of the graded film and of the pure HA film was 3.7 MPa and 3.5 MPa respectively, while that for the uncoated columns was only 1.0 MPa. Thus sputter-coating of the graded film showed a significant enhancement in bonding strength between bone and titanium.

17.3.2 Surface functionalization

Although coating of HA can improve the biocompatibility of titanium for orthopedic and dental devices, brittleness and delamination of HA or Ca-P coatings remain weaknesses for these coatings. Some novel processes have been developed for rendering the surface highly bioactive, without a coating.

Recently Schlegel *et al.* (2008) used anodic plasma-chemical (APC) treatment to fabricate a porous oxide layer incorporating calcium and phosphate directly in the oxide. This produced superior adhesive strength to a conventional calcium phosphate coating, offering potential for long-term osseointegration. They investigated the biocompatibility and osteoconductivity of APC surfaces *in vivo* compared with standard HA coated and uncoated commercially pure titanium implant cortical screws. Sample screws were implanted in female Swiss alpine sheep for 12 weeks. They found no significant differences between the tested coatings, and no delamination was observed with any of the APC-treated surfaces. These results suggest that the APC-treated samples have similar biological performance to HA-coated screws. They concluded that because the APC treatment has a superior bonding strength to the base metal compared to standard HA coatings as well as similar biocompatibility, this approach holds good potential for biomedical applications.

Ion implantation has been used for surface modification of materials for over three decades, and ion implantation processes is being also used to enhance the compatibility of titanium and its alloys with bone.

Hanawa *et al.* (1997) reported on their *in vivo* investigations of calcium ion (Ca^{2+})-implanted titanium inserted into rat tibia for 2, 8, and 18 days. They found that a larger amount of new bone was formed on the Ca^{2+} -treated side than on the untreated side, even at two days after surgery. Bone formation on the untreated side was delayed and the bone did not make contact with the surface. Mature bone with bone marrow formed in eight days. Neither macrophage nor inflammatory cell infiltration was observed. Their results indicate that Ca^{2+} -implanted titanium is superior to titanium alone for bone conduction.

Nayab *et al.* (2005; 2007) investigated the effects of calcium ion implanted Ti on the functional activity of bone cells. They used flow cytometry (FCM) and the reverse transcriptase polymerase chain reaction (RT-PCR) to measure the response of bone-derived cells to key bone-associated components, and found that Ti surfaces implanted with Ca ions can enhance the expression of certain bone-associated components *in vitro*. This effect could be the origin of the benefits of this material for bone *in vivo*.

Maitz *et al.* (2005) formed a bioactive titanium surface by Na plasma immersion ion implantation and deposition (PIII&D) followed by precipitation of calcium phosphate and cell culture. They compared the bioactivity of the plasma-implanted titanium to that of (i) untreated, (ii) Na beam-line implanted, and (iii) NaOH-treated titanium samples. They found that the results could be classified into two groups: non-bioactive (untreated titanium and beam-line Na implanted titanium) and bioactive (Na-PIII&D and NaOH-treated titanium). No cell toxicity was found for the four types of surfaces. They suggested that the use of Na-PIII&D provides an environmentally cleaner technology to improve the bioactivity of Ti compared to conventional wet chemical processes.

Krupa *et al.* (2002, 2004, 2005) investigated the corrosion resistance and biocompatibility of titanium after surface modification by ion implantation of calcium or phosphorus or calcium+phosphorus. They implanted calcium ions or phosphorus ions at a dose of 10^{17} ions/cm². In their *dual* calcium+phosphorus ion implantation, first Ca was implanted and then P, both at a dose of 10^{17} ions/cm², and the ion beam energy was 25 keV. The microstructure, chemical composition, corrosion resistance and biocompatibility *in vitro* were examined. The results revealed that all ion implanted surface layers were amorphous. Electrochemical examinations indicated that calcium, phosphorus and calcium+phosphorus implantation into titanium increases its corrosion resistance under steady conditions after short- and long-term exposures in SBF. But potentiodynamic tests showed that the calcium-implanted samples undergo pitting corrosion during anodic polarization. The

breakdown potentials measured are high (2.5 to 3 V). Good biocompatibility of all the investigated materials was confirmed under the specific examination conditions; however, they pointed out that the calcium implanted titanium was inferior to the unimplanted titanium, a result that is different from the result of Hanawa *et al.* (1997) and Nayab *et al.* (2005, 2007).

Braceras *et al.* (2007) implanted CO^+ ions with an energy of 30 KV and doses from 3 to 6.5×10^{17} ions/cm² into Ti6Al4V disks. They found that on CO^+ ion implanted samples, osteoblast were more spread, star-shaped and flattened. Apoptosis signals were lower on CO^+ ion implanted samples compared with the control sample. Their *in vitro* research proved that CO^+ ion implantation increases alkaline phosphatase (ALP) activity, osteoblast differentiation and accelerated osseointegration. They further did two steps of *in vivo* experiments; first they tested it on 88 dental implants inserted for 3 months into the tibiae of 22 New Zealand albino rabbits. Results revealed that CO^+ ion implanted samples showed an 84.65% bone-to-implant contact (BIC) of bone implant contact on the Ti6Al4V samples, against 52.05% on the control untreated samples. Subsequently, the CO^+ ion implanted treatment has been tested on dental implants in the mandible of beagle dogs for 3 and 6 months, with 72 implants and 12 animals. Results demonstrated again the superior performance of the CO^+ ion implanted samples ($68 \pm 8\%$ and $61 \pm 8\%$ BIC% at month three and six respectively on the histological analysis) against the control samples ($42 \pm 7\%$ and $44 \pm 14\%$ at month three and six respectively). Therefore, these results confirm the claim that CO^+ ion implanted samples show faster and higher osseointegration properties.

Until now, a number of the researches have been done on the bioactivity of ions such as Ca^+ , P^+ , K^+ , Na^+ , Ar^+ , N^+ , NH_2^+ , Mg^+ , Zn^+ , CO^+ and $\text{H}_2\text{O} + \text{H}_2$ gas, implanted in titanium and/or titanium alloy. Among those ions Ca^+ , K^+ , P^+ , Na^+ , NH_2^+ , Mg^+ , CO^+ , and $\text{H}_2\text{O} + \text{H}_2$ gas implanted titanium and/or titanium alloy have been reported as improving osteoblast adhesion and growth. However, there are a number of further researches that need to be done, such as the optimization of species of ions and implanted element distribution which depends on ion implantation energy, dose, as well as treatment temperature. And we need to understand the interaction mechanics of the modified surface with the biological environment.

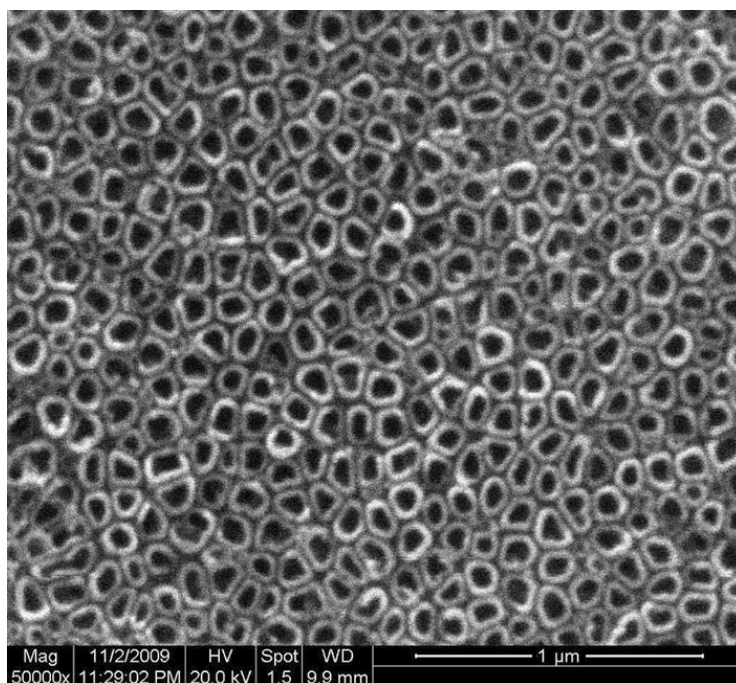
Surface topological modification is another novel research direction with the potential to produce bioactivity without affecting the mechanical characteristics of the material. Fabrication routes for titania nano-architectures can be flexible and cost-effective, enabling realization of desired platform topologies on existing non-planar orthopedic implants.

Xiao *et al.* (2008) fabricated titania nanotube arrays *in situ* on a Ti surface by anodic oxidation in 0.1–0.5% HF solution. They found that the HF concentration and anodic voltage had important effects on the appearance and size of the titania nanotube arrays. In the range of 5–20 V, the nanotube

diameter increased with voltage. They observed that as Na_2HPO_4 was added to the HF electrolyte, apatite could be formed on the arrays. This provides an effective way to prepare bioactive titania. Figure 17.9 shows the morphology of titania nanotube arrays obtained by anodic oxidation in 0.5% HF electrolyte for 20 minutes.

Das *et al.* (2009) evaluated bone cell–anodized Ti surface interactions. They studied human osteoblast cell attachment and growth behavior using an osteoprecursor cell line for 3, 7, and 11 days. They noticed an abundant amount of extracellular matrix (ECM) between neighboring cells on anodized nanotube surface with filopodia extensions coming out from cells to grasp the nanoporous surface of the nanotubes for anchorage. Further, when anodized nanoporous sample surfaces were etched with different patterns, preferential cell attachment was noticed on the nanotube surfaces but almost no cells on an etched plate Ti surface. Immunochemistry studies with alkaline phosphatase showed enhanced osteoblastic phenotype expressions on nanoporous surfaces. Osteoblast proliferation was significantly higher on anodized nanotube surfaces.

Popat *et al.* (2007) also found that nanotubular titania surfaces provide a favorable template for the growth and maintenance of bone cells. The cells cultured on nanotubular surfaces showed higher adhesion, proliferation,



17.9 Titania nanotube arrays.

alkaline phosphatase activity, and bone matrix deposition compared with those grown on flat titanium surfaces. *In vivo* biocompatibility studies suggest that nanotubular titania does not cause chronic inflammation or fibrosis.

Recently, Bjursten *et al.* (2009) compared the bone-bonding ability of two titanium implant surfaces: titanium dioxide (TiO₂) nanotubes and TiO₂ gritblasted surfaces. *In vitro* results showed that the TiO₂ nanotubes improved osteoblast proliferation and adhesion compared with gritblasted titanium surfaces. They further did an *in vivo* experiment of four weeks of implantation of two kinds of samples in rabbit tibias. Pull-out testing indicated that TiO₂ nanotubes significantly improved bone-bonding strength by as much as nine-fold compared with TiO₂ gritblasted surfaces. Histological analysis confirmed greater bone-implant contact area, new bone formation, and calcium and phosphorus levels on the nanotube surfaces.

Bimolecular immobilization on a titanium surface is also a novel channel for functionalization. Brandley and Schnaar (1988) reported cell-binding peptides containing the Arginine-Glycine-Aspartic acid (RGD) sequence to be effective for promoting cell adhesion on materials; numerous studies have demonstrated that peptide modified surfaces influence short- and long-term cell response, such as attachment, shape and function. These responses are mediated via cell receptors known as integrins, which bind specifically to short peptide sequences from larger proteins. Integrins transduce information to the nucleus through several cytoplasmic signaling pathways.

Ferris *et al.* (1999) evaluated the quality and quantity of the new bone formed in response to titanium rods surface-coated with the peptide sequence Arg-Gly-Asp-Cys (RGDC) using gold-thiol chemistry and implanted in rat femurs. Histomorphometric analysis of cross-sections perpendicular to the implant long axis showed a significantly thicker shell of new bone formed around RGDC-modified versus plain implants at two weeks. They observed a significant increase in bone thickness for RGDC implants at four weeks while bone surrounding controls did not change significantly in thickness. Mechanical pull-out testing conducted at four weeks revealed that the average interfacial shear strength of peptide modified rods was 38% greater than control rods. Their data suggest that an RGDC peptide coating may enhance titanium rod osseointegration in the rat femur.

It has recently been demonstrated that phosphatidylserine-rich phospholipid coatings can induce fast mineralization of titanium implant surfaces on incubation in simulated body fluids. Bosetti *et al.* (2007) investigated the biocompatibility of these coatings in terms of cytotoxicity and their ability to support osteoblast adhesion and activity. Their results showed that the fast mineralization of the phospholipid matrix, obtained *in vitro* by pre-treatment in a SBF, exposes the cells to an environment similar to that present in the bone during its natural formation which allows cells to adhere, proliferate and produce proteins fundamental for bone growth. The biocompatibility

of these phospholipid-based coatings, in combination with their ability to initiate rapid mineralization, provides a promising material that could create bone cell interactions and bone integration *in vivo*.

17.4 Future trends

Biocompatibility is a prerequisite for biomaterials. The traditional considerations of biocompatibility are non-toxicity, not causing any inflammatory or allergic reactions in the human body, not causing thrombus formation and blood component decomposition, non-carcinogenicity and non-irritating. These ideas are based on the notion that biomaterials should play an inert role, maintaining low chemical reactivity with the body.

In the past two decades, attempts to introduce biological activity into biomaterials have been realized in research. The concept of tissue engineering and regeneration has prompted much progress in biomaterials research. Today, much biomaterial research is focused on enhancing the interaction between biomaterials and biological systems by means of chemical, physical, biochemical, and physiological processes, to produce specific and positive consequences of the interaction. The tendency of surface modification of a biomaterial in the aspect of controlling the interactions between the material and its biological environment can be summarized as from bioinert to bioactive, and further to be biospecific and bioinducing. Thus the concept of biocompatibility has been expanded: 'Biocompatibility refers to the ability of a biomaterial to perform its desired function with respect to a medical therapy, without eliciting any undesirable local or systemic effects in the recipient or beneficiary of that therapy, but generating the most appropriate beneficial cellular or tissue response in that specific situation, and optimising the clinically relevant performance of that therapy' (Williams, 2008).

In the case of titanium-based biomaterials, much effort has been made to improve biocompatibility and surface mechanical properties via a surface engineering approach. As discussed in Sections 17.2 and 17.3, surface functionalization becomes a hot-point of surface engineering research for Ti-based biomaterials. There are two major directions for the surface functionalization to mimic biological substances and their functions: one is the topographical mimic, such as the construction of micro and nano patterns on titanium surfaces to guide cell growth, which plays a role similar to the topography of extracellular matrix (ECM) which can contribute to cell growth. A typical example is the recently developed titanium oxide nanotube on Ti which brings benefit not only for promoting bone cell growth, but has newly been proved to enhance endothelial cell growth and prevent smooth muscle cell growth (Lily *et al.*, 2009). Therefore, the titanium nanotube may be applied in both orthopedic and cardiovascular devices for the surface biomimetic modification. The other direction is the surface immobilization

of biomolecules to mimic the role of the molecular structure of ECM to the cells. The cell adhesive molecules in the ECM, such as RGD, fibronectin (FN) and laminin (LN), can specifically recognize cells and promote their growth, and therefore the binding of those molecules on titanium surfaces can significantly promote cell growth. It is expected that combining the topography and biomolecular modification to materials surface can be more prospective to the surface functionization of titanium and produce more closely ideal Ti implants for human health care.

17.5 Sources of further information and advice

- K. E. Tanner, Titanium in Medicine, *Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine*, Volume 216, Number 3/2002, Professional Engineering Publishing
- J. Breme, J. Kirkpatrick, R. Thull, *Metallic Biomaterial Interfaces*, February 2008, John Wiley and Sons Ltd
- Y. Oshida, *Bioscience and Bioengineering of Titanium Materials*, December 2006, Elsevier Science
- D. M. Brunette, P. Tengvall, M. Textor, *Titanium in Medicine: Material Science, Surface Science, Engineering, Biological Responses and Medical Applications* (Engineering Materials), January 2001, Springer
- D. A. Jones, *Principles and Prevention of Corrosion*, 1996, 2nd Edition, Prentice Hall, New Jersey

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17.7 References

- Allen M, Myer B and Rushton N (2001), 'In vitro and in vivo investigations into the biocompatibility of diamond-like carbon (DLC) coatings for orthopaedic applications', *J Biomed Mater Res*, 58, 319–328.
- Amiji M and Park K (1993), 'Surface modification of polymeric biomaterials with poly-(ethylene oxide), albumin and heparin for reduced thrombogenicity', *J Biomater Sci. Polymer Edn*, 3, 217–223.
- Andara M, Agarwal A, Scholvin D, Gerhardt R A, Doraiswamy A, Chunming J, Narayan R J, Shin C C, Shin C M, Lin S J and Su Y Y (2006), 'Hemocompatibility of diamond like carbon–metal composite thin films', *Diamond & Related Materials*, 15, 1941–1948.
- Arru P, Rinaldi S, Stacchino C and Vallana F (1996), 'Wear assessment in bileaflet heart halves', *J Heart Valve Dis*, 5 Suppl 1, 144–148.
- Binahmed A, Stoykewych A, Hussain A, Love B and Pruthi V (2007), 'Long-term follow-

- up of hydroxyapatite-coated dental implants – a clinical trial', *Int J Oral Maxillofac Implants*, 22, 963–968.
- Bjursten L M, Rasmusson L, Lh S, Smith G C, Brammer K S and Jin S (2009), 'Titanium dioxide nanotubes enhance bone bonding *in vivo*', *J Biomed Mater Res A*, 88A, doi: 10.1002/jbm.a.32463
- Blackwood D J (2003), 'Biomaterials: Past Successes and Future Problems', *Corrosion Reviews*, 21, 97–124.
- Bosetti M, Santin M, Lloyd A W, Denyer S P, Sabbatin M and Cannas M (2007), 'Cell behaviour on phospholipids-coated surfaces', *J Mater Sci Mater Med*, 18, 611–617.
- Braceras I, Alava J I, Goikoetxea L, Maeztu M A and Onate J I (2007), 'Interaction of engineered surfaces with the living world: Ion implantation vs. osseointegration', *Surface & Coatings Technology*, 201, 8091–8098, doi:10.1016/j.surfcoat.2006.03.052.
- Brandley B K and Schnaar R L (1988), 'Covalent attachment of an Arg-Gly-Asp sequence peptide to derivatizable polyacrylamide surfaces: Support of fibroblast adhesion and long-term growth', *Anal Biochem*, 172, 270–278.
- Brizuela M, Garcia-Luis A, Viviente J L, Braceras I and Oñate J I (2002), 'Tribological study of lubricious DLC biocompatible coatings', *J Mater Sci Mater Med*, 13, 1129–1133.
- Chang J K, Chen C H, Huang K Y and Wang G J (2006), 'Eight-year results of hydroxyapatite-coated hip arthroplasty', *J Arthroplasty*, 21, 541–546.
- Chen J Y, Wang L P, Fu K Y, Huang N, Leng Y, Leng Y X, Yang P, Wang J, Wan G J and Sun H (2002), 'Blood compatibility and sp^3/sp^2 contents of diamond-like carbon (DLC) synthesized by plasma immersion ion implantation–deposition', *Surf Coat Technol*, 156, 289–294.
- Choi H W, Lee K R, Wang R and Oh K H (2006), 'Fracture behavior of diamond-like carbon films on stainless steel under a microtensile test condition', *Diamond Relat Mater*, 15, 38–43.
- Chu C L, Hu T, Wu S L, Dong Y S, Yin L H, Pu Y P, Lin P H, Chung C Y, Yeung K W and Chu P K (2007), 'Surface structure and properties of biomedical NiTi shape memory alloy after Fenton's oxidation', *Acta Biomater*, 3, 795–806.
- Clerc C O, Jedwab M R, Mayer D W, Thompson P J and Stinson J S (1997), 'Assessment of wrought ASTM F1058 cobalt alloy properties for permanent surgical implants', *J Biomed Mater Res*, 38, 229–234.
- Das K, Bose S and Bandyopadhyay A (2009), 'TiO₂ nanotubes on Ti: Influence of nanoscale morphology on bone cell–materials interaction', *J Biomed Mater Res A*, 90, 225–237, doi: 10.1002/jbm.a.32088.
- Davidson J A, Daigle K P and Kovacs P (1996), 'Wear-resistant, hemocompatible Ti-Nb-Zr and Zr-Nb alloys to improve blood pump design and performance', *Artif Organs*, 20, 513–522.
- Dion I, Roques X, Baquey C, Baudet E, Basse Cathalinat B and More N (1993), 'Hemocompatibility of diamond-like carbon coating', *Biomed Mater Eng*, 3, 51–55.
- Eisenbarth E, Velten D, Muller M, Thull R and Breme J (2004), 'Biocompatibility of β -stabilizing elements of titanium alloys', *Biomaterials*, 25, 5705–5713.
- Ferris D M, Moodie G D, Dimond P M, Gioranni C W, Ehrlich M G and Valentini R F (1999), 'RGD-coated titanium implants stimulate increased bone formation *in vivo*', *Biomaterials*, 20, 2323–2331.
- Filiaggi M J, Pilliar R M and Abdulla D (1996), 'Evaluating sol–gel ceramic thin films for metal implant applications. II. Adhesion and fatigue properties of zirconia films on Ti-6Al-4V', *J Biomed Mater Res*, 33, 239–256.

- Firstov G S, Vitchev R G, Kumar H, Blanpain B and Van Humbeeck J (2002), 'Surface oxidation of NiTi shape memory alloy', *Biomaterials*, 23, 4863–4871.
- Fischer H, Luk M, Oedekoven B, Telle R and Mottaghy K (2007), 'Hemocompatibility of high strength oxide ceramic materials: An *in vitro* study', *J Biomed Mater Res*, 81, 982–986.
- Hanawa T, Kamiura Y, Yamamoto S, Kohgo T, Amemiya A, Ukai H, Murakami K and Asaoka K (1997), 'Early bone formation around calcium-ion-implanted titanium inserted into rat tibia', *J Biomed Mater Res*, 36, 131–136.
- Hasebe T, Shimada A, Suzuki T, Matsuoka Y, Saito T, Yohena S, Kamijo A, Shiraga N, Higuchi M, Kimura K, Yoshimura H and Kuribayashi S (2006), 'Fluorinated diamond-like carbon as antithrombogenic coating for blood-contacting devices', *J Biomed Mater Res A*, 76, 86–94.
- Hong J, Andersson J, Ekdahl K N, Elgue G, Axén N, Larsson R and Nilsson B (1999), 'Titanium is a highly thrombogenic biomaterial, possible implications for osteogenesis', *Thromb Haemost*, 82, 58–64.
- Huang N, Chen Y R, Luo J M, Yi J, Lu R, Xiao J, Xue Z N and Liu X H (1994), 'In vitro investigation of blood compatibility of Ti with oxide layers of rutile structure', *J Biomater Appl*, 8, 404–412.
- Huang N, Yang P, Leng Y X, Chen J Y, Sun H, Wang J, Wan G J, Ding P D, Xi T F and Leng Y (2003), 'Functional inorganic films fabricated by PIII(-D) for surface modification of blood contacting biomaterials: Fabrication parameters, characteristics and antithrombotic properties', *Biomaterials*, 24, 2177–2187.
- Huang N, Yang P, Leng Y X, Wang J, Sun H, Chen J Y and Wan G J (2004), 'Surface modification of biomaterials by plasma immersion ion implantation', *Surface & Coatings Technology*, 186, 218–226.
- Huang N, Leng Y X, Yang P, Chen J Y, Sun H, Wang J, Wan G J, Zhao A S and Ding P D (2006), 'Surface modification of coronary artery stent by Ti-O/Ti-N complex film coating prepared with plasma immersion ion implantation and deposition', *Nuclear Instruments and Methods in Physics Research B*, 242, 18–21.
- Jones M I, McColl I R, Grant D M, Parker K G and Parker T L (2000), 'Protein adsorption and platelet attachment and activation, on TiN, TiC, and DLC coatings on titanium for cardiovascular applications', *J Biomed Mater Res*, 52, 413–421.
- Jozwik K and Karczewska A (2007), 'The new generation Ti6Al4V artificial heart valve with nanocrystalline diamond coating on the ring and with Derlin disc after long-term mechanical fatigue examination', *Diamond & Related Materials*, 16, 1004–1009.
- Karagkiozaki V, Logothetidis S, Kalfagiannis N, Lousinian S and Giannoglou G (2009), 'Atomic force microscopy probing platelet activation behavior on titanium nitride nano-coatings for biomedical applications', *Nanomedicine*, 5, 64–72.
- Khor K A, Srivatsan T S, Wang M, Zhou W and F Boey (eds) (2000), *Processing and Fabrication of Advanced Materials VIII*, Singapore, World Scientific Publishing.
- Kim J G, Lee K R and Yang S J (2008), 'Wear-corrosion performance of Si-DLC coatings on Ti-6Al-4V substrate', *J Biomed Mater Res A*, 86, 41–47.
- Krupa D, Baszkiewicz J, Kozubowski J A, Barcz A, Sobczak J W, Biliński A, Lewandowska-Szumieł M and Rajchel B (2002), 'Effect of phosphorus-ion implantation on the corrosion resistance and biocompatibility of titanium', *Biomaterials*, 23, 3329–3340.
- Krupa D, Baszkiewicz J, Kozubowski J A, Lewandowska-Szumieł M, Barcz A, Sobczak J W, Biliński A and Rajchel A (2004), 'Effect of calcium and phosphorus ion implantation on the corrosion resistance and biocompatibility of titanium', *Biomed Mater Eng*, 14, 525–536.

- Krupa D, Baszkiewicz J, Kozubowski J A, Barcz A, Sobczak J W, Biliński A, Lewandowska-Szumiel M and Rajchel B (2005), 'Effect of dual ion implantation of calcium and phosphorus on the properties of titanium', *Biomaterials*, 26, 2847–2856.
- Kwok S C H, Wang J and Chu P K (2005), 'Surface energy, wettability, and blood compatibility of phosphorus doped diamond-like carbon films', *Diamond Relat Mater*, 14, 78–85.
- Landor I, Vavrik P, Sosna A, Jahoda D, Hahn H and Daniel M (2007), 'Hydroxyapatite porous coating and the osteointegration of the total hip replacement', *Arch Orthop Trauma Surg*, 127, 81–89.
- Leng Y X, Chen J Y, Yang P, Sun H, Wan G J and Huang N (2003), 'Mechanical properties and platelet adhesion behavior of diamond-like carbon films synthesized by pulsed vacuum arc plasma deposition', *Surf Sci*, 531, 177–184.
- Liang P G, Ferguson E S and Hodge E S (1967), 'Plate fixation for open mandibular fractures', *J Biomed Mater Res*, 1, 135–149.
- Logothetidis S, Gioti M, Lousinian S and Fotiadou S (2005), 'Haemocompatibility studies on carbon-based thin films by ellipsometry', *Thin Solid Films*, 482, 126–132.
- Maguire P D, McLaughlin J A, Okpalugo T I T, Lemoine P, Papakonstantinou P, McAdams E T, Needham M, Ogwu A A, Ball M and Abbas G A (2005), 'Mechanical stability, corrosion performance and bioresponse of amorphous diamond-like carbon for medical stents and guidewires', *Diamond Relat Mater*, 14, 1277–1288.
- Maitz M F, Poon R W, Liu X Y, Pham M T and Chu P K (2005), 'Bioactivity of titanium following sodium plasma immersion ion implantation and deposition', *Biomaterials*, 26, 5465–73.
- Maitz M F and Shevchenko N (2006), 'Plasma-immersion ion-implanted nitinol surface with depressed nickel concentration for implants in blood', *J Biomed Mater Res A*, 76, 356–365.
- McGregor D B, Baan R A, Partensky C, Rice J M and Wilbourn J D (2000), 'Evaluation of the carcinogenic risks to humans associated with surgical implants and other foreign bodies – a report of an IARC Monographs Programme Meeting. International Agency for Research on Cancer', *Eur J Cancer*, 36, 307–313.
- Meireles G C, de Abreu L M, Forte A A, Sumita M K, Sumita J H and Aliaga J C (2007), 'Randomized comparative study of diamond-like carbon coated stainless steel stent versus uncoated stent implantation in patients with coronary artery disease', *Arq Bras Cardiol*, 88, 390–395.
- Miller P D and Holladay J W (1958), 'Friction and wear properties of titanium', *Wear*, 59, 133–140.
- Mueller H J and Greener E H (1970), 'Polarization studies of surgical materials in Ringer's solution', *J Biomed Mater Res*, 4, 29–41.
- Nag S, Banerjee R and Fraser H L (2005), 'Microstructural evolution and strengthening mechanisms in Ti-Nb-Zr-Ta, Ti-Mo-Zr-Fe and Ti-15Mo biocompatible alloys', *Materials Science and Engineering: C*, 25, 357–362.
- Nayab S N, Jones F H and Olsen I (2005), 'Effects of calcium ion implantation on human bone cell interaction with titanium', *Biomaterials*, 26, 4717–4727.
- Nayab S N, Jones F H and Olsen I (2007), 'Effects of calcium ion-implantation of titanium on bone cell function *in vitro*', *J Biomed Mater Res A*, 83, 296–302.
- Niinomi M (2001), 'Cyto-toxicity and fatigue performance of low rigidity titanium alloy', *Met Mater Trans*, 32A, 477–486.
- Onate J I, Comin M, Braceras I, Garcia A, Viviente J L, Brizuela M, Garagorri N, Pris J I and Alava J I (2001), 'Wear reduction effect on ultra-high-molecular-weight

- polyethylene by application of hard coatings and ion implantation on cobalt chromium alloy, as measured in a knee wear simulation machine', *Surf. & Coat Technol.*, 142–144, 1056–1062.
- Ong S E, Zhang S, Du H, Too H C and Aung K N (2007), 'Influence of silicon concentration on the haemocompatibility of amorphous carbon', *Biomaterials*, 28, 4033–4038.
- Ozeki K, Yuhta T, Fukui Y, Aoki H and Nishimura I (2002), 'A functionally graded titanium/hydroxyapatite film obtained by sputtering', *J Mater Sci Mater Med*, 13, 253–258.
- Peng L, Eltgroth M L, Latsempa T J, Grimes C A and Desai T A (2009), 'The effect of TiO₂ nanotubes on endothelial function and smooth muscle proliferation', *Biomaterials*, 30, 1268–1272.
- Plant S D, Grant D M and Leach L (2005), 'Behaviour of human endothelial cells on surface modified NiTi alloy', *Biomaterials*, 26, 5359–5367.
- Popat K C, Leoni L, Grimes C A and Desai T A (2007), 'Influence of engineered titania nanotubular surfaces on bone cells', *Biomaterials*, 28, 3188–3197.
- Reikerås O and Gunderson R B (2002), 'Failure of HA coating on a gritblasted acetabular cup: 155 patients followed for 7–10 years', *Acta Orthop Scand*, 73, 104–108.
- Restrepo C, Lettich T, Roberts N, Parvizi J and Hozack W J (2008), 'Uncemented total hip arthroplasty in patients less than twenty-years', *Acta Orthop Belg*, 74, 615–22.
- Roy R K and Lee K R (2007), 'Biomedical Applications of Diamond-like Carbon Coatings', *J Biomed Mater Res B Appl Biomater*, 83, 72–84.
- Saikko V, Ahlroos T, Calonius O and Knen J K (2001), 'Wear simulation of total hip prostheses with polyethylene against CoCr, alumina and diamond-like carbon', *Biomaterials*, 22, 1507–1514.
- Salahas A, Vrahatis A, Karabinos I, Antonellis I, Ifantis G, Gavaliatsis I, Anthopoulos P and Tavernarakis A (2007), 'Success, safety, and efficacy of implantation of diamond-like carbon-coated stents', *Angiology*, 58, 203–210.
- Schlegel P, Hayes J S, Frauchiger V M, Gasser B, Wieling R, Textor M and Richards R G (2008), 'An *in vivo* evaluation of the biocompatibility of anodic plasma chemical (APC) treatment of titanium with calcium phosphate', *J Biomed Mater Res B*, 90B, 26–34. doi: 10.1002/jbm.b.31249
- Shi D L (eds) (2005), *Introduction to Biomaterials*, Beijing, PR China, Tsinghua University Press
- Sun L, Berndt C C, Gross K A and Kucuk A (2001), 'Material fundamentals and clinical performance of plasma-sprayed hydroxyapatite coatings: A review', *J Biomed Mater Res*, 58, 570–592.
- Sunny M C and Sharma C P (1991), 'Titanium–protein interaction, changes with oxide layer thickness', *J Biomater Appl*, 6, 89–98.
- Taeger G, Podleska L E, Schmidt B, Ziegler M and Nast-Kolb D (2003), 'Comparison of diamond-like carbon and alumina articulating with polyethylene in total hip arthroplasty', *Mat-wiss Werkstofftech*, 34, 1094–1100.
- Takemoto S, Yamamoto T, Tsuru K, Hayakawa S, Osaka A and Takashima S (2004), 'Platelet adhesion on titanium oxide gels: Effect of surface oxidation', *Biomaterials*, 25, 3485–3492.
- Tanaka Y, Matsuo Y, Komiya T, Tsutsumi Y, Doi H, Yoneyama T and Hanawa T (2009), 'Characterization of the spatial immobilization manner of poly(ethylene glycol) to a titanium surface with immersion and electrodeposition and its effects on platelet adhesion (p NA)', *J Biomed Mater Res A*, doi: 10.1002/jbm.a.32375
- Wapner K L (1991), 'Implications of metallic corrosion in total knee arthroplasty', *Clin Orthop Relat Res*, 271, 12–20.

- Wan G J, Huang N, Zhao A S, Yang P and Chu P K (2007), 'Behaviors of Platelets Adherent on Si-N(H) Surface Prepared from Ammonia Plasma-Implanted Silicon', *Key Engineering Materials*, 330–332, 889–892.
- Wang H, Eliaz N, Xiang Z, Hsu H P, Spector M and Hobbs L W (2006), 'Early bone apposition *in vivo* on plasma-sprayed and electrochemically deposited hydroxyapatite coatings on titanium alloy', *Biomaterials*, 27, 4192–4203.
- Weng Y J, Hou R X, Xie D, Wang J and Huang N (2007), 'Covalent Immobilization of Heparin on Anatase TiO₂ Films via Chemical Adsorbent Phosphoric Acid Interface', *Key Engineering Materials*, 330–332, 865–868.
- Weng Y J, Qi F, Huang N, Wang J, Cheng J Y and Leng Y X (2008), 'Photochemical immobilization of bovine serum albumin on Ti-O and evaluations *in vitro* and *in vivo*', *Applied Surface Science*, 255, 489–493.
- Williams D F (2008), 'On the mechanism of biocompatibility', *Biomaterials*, 29, 2941–53.
- Xiao X F, Liu R F and Tian T (2008), 'Preparation of bioactive titania nanotube arrays in HF/Na₂HPO₄ electrolyte', *Journal of Alloys and Compounds*, 466, 356–362.
- Yamazaki K, Kihara S, Akimoto T, Tagusari O, Kawai A, Umezu M, Tomioka J, Kormos R L, Griffith B P and Kurosawa H (2002), 'EVAHEART, an implantable centrifugal blood pump for long-term circulatory support', *Jpn J Thorac Cardiovasc Surg*, 50, 461–465.
- Yamazaki K, Litwak P, Tagusari O, Mori T, Kono K, Kameneva M, Watach M, Gordon L, Miyagishima M, Tomioka J, Umezu M, Outa E, Antaki J F, Kormos R L, Koyanagi H and Griffith B P (1998), 'An implantable centrifugal blood pump with a recirculating purge system (Cool-Seal system)', *Artif Organs*, 22, 466–474.
- Yang W M, Liu Y W, Zhang Q, Leng Y X, Zhou H F, Yang P, Chen J Y and Huang N (2007), 'Biomedical response of tantalum oxide films deposited by DC reactive unbalanced magnetron sputtering', *Surface and Coatings Technology*, 201, 8062–8065.

Plasma electrolytic oxidation and anodising of aluminium alloys for spacecraft applications

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Abstract: This chapter describes an environmentally safe and emerging surface technology for aluminium alloys commonly known as plasma electrolytic oxidation (PEO). Although anodising is commonly used on aluminium alloys, there are recent issues related to both environmental legislation and the need for more durable, multi-functional surface characteristics. In particular, spacecraft hardware must survive environments at the launch-site, during launch, in space and during re-entry to Earth. The chapter provides results from various laboratory tests following the space industry standards. The PEO process is compared to a conventional anodising process. A number of applications and case studies are finally introduced.

Key words: plasma electrolytic oxidation, anodising, thermo-optical properties, fretting and impact wear, cold welding.

18.1 Introduction

Surface treatments such as chemical conversion, laser enhancement, thermal spraying, plating, physical vapour deposition (PVD), and organic finishing methods are all considered for the surface treatment and protection of aluminium and other lightweight alloys. These methods are covered in detail in various chapters of this book and also in the literatures (Davies, 1993; Cramer and Covino, 2005; Reidenbach, 1994; Davenport *et al.*, 2000). This particular chapter focuses on an emerging surface treatment process called plasma electrolytic oxidation (PEO) together with the very widely adopted anodising and hard anodising processes for comparison. Both processes will be considered with respect to their properties and their use for spacecraft hardware applications.

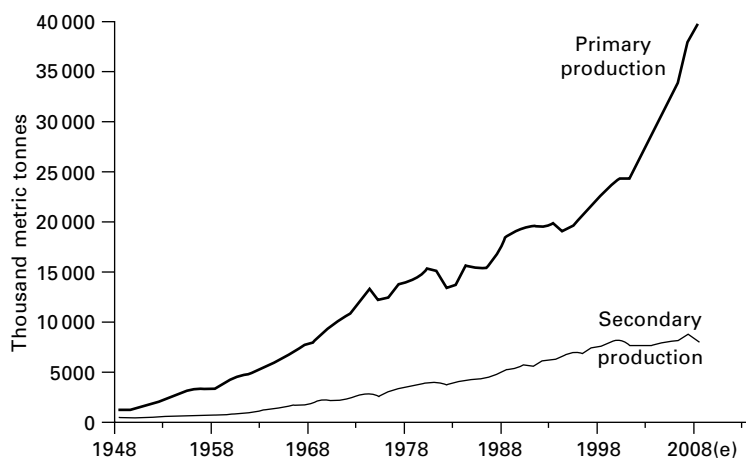
Although initial developments in Russia on PEO for aluminium alloys date back nearly 35 years (Markov *et al.*, 1976), this technology is receiving a widespread interest outside Russia only during recent years. PEO has been researched in academia (Yerokhin *et al.*, 1999; Curran and Clyne, 2005, 2006; Monfort *et al.*, 2006, 2007) and is successfully being commercialised by industries under the trade names of Keronite and Keplacoat. Its growing portfolio of applications includes the space and aerospace industries (Suminov *et al.*, 2005; Shrestha *et al.*, 2003, 2006; Choppy *et al.*, 2007), automotive

(Rao *et al.*, 1997; Mistry *et al.*, 2008; Dahm *et al.*, 2009; Shrestha *et al.*, 2006, 2007), oil and gas, textile (Yerokhin *et al.*, 1999), computing/communications/consumables (3Cs), ship-building, medical devices and bio-medical equipment, as well as the packaging industries.

While black-anodising and hard-anodising have been used to-date on aluminium alloys in various space and aerospace applications, this chapter will attempt to highlight some key benefits of the emerging PEO technology that can offer enhanced properties required for future launchers, space transportations vehicles, and satellites. Stringent environmental legislation can mean that the electrolytes used for anodising processes may be either restricted, or difficult to dispose of after use. Of greater consideration will be the increasing requirements for superior performance, greater durability, and a need for multi-functional surfaces.

18.2 Aluminium (Al) alloys for aerospace applications

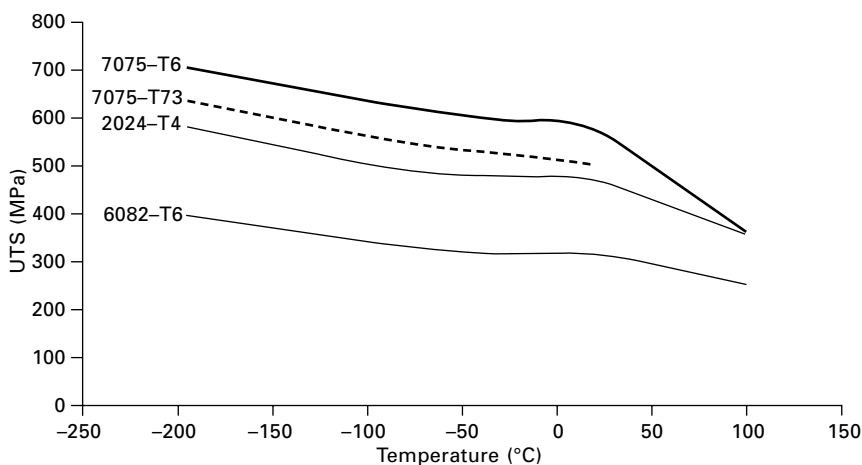
Aluminium is the world's second most produced metal, after iron, and its usage continues to increase (Fig. 18.1). Another significant fact is that the use of recycled aluminium is also growing steadily and accounts for nearly 30% of the production of primary metal (Anon., 1997). The wide variety of applications that have been developed with aluminium, and the sustained rise in consumption, are due to a number of deciding factors when designers, manufacturers and users come to select materials. Aluminium's main advantages include: lightness, high specific strength, high thermal and



18.1 World aluminium production 1948–2008 (e – estimate) (Source: USGS).

electrical conductivities, good formability, excellent machinability, corrosion resistance depending upon environment, diversity of aluminium alloys, extensive range of forms and options (e.g. rolling, extrusions, stampings, forgings, and castings), and suitability for a diverse range of joining techniques, surface treatment and recyclability.

Design engineers employed in the space industry are continually attempting to reduce the weight and improve the strength of the structures and piece-parts used in the construction of launchers and satellites – each component for space applications can be a candidate for weight-saving. Lightweight materials such as aluminium alloys are primarily used with a view to minimise fuel consumption and associated launch costs; their use will enable a larger, more efficient payload to be flown, possibly with improved performance. Light alloys, such as those composed of mainly aluminium with the addition of other elements such as beryllium, magnesium, copper and zinc, are of particular interest for use in spacecraft components due to their light weight and high specific strength. Also, aluminium alloys respond well to low temperatures and, unlike steels, they have no transition temperature between ductile fracture and brittle fracture at low temperatures (Anon., 1997). These alloys and their surface coating requirements have been reported in relation to the James Webb Space Telescope (JWST) near infra-red spectrum (NIRSpec) cryogenic light shield mechanism (Sharma, 2007), PLANK telescopes (Barucci *et al.*, 2003), cryogenic tanks for launch vehicles (Nebiolo *et al.*, 2001) and shuttle orbiter (Dunn, 1984). Tensile strength values for some typical commercial alloys are shown in Fig. 18.2. The reduction in strength with increase in temperature is quite pronounced.



18.2 Variations of ultimate tensile strength (UTS) of aluminium alloys at different temperatures. Values at 100°C are after 1000 h of heat treatment (Source: Pechiney Rhenalu).

In addition to standard alloys, more recent alloy developments include the following:

- Additions of lithium to aluminium for increased mechanical performance and a decrease in density
- Reinforced alloys (e.g. metal matrix composites – MMC) consisting of aluminium alloys reinforced with whiskers, metal wires, boron or carbon fibres
- Sandwich material, e.g. Al-alloy sheets with layers of fibre-reinforced polymer composite in between (Fibre metal laminates – FML)

Basic properties of some commonly used aerospace-grade aluminium alloys are given in Table 18.1. A list of aluminium alloys that have been approved for space applications are given in Table 18.2.

For space applications, aluminium alloy forgings, extrusions and plates are used mainly in primary and secondary structures. Aluminium tubes may be used as heat distribution pipes and plumbing, and other applications will include boxes for the housing of electronic systems. Aluminium alloy AA2219 was used extensively throughout the modular pressure shell and Igloo structure for the Spacelab project of the European Space Agency (ESA), due to its mechanical strength, good weldability, fracture toughness and resistance to general corrosion and stress corrosion cracking (Dunn, 1984; Dunn and Stanyon, 1997). It is now a preferred alloy for launch vehicles and manned spacecraft such as the various modules of the International Space Station (ISS) shown in Fig. 18.3.

18.3 Requirements from engineering components in space

Protection of aluminium alloys and their successful long-term applications in a space environment present a number of challenges and stringent requirements, e.g. resistance to corrosion prior to launch, corrosion fatigue, stress corrosion cracking (SCC), galvanic or bimetallic corrosion (Dunn, 1984; Rooij, 1989), cold welding, fretting and impact wear (Merstallinger *et al.*, 2003). Coatings may be of organic or inorganic type; they are generally applied to offer surface protection to the underlying light alloys and for achieving additional surface characteristics, e.g. thermo-optical properties with desired absorptance and emittance values, and for applications concerned with low earth orbit (LEO) environments.

Equipment inside the manned habitats of the International Space Station (Fig. 18.3) can experience humidity levels up to 70% RH. It should also be remembered that most space launch vehicles, including the shuttle orbiter (Fig. 18.4) are stored for long periods in warm, humid environments (both the Kennedy Space Centre and the Guyanese Space Centre are sited in tropical,

Table 18.1 Aluminium alloys used in space applications (all data are for room temperature) (Source: ECSS-Q-70-71A rev 1)

Material	Chemical composition	Specific gravity	Ultimate tensile strength (MPa)	Proof stress (0.2%) (MPa)	Elongation at break (%)	Thermal conductivity ($\text{Wm}^{-1}\text{°C}^{-1}$)	Atmospheric corrosion resistance	Typical applications
ISO Al 99.5	99.5% Al	2.71	75–146	55–133	25	230	Good	Light reflectors, heat exchangers
ISO AlCu4Mg1	4.5Cu 1.5Mg 0.6Mn Bal.Al	2.77	385–495	260–470	3–16	150–180	Poor	–
ISO Al Mg2	1.7–2.4Mg Bal.Al	2.69	180–250	87–190	16	155		–
ISO Al MgSi	0.4–0.9Mg 0.3–0.7Si Bal.Al	2.7	155–210	90–180	8–14	197–201	Moderate	–
AA2190	2.7Cu, 0.25Mg 2.25Li, 0.12Zr Bal. Al	2.5–2.6	455	455			Poor	Aircraft structures and cryogenic tankage structures
AA2195	4Cu 1.0Li 0.4Mg 0.3Ag 0.15Zr Bal. Al	2.55–2.6	–	–	–	–	Poor	Aircraft and spacecraft structures, cryogenic tankage structures
AA2219	5.8–6.8Cu 0.2–0.4Mn Bal. Al	2.84	172–476	70–395	7–20	116–170	Poor	Aircraft and spacecraft structures
AA2618	0.1–0.25Si 0.9–1.3Fe 1.92.7Cu 1.3–1.8Mg 0.1Zn 0.9–1.2Ni <0.1Ti Bal.Al	2.76	441	372	10			Aircraft and spacecraft structures
AA7075	5.6Zn 2.5Mg 1.6Cu 0.3Cr Bal.Al	2.8	400–650	340–595	3–8	134	Poor	Aircraft structural parts and other highly stressed applications

Table 18.2 Alloys with high resistance to stress corrosion cracking. These materials should be used for space applications. For aluminium alloys with other heat treatment, detailed justification for use shall be provided. (ECCC-Q-70-36A, 1998)

Wrought ^{1,2}		Cast	
Alloy	Condition	Alloy ³	Condition
1000 series	All	355.0, C355.0	T6
2011	T8	356, A356.0	All
2024, rod bar	T8	357.0	All
2219	T6, T8	B358.0 (Tens-50)	All
(E) 2419	T8	359.0	All
(E) 2618	T6, T8	380.0 A380.0	As cast
3000 series	All	514.0 (214)	As cast ⁵
5000 series	All ^{4, 5}	518.0 (218)	As cast ⁵
6000 series	All	535.0 (Almag 35)	As cast ⁵
(E) 7020	T6 ⁶	A712.0, C712.0	As cast
7049	T73		
7149	T73		
7050	T73		
7075	T73		
7475	T73		

¹ Mechanical stress relieved (TX5X or TX5XX) where possible

² Including weldments of the weldable alloys

³ The former designation is shown in parentheses when significantly different

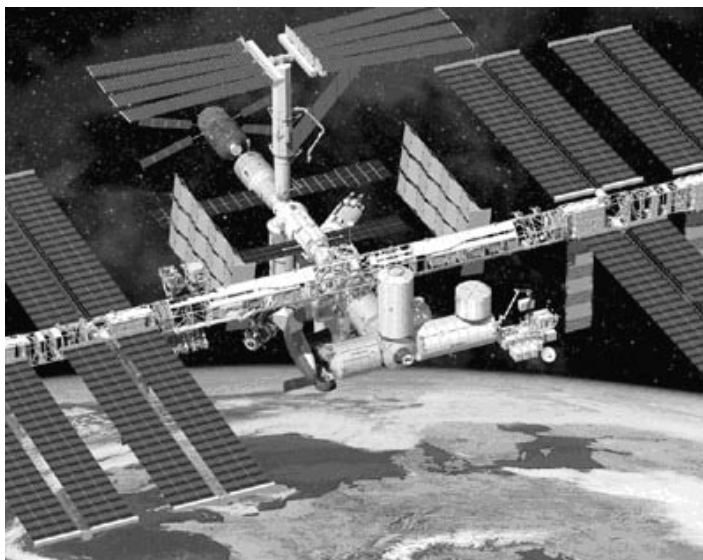
⁴ High magnesium content alloys 5456, 5083 and 5086 should be used only in controlled tempers (H111, H1112, H116, H117, H323, H343) for resistance to stress corrosion cracking and exfoliation

⁵ Alloys with magnesium content greater than 3.0% are not recommended for high temperature application, 66°C and above

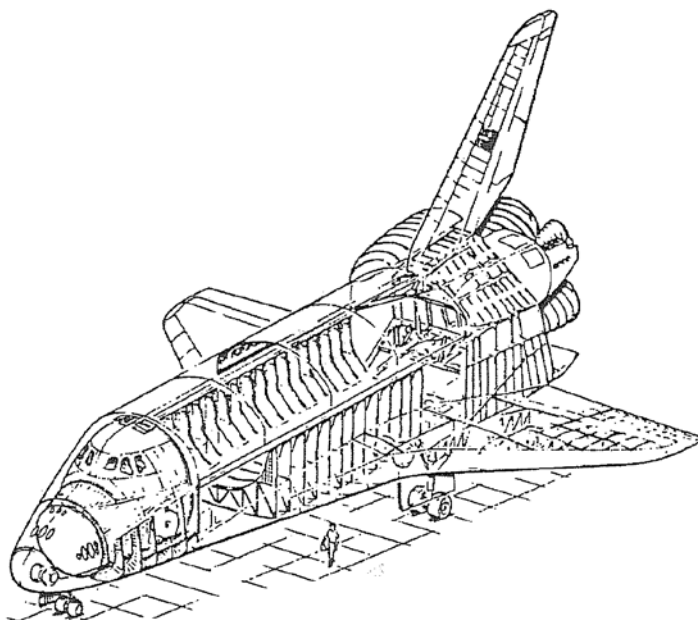
⁶ Excluding weldments

maritime locations). Similarly, equipment and spacecraft frequently have to be stored at these potentially corrosive sites for considerable periods of time. Manned launch vehicles and those spacecraft that return to earth during several missions are often exposed to appreciably corrosive environments.

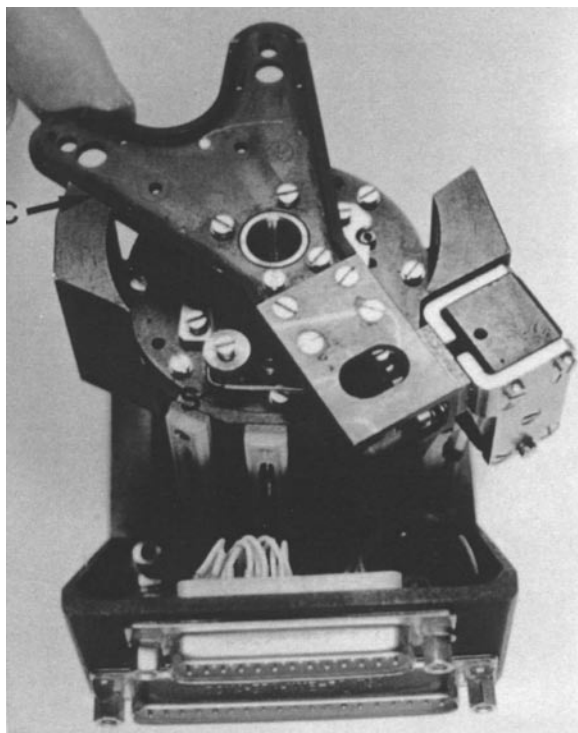
During space flight, the repetitive mechanical contacting of aluminium alloys either with similar materials or with dissimilar materials in vacuum can lead to seizure by cold welding. Mechanisms and parts that suffer from cold welding can include hold-down points, end-stops (Fig. 18.5), bolted/riveted/pinned/keyed or press-fitted areas, couplings, bearings, clutches, spindles and seals; and base plates, universal joints and shackles. Cold welding can result from contact surfaces that impact or fret against each other. Consequently, surface coatings are required to offer functional properties including stability in vacuum, resistance to thermal shocks, UV degradation, debris formation, out-gassing, high humidity, atomic oxygen and dielectric characteristics.



18.3 A view of the International Space Station (ISS). The structural skins of all the modules are constructed from either AA7075 or AA2219. These have been delivered by US, European and Japanese companies (Source: European Space Agency).



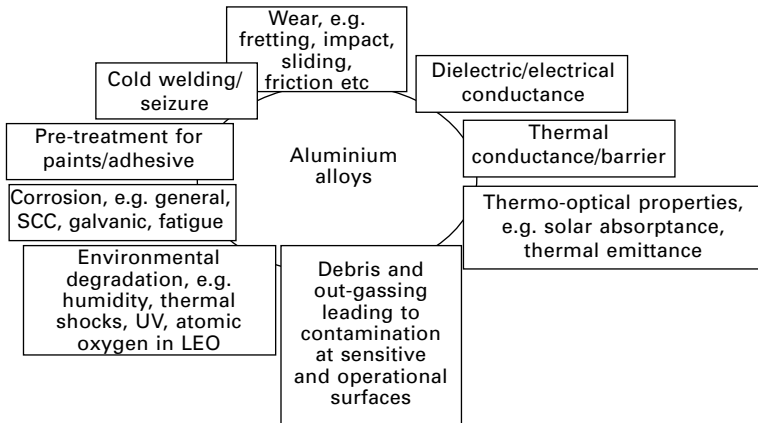
18.4 AA2219 was the major structural material for the NASA Orbiter (Dunn, 1984).



18.5 Mechanism of a satellite anchor malfunctioned due to cold welding (Merstallinger *et al.*, 2003).

18.4 Advanced coatings and multi-functionality

Hard coatings are generally considered to offer protection from corrosion, wear, cold welding and other functional requirements, but due to their generally brittle nature they rarely offer any improvement in strength. In fact, anodic coatings in general reduce the fatigue strength of components and structures. However, if the coating is deemed to protect the aluminium substrate from corrosive pitting or exfoliation, then it can be considered as preventing the premature failure of engineering components as a consequence of the corrosive environment. Spacecraft components require multifunctional properties, as shown in Fig. 18.6, and it is often difficult to achieve these multiple properties from one surface coating type. In this respect, often a variety of surface engineering processes are considered for light alloys, which include anodising, chemical conversion, metallic coatings, thermal barrier, thermo-optical coatings, etc. While a number of existing coatings do offer reasonably satisfactory characteristics, the search for modern and advanced coatings continues with the aim of delivering multi-functionality for use in extremely demanding environments.



18.6 Multifunctional properties required from surface coatings on aluminium alloys used in spacecraft hardware.

18.5 Environmental aspects of engineering components in space

Environmental legislations in the space industry continue to become more stringent with prohibition imposed by EC directive 2002/95/EC on surface finishing for aluminium alloys that uses Cr^{+6} . The most often used corrosion protection layer, a chemical conversion coating that can be easily applied by dipping or painting, is known commercially as Alodine 1200. This layer is used on all aluminium alloys as a base for paint systems, but it does contain Cr^{+6} . While space hardware is still exempted from the Restrictions of Hazardous Substances (RoHS) directive, space agencies such as ESA and NASA are actively seeking to comply with RoHS (Rohr *et al.*, 2008). Recently, extensive studies have been conducted by ESA in order to find suitable chemical conversion coatings that are free from Cr^{+6} . New chemical conversion coating products that comply with RoHS, such as Alodine 5700, Nabutan and Iridite NCP, which have no Cr^{+6} content, have been tested but do not provide suitable protection for spacecraft hardware (Pereira *et al.*, 2008).

Conventional black-anodised coatings with organic dyes used as spacecraft thermal control materials do not have thermo-optical stability after prolonged exposures to a space environment. The recommended black anodising uses nickel sulphide or cobalt sulphide as an inorganic black dye (ECSS-Q-ST-70-03C, 2008) and other chemicals that are quite toxic and considered harmful to the environment. Furthermore, hard anodising techniques employ large quantities of strong acids and, once used, they are difficult to dispose off as they contain high levels of total dissolved solids (TDS). Consequently, there exists a need to identify new coating processes that can meet the requirements

of recent environmental legislations and the desire for increased performance and multi-functionality.

18.6 Most commonly used coating processes for Al alloys

18.6.1 Anodising

Anodising process is covered in greater detail in Chapter 4. This section highlights only some general aspects of the anodising process relevant to space hardware coating. Anodising is an electrolytic process for producing thick oxide coatings, usually on aluminium and its alloys. The oxide layer is typically 5 to 25 μm in thickness and is used to give improved surface resistance to wear and corrosion, or as a decorative layer. During the process, the component to be treated is made an anode in acid solutions normally under DC voltages. Oxidation occurs at the component surface, resulting in the formation of a coherent oxide film that is adherent to the underlying metal substrate. In the space industry, the final objective for many aluminium structures and sub-systems is that they possess black finishes with defined optical characteristics, especially absorption–reflectance ratios (e.g. α/ϵ). Before anodising can be undertaken, the aluminium alloy surface needs to be given a pre-treatment. This pre-treatment will influence the final appearance and properties of the anodised coating. The types of pre-treatment can range from mechanical processes such as abrasive polishing, to chemical treatments such as chemical brightening or electrolytic polishing. In addition, any machining, drilling or welding of the component should be carried out before anodising. Extensive information on anodising and hard anodising can also be found in the literature (Sheasby and Pinner, 2001; MIL-A-8625F, 1993).

One type of electrolyte solution commonly used with the anodising process is a 10–15% solution of sulphuric acid at 25°C. This electrolyte gives a coating formation rate of about 25 $\mu\text{m/hr}$. These conventional anodised coatings are porous and clear, and are normally used with inorganic dyes in applications, for example, to manage passive thermal control on spacecraft for avoiding stray light in optical instruments. Recently, black anodised (following ESA ECSS-Q-ST-70-03C, 2008) 2xxx and 7xxx series aluminium alloys have been reported to have premature failures due to spalling of the anodised coating after thermal cycling. Such coating degradation could generate particulate contamination in satellites and might affect mission lifetime (Goueffon *et al.*, 2009). Black anodising, as a process, is suitable for unalloyed aluminium or alloys with less than, individually, 5%Cu, 6%Zn or 5%Si (ECSS-Q-ST-70-03C, 2008). This means that the alloy type AA2219 with Cu 5.8–6.8% (see Table 18.1) would result in a coating that would not meet the space hardware

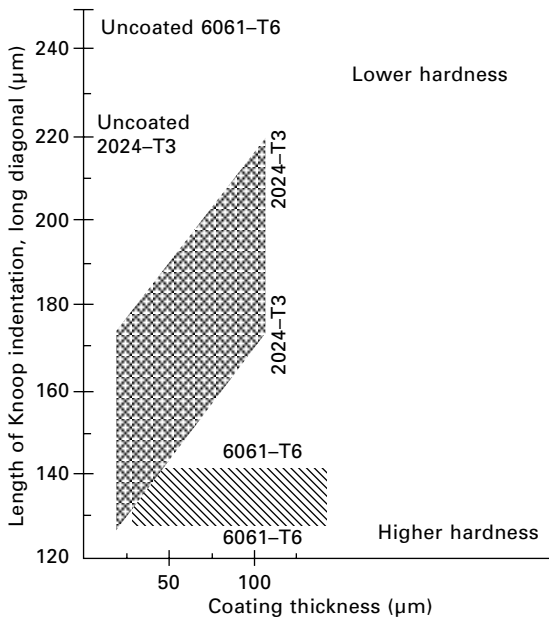
requirements with respect to corrosion, humidity, adhesion and exposures to thermal cycles (Corocher and Martin, 2004). Experience has shown that the alloy AA7075, which has a zinc content close to 6%, can also produce coatings that are of poor quality and are liable to spall off (Goueffon *et al.*, 2009).

'Hard anodising' refers to the preparation of thicker oxide coatings, typically $> 25\mu\text{m}$, with higher hardness of typically 250–500 HV; these are used to give a wear-resistant surface to aluminium alloys, which is achieved by using a sulphuric acid/oxalic acid mixture at higher concentrations and at lower temperatures of about 0–10°C. The coatings produced are grey to black in colour and are less-porous than with conventional anodising. Not all aluminium alloys can be hard anodised. The 5xxx and 6xxx series alloys respond well to hard anodising, whereas 2xxx, 7xxx alloys and others, including casting alloys with high copper and silicon contents, do not. For these higher silicon and copper-containing alloys, the anodised layer tends to be highly porous and of low hardness. For example, the hard anodised coating on an alloyed aluminium such as AA2024/AA7075 will have a hardness of about 250 HV compared to 700 HV for that on a less alloyed material (Wang *et al.*, 2000). Thus, high strength alloys of 2xxx and 7xxx series will have poorer corrosion and wear (impact, fretting, and abrasion) resistance, due to pores and defects in the anodised layer. Coating thicknesses vs Knoop indentation lengths for hard anodised coatings are shown in Fig. 18.7, which shows hardness values for the coating on the AA2024 alloy to scatter over a wide range.

Hard anodising often gives a relatively low cost, wear-resistant coating that can be applied to aluminium alloys and is particularly suitable for protecting against low-stress abrasion. As a result, hard anodised coatings are frequently used with aluminium components in sliding systems. These coatings also have some use for protecting aluminium components that experience fluid-assisted wear, slurry erosion, solid particle erosion and liquid erosion. They are also resistant to many chemicals with the notable exception of alkalis. Anodising is not used for impact wear applications due to the brittle nature of the coating.

18.6.2 Plasma Electrolytic Oxidation (PEO)

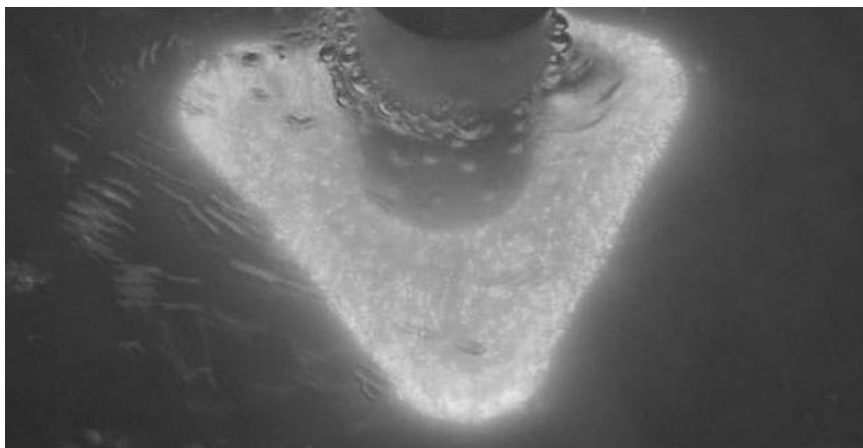
Details on fundamentals, processing, properties and general applications of PEO coatings are covered in Chapter 5. This section highlights some basics of PEO that are relevant, in general, to space applications. PEO is an emerging technology and offers versatility in terms of coating a range of aluminium alloys, including those with high Cu, Zn or Si content in all forms, such as cast, extrusions and sheets. There are some similarities between the anodising and the PEO processes, since both are electrolytic bath processes



18.7 Hard anodised coating thickness vs Knoop indentation length (Sheasby and Pinner, 2001).

that involve oxidation of the substrate. However, the similarities end there. Major distinctions remain in the use of electrolyte formulations, electrical parameters, co-deposition from the electrolyte and the presence of genuine plasma chemistry at the surface of the part. The PEO process results in the formation of primarily crystalline-based ceramic coatings. The term ‘ceramic’ comes from the Greek word ‘keramikos’, which means ‘burnt stuff’, and its use indicates that enhanced properties of PEO coatings similar to that of ceramics are achieved through high-temperature of plasma chemical reactions in a specially formulated electrolyte where discharge temperatures of around 10 000°C have been reported (Yerokhin *et al.*, 1999). On one hand, electrolyte constituents are important which allow complex interactions such as ionic, charge and mass transfers to occur, resulting in the formation of specific oxides/phases. On the other hand, electrical parameters such as voltage, frequency, current, pulse shape and time, play important roles in the subsequent voltage breakdown, local melting and oxidation of the substrate, molten pool formation, quenching and re-crystallisation processes.

Coating of aluminium alloys by plasma electrolytic oxidation involves the creation of a plasma discharge around a component immersed in an electrolyte (Fig. 18.8), most successful being alkaline types but also can be extended to various acidic forms (Yerokhin *et al.*, 1999). Compositions and concentrations of the electrolyte constituents are proprietary to the



18.8 Plasma electrolytic oxidation of a component immersed in electrolyte.

commercial companies, such as Keronite International Ltd, and are often reported to be of low concentration alkaline type of typically < 4% of total dissolved solids (TDS). However, there are a growing number of research publications where various salt compositions have been reported (Yerokhin *et al.*, 1999; Suminov, 2005; Rama Krishna *et al.*, 2006; Curran and Chyne, 2006; Godja, 2009). Obviously, secret to the formation of optimised coatings and successful industrial exploitations will include: electrolyte recipe with long electrolyte life and electrical process parameters, followed by other engineering aspects such as jiggling techniques, electrolyte flow management, and counter electrode management. The mechanism of oxide layer formation during the PEO process represents complex combinations of oxide growth, with subsequent fusing and re-crystallisation of the oxide film, and also involves partial substrate metal dissolution at microscopic levels. While the PEO process can be considered very aggressive due to occurrence of extensive plasma discharges on the surface and oxide eruptions at very high local temperatures and pressures ($T \sim 10^4^\circ\text{C}$ and $p \sim 10^2$ GPa, Yerokhin *et al.*, 1999), these discrete processes occur at microscopic levels and the treated component, including the working surface, encounters negligible heat-affected zones or distortion. The process temperature and the component are typically in the range of 12–30°C. The resulting oxidation of the alloy surface can also include some elemental co-deposition from the electrolyte, creating a ceramic layer that contains both crystalline and amorphous phases. Typical process parameters during the Keronite PEO and hard anodising/black anodising of AA7075 alloy are given in Table 18.3. A summary of key advantages and disadvantages of the PEO process against hard anodising and plasma spray ceramic is given in Table 18.4.

Table 18.3 Typical process parameters during Keronite PEO and hard anodising/black anodising of AA7075 alloy

Coating process	Aluminium alloy	Pre-treatment	Coating electrolyte	Total salt content (%)	Typical pH	Nominal thickness (μm)	Coating rate ($\mu\text{m}/\text{min}$)	Voltage (V)	Current density (A/dm^2)	Process temp ($^{\circ}\text{C}$)	Post-treatment	Coating formation method	Surface appearance
Keronite PEO (AC)	7075	Often degrease only is sufficient	Proprietary alkaline free of Cr, V, Ni or other heavy metals	< 4	7–12	15–60	1–4	200–900	Up to 30	12 to 30	Rinse/dry/seal with silicate/sol-gel	Plasma oxidation	Grey to charcoal black natural
Hard Anodising (DC)	7075	Degrease and chemical clean in alkaline solution	Sulphuric acid H_2SO_4	15–20	< 3	< 60	0.8–1	45–50	1–2	–10 to 0	Hot water seal	Oxidation without plasma	Bluish black natural
Black Anodising (DC)	7075	Vapour degrease in trichloro-ethylene, etching in trisodium phosphate+ sodium carbonate at 90–95 $^{\circ}\text{C}$, rinsing, deoxidising in nitric acid, rinsing	Sulphuric acid H_2SO_4	12–18	< 3	25–35	< 1	~ 50	1–2	25 $\pm$ 1	Cobalt acetate or nickel acetate solutions	Oxidation without plasma	Black obtained by inorganic dye

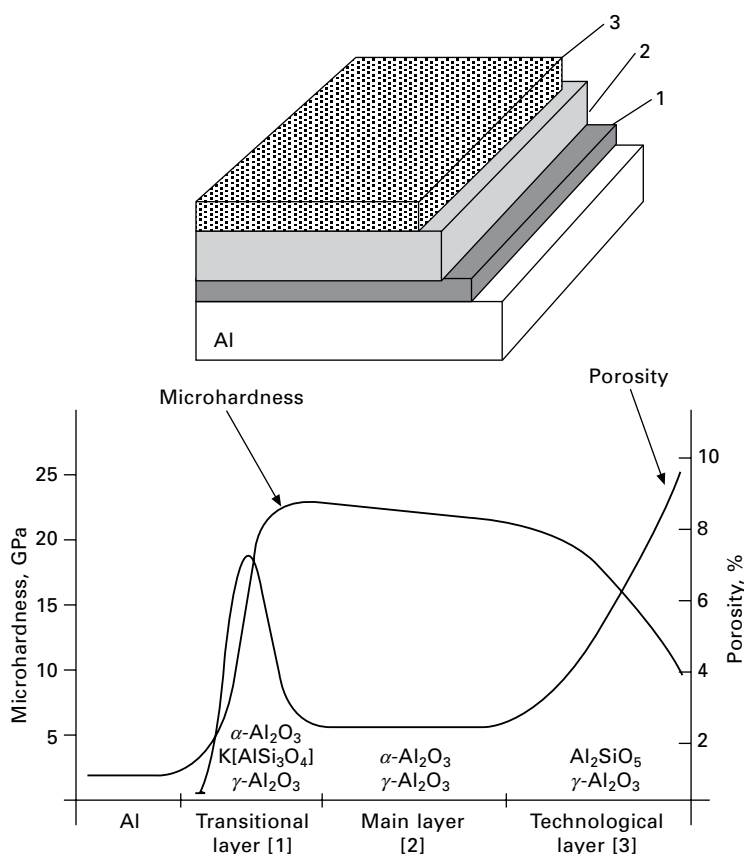
Table 18.4 Key advantages of PEO vs hard anodising and plasma spray Al₂O₃ on Al alloys

	PEO vs hard anodising	PEO vs plasma spraying
Advantages	– Higher micro-hardness and wear resistance – Higher corrosion resistance – Suitability for a wide range of aluminium alloys including higher Cu (>5%) and Si (up to 25%) contents – Possibility to ensure uniform layer thickness for complicated surfaces – Room temperature process (electrolyte operational temperature in a range of 10–30°C) – Faster coating speed/oxidation rate – Possibility of retaining initial dimensions of the treated parts – Minimal requirements of preliminary preparation of surface before coating – Environmentally friendly due to use of ecologically safe electrolyte that contains no heavy metals – No cracks around corners or sharp radius	– Much higher adhesion because the coating is formed due to oxidation of the substrate alloy – No requirement of surface preparation e.g. by grit blasting – Possibility to ensure uniform layer thickness for complicated surfaces – Possibility to coat inner surface, holes and geometries with restricted access – Possibility to coat sharp corners – Investment costs are less than plasma spraying
Disadvantages	– Higher equipment costs – Supplied as proprietary electrolyte and machinery – Higher production costs for low volume applications	– Process limited to light alloys only whereas plasma spray is suitable for most substrate materials

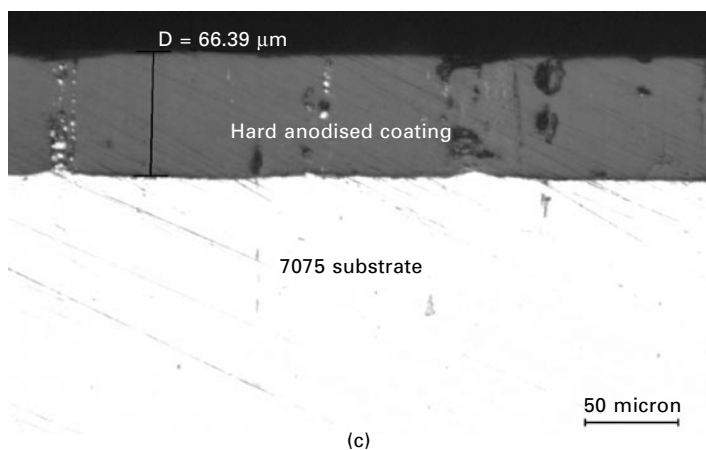
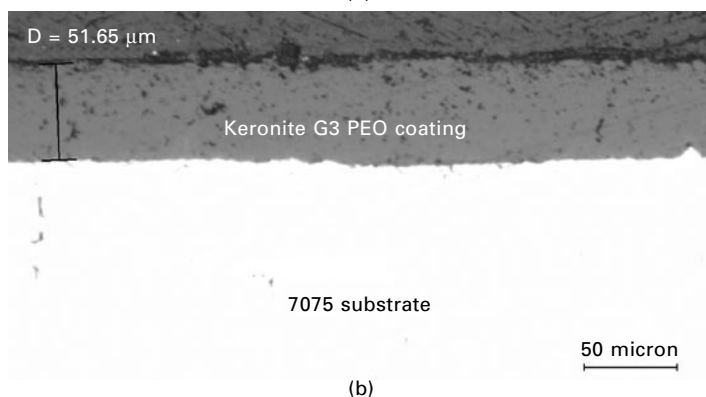
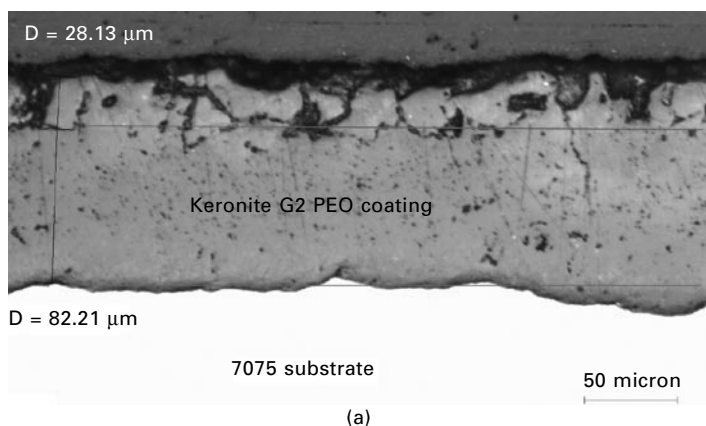
18.7 PEO and anodised coating characteristics and properties

18.7.1 Coating structure

Structural studies typically show three distinct regions in the coatings produced on aluminium alloys by the PEO technique. A schematic representation of such a coating type is shown in Fig. 18.9 and optical microscope images of the PEO coating on AA7075 alloy are shown in Fig. 18.10a. The outer region, which possesses the highest porosity and lower hardness, often referred to as the 'technological layer', can present 5–40% of the total coating thickness and is typically comprised of fused ceramic α - Al_2O_3 and other compositions formed from the electrolyte. Often for applications involving wear, this layer is removed by polishing or honing. Under the technological layer is



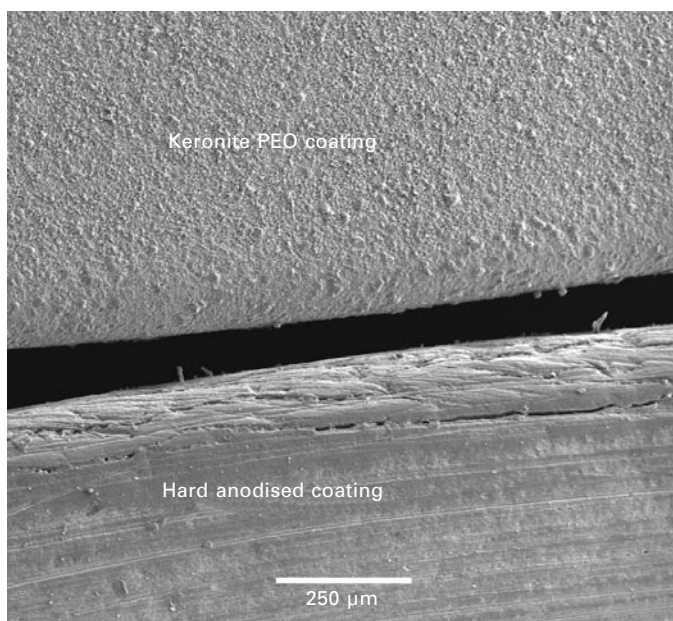
18.9 Schematic representations of PEO coating structure and microhardness. (Suminov *et al.*, 2005).



18.10 Evolution in the PEO coating technology: (a) G2 (Lower frequency) technology showing porous technological layer and a more roughened/etched substrate; (b) G3 (Higher frequency) technology with almost no technological layer; (c) hard-anodised coating showing large and through-thickness pores and residual intermetallic particles within anodised layer.

a middle region, with finer microstructure, referred to as the 'main layer' or 'working layer', which possesses the highest hardness and comprises primarily α -Al₂O₃ and γ -Al₂O₃. A very thin layer lies immediately above the substrate interface region and is called the 'transitional' or 'barrier' layer; that is extremely well adhered to the base material. The relative sizes of the various layers, their structure, porosity, composition and hardness are influenced by substrate composition, electrolyte composition and electrical process parameters/power supply. Advanced versions, such as the Keronite G3 (higher frequency) technology can produce PEO coatings that are much denser and have almost no technological layer (Fig. 18.10b). Also, these newer modules are capable of producing coatings with near 100% inward growth, thus maintaining the initial part dimension and needing only minimal post-finishing requirements. Older versions, such as G2 (lower frequency) technology, typically result in 50/50 outward/inward coating growth and need post-finishing, e.g. polishing, honing requirements such as a cross-section shown in Fig. 18.10a. A sulphuric acid, hard anodised coating on the same AA7075 alloy is shown in Fig. 18.10c, with an abundance of defects and larger pores. Porosity levels of up to 40% for hard anodised coatings have been reported elsewhere (Rama Krishna *et al.*, 2006; Sheasby and Pinner, 2001). Further discussion concerning the coating structures can be found in Chapter 4.

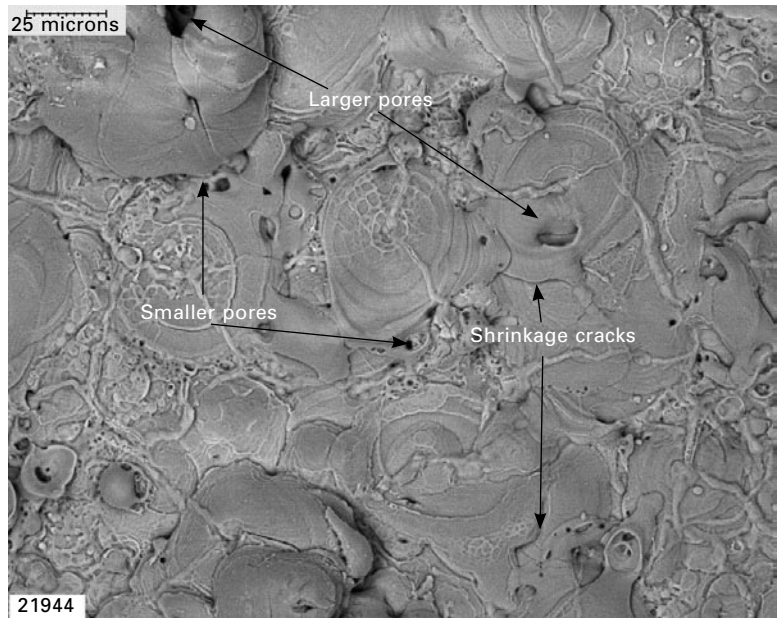
An SEM image of an as-prepared surface of a PEO layer is presented in Fig. 18.11, which shows an abundance of spherical and irregular-shaped particle-like structures formed during the PEO process. A higher magnification SEM image of a PEO coating on AA6082 alloy (Fig. 18.12) is typical of this coating type, with the top surface containing an abundance of fused ceramic grains in circular and semi-circular shapes. These are formed by quenching of erupted molten pools, and the subsequent formation of smaller and larger-scale pores, and shrinkage cracks. As-prepared surface roughness values of $\sim 1\text{ }\mu\text{m Ra}$ down to $<0.5\text{ }\mu\text{m Ra}$ with certain electrolyte types for a 20–30 μm coating thickness are achievable for the PEO coatings on aluminium alloys. The layer contains some micro-scale porosity, as would be expected from the PEO process, but the coating can be considered relatively dense. An as-prepared surface of the hard-anodised layer (Fig. 18.11) shows edge problems in the form of parallel lines that form vertical through-thickness cracks. A typical cross-section of the PEO coating on AA7075 alloy at the outer corner/edge is shown in Fig. 18.13a. A typical cross-section of a hard-anodised layer on the same alloy (Fig. 18.13b) shows the presence of extensive 'V-shaped' and 'columnar' cracks. These cracks are seen through the entire coating thickness and extend down to the underlying substrate, and in several areas even expose the bare metal substrate.



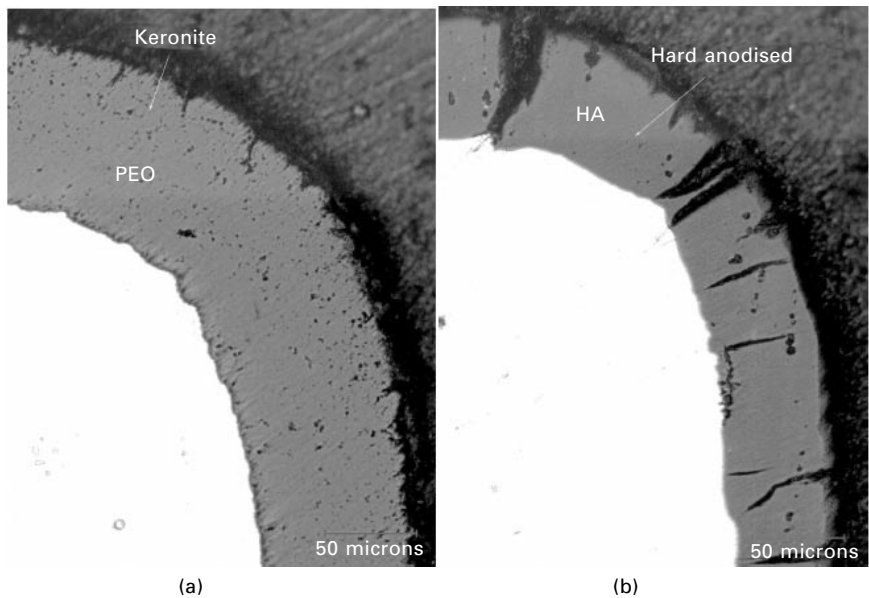
18.11 SEM image showing a sharp edge/corner of the coating on AA7075: (top) good and uniform coating retention with the Keronite PEO layer; and (bottom) wide-opening cracks with the hard anodised layer. Also the hard anodised mimics the machining lines of the underlying substrate.

18.7.2 Mechanical properties

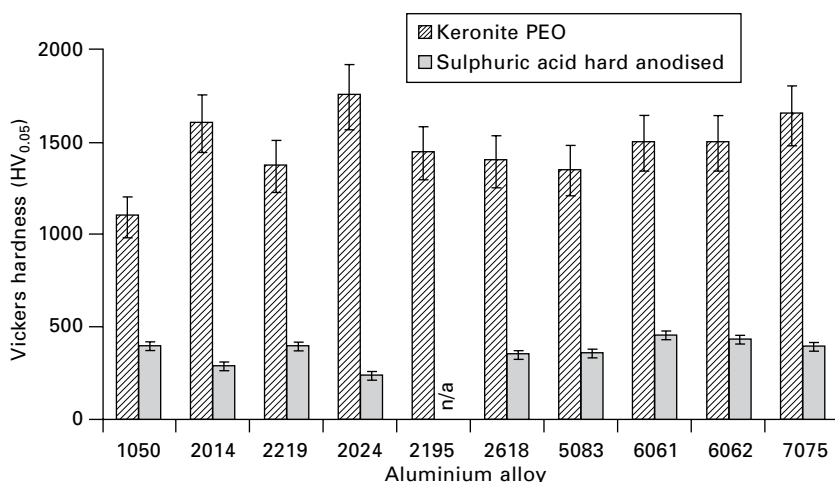
Aerospace and spacecraft components require high-quality surface finishes that are able to survive operational environments. These need to be manufactured with processing procedures that provide for consistent, reproducible service characteristics. Meeting such requirements is possible with thick oxide coatings of up to 100 μm thickness with low porosity and low roughness – achievable by the PEO process. Considerably higher thickness coatings are also possible but these are often of little use for most engineering applications due to production time, costs and deterioration in the coating quality. A layer thickness of 50–100 μm and of very high hardness tends to offer very good load support. High hardness of the PEO coatings is one of the key features that make the technology attractive where performance and durability are critical. The hardness of PEO coatings can be three to five times higher than that of hard anodised coatings, with greater differences seen on alloys such as 2xxx and 7xxx series. Some hardness values of the PEO and the sulphuric acid hard anodised coatings on various aluminium alloys are given in Fig. 18.14. Obviously, such high hardness of the PEO coatings can be expected due to the presence of a primarily crystalline Al_2O_3 .



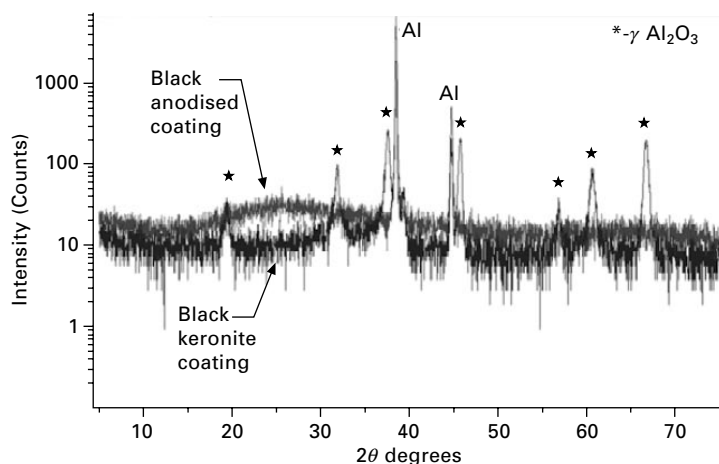
18.12 Secondary electron SEM image of Keronite PEO surface on AA6082 alloy showing fused ceramic layer with micro-scale $<2\text{ }\mu\text{m}$ and some larger-scale $5\text{--}10\text{ }\mu\text{m}$ size porosity and shrinkage cracks formed during the PEO process.



18.13 Optical micrographs of: (a) Keronite coating showing a uniform coating coverage and good edge retention; and (b) hard anodised coating showing extensive V-shaped through-thickness columnar cracks extending down to the substrate on the edge.

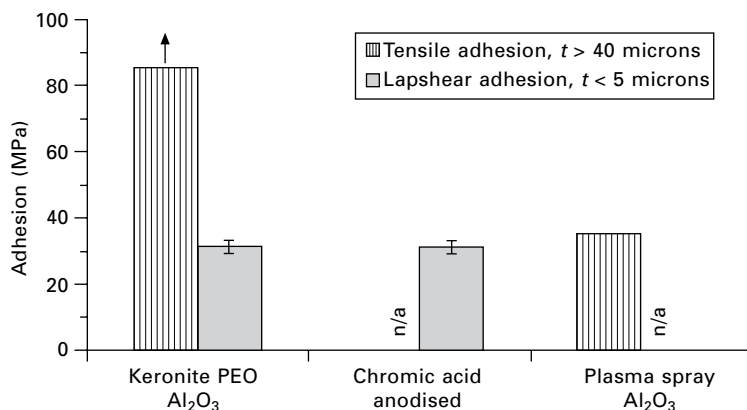


18.14 Micro-indentation hardness values of PEO and sulphuric acid hard anodised coatings on various aluminium alloys.



18.15 XRD patterns of the Keronite PEO coating showing the presence of crystalline γ - Al_2O_3 and hard anodised coating showing the presence of amorphous alumina.

phase content, compared with the entirely amorphous phase present in the hard anodised coating (Fig. 18.15). In addition, oxidation of the base metal itself results in the PEO coatings having a very high bond strength. Tensile bond strengths of typically 40 μm PEO coatings have been found to exceed 80 MPa, which is significantly higher than those of plasma sprayed Al_2O_3 on aluminium substrates. Lap shear strengths of thinner PEO coatings (<5 μm) are typically around 25 MPa, which is similar to those of chromic acid anodised coatings (Fig. 18.16).



18.16 Bond strength of PEO coatings measured following the ASTM-C633-01 (2008) standard.

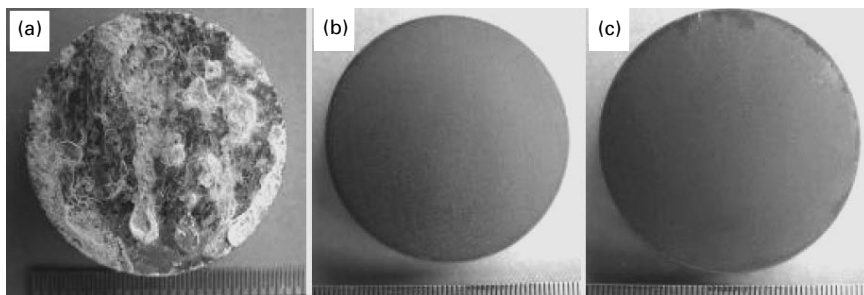
18.7.3 Resistance to environmental exposures – corrosive, humidity, UV and thermal shocks

Spacecraft structural components and sub-systems can degrade during many phases of their lifetimes. At the launch pads at both the Kennedy space centre and the French Guiana site, there is exceedingly high chloride contamination due to the seacoast environments. During the launch, there is exceptionally high exposure to vibrations and acoustic noise. And finally, in space, all surfaces are exposed to thermal cycling under vacuum as the spacecraft is heated by the sun then cooled in eclipse. Such temperature excursions can be between -50°C and $+150^\circ\text{C}$.

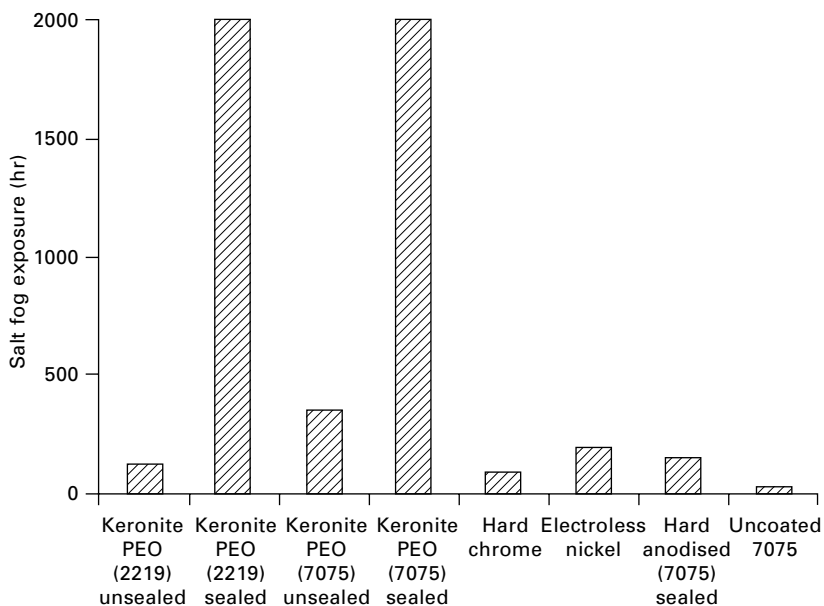
Hard anodised coatings require inorganic colorant/sealer for use in an UV environment and such finish can only be achieved using inorganic dyes that have environmental issues. PEO coatings do not require dyes e.g. for obtaining black ceramic surface finishes on aluminium alloys. Such black PEO coatings have been tested and reported to offer very good resistance in UV, humidity and thermal shock environments (Shrestha *et al.*, 2003). Such stability to environmental exposures can be expected from PEO ceramic coatings owing to the fine-scale porosity and high concentration of shrinkage cracks, which create a relatively low global stiffness for PEO coatings (an order of magnitude lower than that of fully dense alumina). The resulting low residual stress (Curran and Clyne, 2006) and very high adhesion of the PEO coatings make them resistant to severe thermal shocks. The corrosion resistance of sealed, hard-anodised coatings is generally good and can meet the salt fog corrosion resistance of maximum to about 160 h for the Cu-containing alloys such as AA7075, whereas the PEO coatings perform much better on similar alloys (Shrestha *et al.*, 2003, 2006). Such superior corrosion resistance can be expected from PEO coatings due to a

denser coating microstructure and the electrochemically neutral nature of the ceramic layer with respect to the underlying substrate. This is especially marked at corners and edges due to a uniform coverage of the corners and edges, whereas hard-anodised coatings are well known to fail prematurely due to the above-mentioned truncated and widely opened 'V' and through-thickness cracks, as shown in Fig. 18.13.

A typical salt fog resistance of PEO vs hard anodised coatings is shown in Fig. 18.17. The data in Fig. 18.18 demonstrate the good corrosion resistance



18.17 Surfaces of (a) uncoated; (b) sealed Keronite PEO; and (c) sealed hard-anodised coating after 25 thermal shocks between -196°C and $+100^{\circ}\text{C}$ followed by 360 h of salt spray exposure.

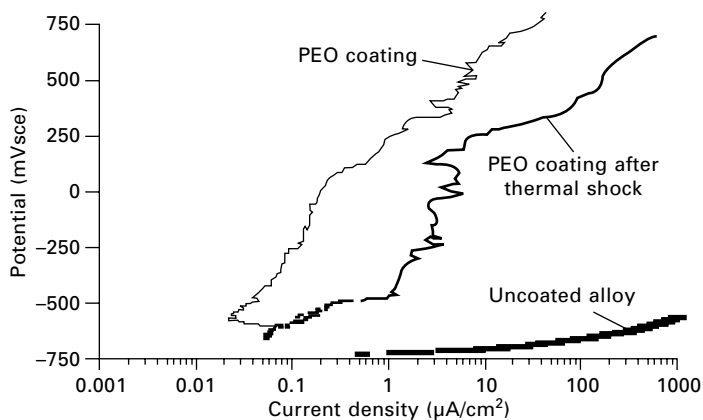


18.18 Corrosion resistance of the coating without damage to the coating (subjective rating as per ASTM D1654 to 9*) in a 5 wt% salt fog environment.

of PEO and anodised coatings on 2xxx or 7xxx series aluminium alloys, which otherwise have inherently poor corrosion resistance. The corrosion behaviour of PEO coatings on AA2219 alloy has been also demonstrated by electrochemical studies, as shown in Fig. 18.19. The very poor corrosion resistance of the uncoated alloy was shown by an active response (seen as rapid increase of the current density) upon shifting the potential just a few milli-volts in the positive direction from the rest potential. The as-prepared coatings demonstrated very high corrosion resistance, followed by the coating surfaces that had undergone 50 thermal shocks, as shown by their passivity, i.e. very small current densities of $<0.3 \mu\text{A}\cdot\text{cm}^{-2}$ and $<7 \mu\text{A}\cdot\text{cm}^{-2}$ respectively. The coating started to display signs of passivity breakdown at potentials significantly higher than the free corrosion potential.

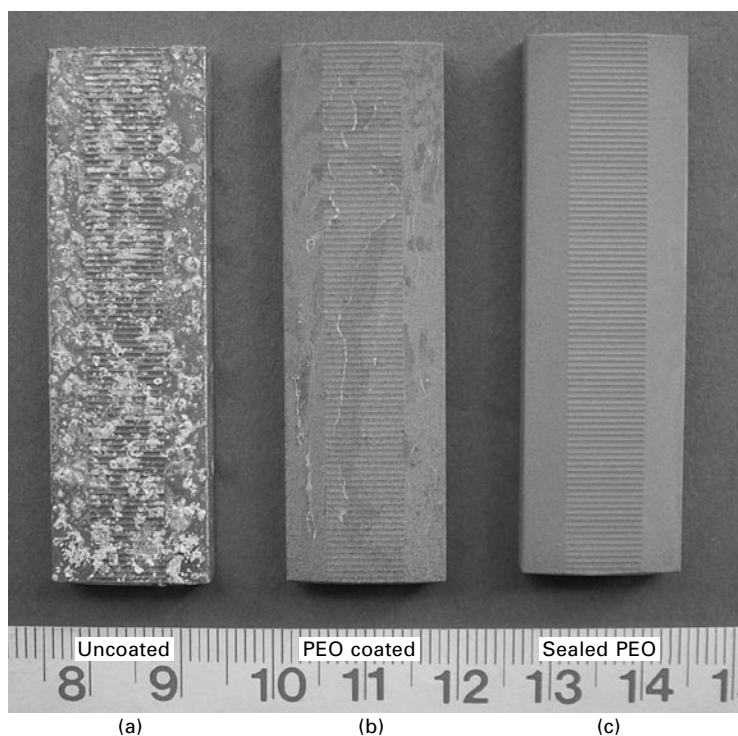
18.7.4 Fatigue and corrosion fatigue

As stated in the previous section, spacecrafts during launch are subjected to high vibrational loads that can lead to the fatigue failures of aluminium alloy structures. Hard anodising can reduce the fatigue strength by up to 50%, with the columnar cracks considered partly responsible by acting as stress raisers. While there are not many published data available, it is often mentioned that fatigue reductions with PEO coatings are substantially lower. Rotating bending tests with Keronite PEO coated AA7075 alloy had a fatigue reduction of $< 15\%$ (Poeton, 2008) and of $< 10\%$ for Keronite PEO treated Mg alloys (Yerokhin *et al.*, 2004). The fatigue problem is even worse when corrosion is present and this results in substantially premature failures due

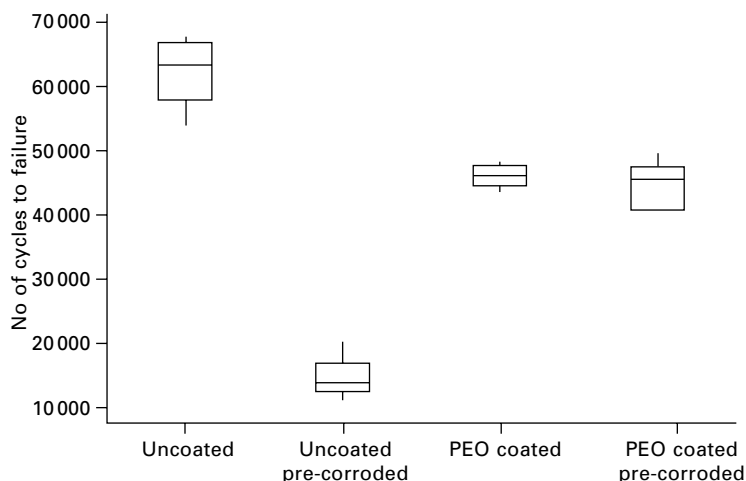


18.19 Electrochemical corrosion behaviour of the Keronite PEO coating on AA2219 alloy in as prepared condition, after 50 thermal shocks (-193°C liquid nitrogen and $+100^\circ\text{C}$ boiling water) and the uncoated alloy.

to the corrosion-initiated pitting of engineering components. Surfaces of 2xxx series aluminium alloy after 24 h exposure to 5wt% atomised NaCl fog to ASTM B117, shown in Fig. 18.20, clearly indicates that significant corrosion protection is offered by a thin layer of PEO coating. Three-point bending fatigue test results of the uncoated; the uncoated + pre-corroded (24 h salt fog); the PEO coated; and the PEO coated + pre corroded (24 h salt fog) specimens are shown in Fig. 18.21. The Y axis on the box plots is the number of cycles to failure and the distribution of the whole test population is represented by the vertical line. The box represents 50% of the population (i.e. from the 25th percentile to the 75th percentile) while the line in the middle is the median line (i.e. the 50th percentile). The plots in Fig. 18.21 show that the fatigue life after corrosion significantly drops for the uncoated samples while for the PEO coated sample the fatigue life remains very similar, showing that the exposure to corrosion does not affect the fatigue life when the coating is present. However, some fatigue reduction due to the coating was evident when compared to the uncoated alloy.



18.20 Surfaces of (a) uncoated 2xxx series Al-alloy fatigue test specimens showing extensive corrosion; (b) Keronite 5–7 μm thickness coated (with mild corrosion); and (c) Keronite 3–5 μm sealed (with no visible corrosion), after 24 h of exposure to a 5 wt% atomised salt fog environment to ASTM B117.



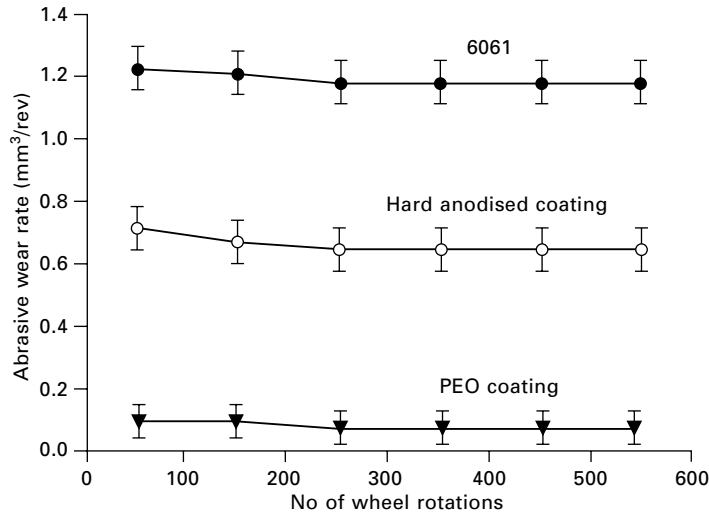
18.21 Box plot data showing number of cycles to failure for fatigue samples (alloy 2xxx series): uncoated, uncoated + pre-corroded, PEO coated, PEO coated + pre-corroded. Pre-corrosion means 24 h of exposure to a 5 wt% atomised salt fog prior to fatigue tests.

18.7.5 Wear and friction

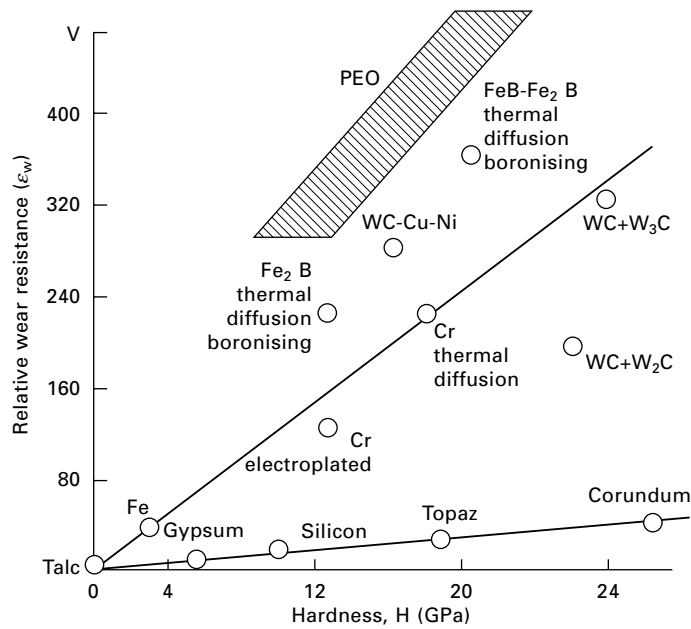
The very high hardness of the PEO ceramic accompanied by fine-scale porosity (Curran and Clyne, 2006) and low global stiffness ($E \sim 30\text{GPa}$, Curran and Clyne, 2005) offer these coatings superior abrasive wear resistance when compared to hard-anodised coatings (Fig. 18.22), comparable to that of WC-based composites, boride diffusion coatings and corundum (Fig. 18.23).

The friction coefficients of PEO coatings on Al-6%Mg alloy against carburised or nitrided steel in lubricated reciprocating sliding wear tests under extreme pressures (from $\sim 222 - 2923\text{ MPa}$) were reported to be ~ 0.15 over 150 m of sliding distance (Dearnley *et al.*, 1999). The authors also reported that, even when the maximum sub-surface shear stress was located beneath the coating layer, and was sufficient to cause plastic deformation of the aluminium alloy, no collapse of the coating took place.

The friction coefficient of ceramic-to-ceramic in an un-lubricated condition is usually high, and for the Keronite PEO coating against itself has been reported to be about 0.5–0.6 (Shrestha *et al.*, 2003). Such high friction can be substantially reduced to an extremely low value of about 0.04 by impregnating the porosity in the coating with, for example, solid lubricants. Keronite PEO composite coatings where the natural pores that are present in the PEO coating are impregnated with solid lubricants such as MoS_2 or PTFE have been developed to provide tribological surfaces with very low sliding friction coefficients, maximum resistance to wear, minimum debris generation, vacuum compatibility, resistance to thermal shock and with



18.22 Volumetric abrasive wear rate of PEO and hard-anodised coatings in comparison with AA6061 alloy at 1 N normal load (Rama Krishna *et al.*, 2006).



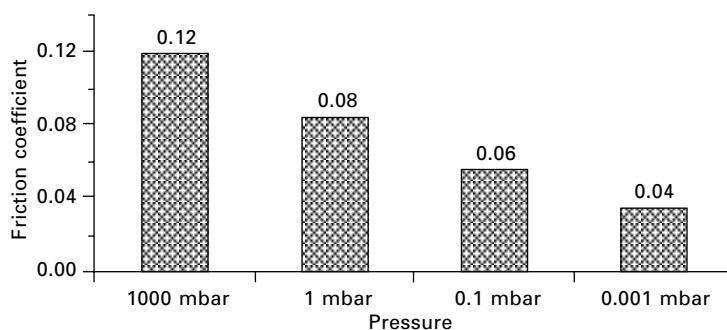
18.23 Relative wear resistance (ϵ_w) diagrams for some materials in respect to talc. (Yerokhin *et al.*, 1999, Elsevier).

thermal conductivity better than plastics (Fig. 18.24). Recently, Instituto de Astrofísica de Canarias (IAC) and Keronite have undertaken a co-operative research on cryogenic, plain sliding bearings.

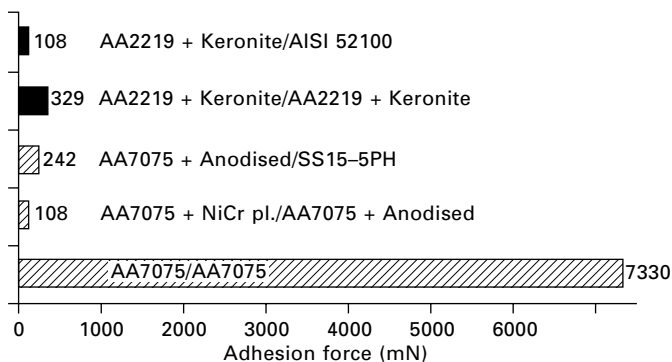
18.7.6 Fretting, impact and cold welding in vacuum

On spacecraft, a variety of engineering mechanisms exhibit ball-to-flat surface contacts, which are periodically closed and opened several thousand times. Vibrations occurring during launch or during movement of, e.g. antennas in space, can lead to small oscillating movements in the contact area, which occurrence is referred to as ‘fretting’. This ‘fretting’ movement can eventually degrade the space mechanism’s surface layers, whether they are natural oxides, chemical conversion films or even metallic coatings. The lateral motion causes severe destruction of the contact areas, resulting in an increase of adhesion forces between the mating parts. In turn, this dramatically increases the tendency of these contacting surfaces to experience ‘cold-welding’ (i.e. adhesion or galling), which may lead to eventual failure of the space mechanism (Merstallinger *et al.*, 2003).

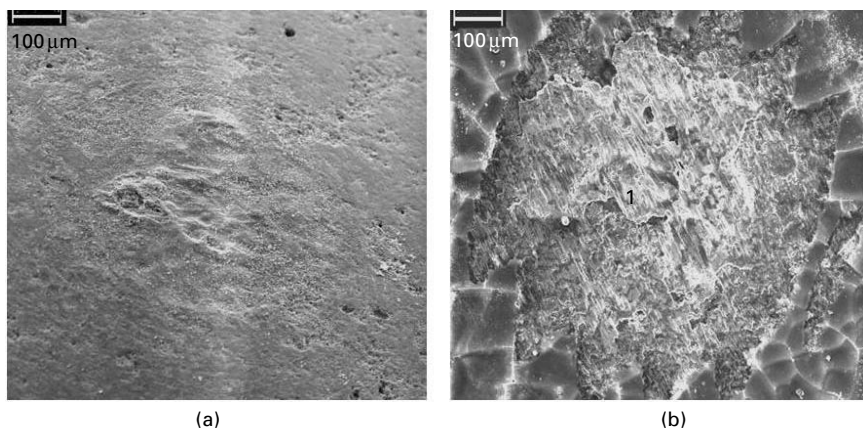
The Keronite PEO ceramic surface on AA2219 alloy, after fretting tests against a 52100 steel ball in vacuum, was shown to have very low adhesion (Fig. 18.25). Adhesion values of the Keronite PEO coated AA2219 against a 52100 steel ball and of NiCr plated AA7075 against an anodised AA7075 are similar. An aluminium alloy without a coating results in extremely high adhesion after fretting. The Keronite PEO coating surface against itself displayed a higher adhesion than against a steel surface by about three times. Despite the low adhesion values displayed by the Keronite and hard anodised coatings against steel surfaces, the Keronite PEO coating displayed superiority over the anodised coating in terms of surface wear. The Keronite PEO coating showed no sign of surface damage, whereas the anodised



18.24 Friction coefficient of Keronite PEO composite coating after sliding wear tests in a cryogenic environment (Shrestha *et al.*, 2006).



18.25 Adhesion measured during fretting tests. (Merstallinger *et al.*, 2003).



18.26 Surface after fretting test of: (a) Keronite coating (no visible damage); and (b) anodised coating (showing extensive surface cracks).

coating displayed extensive cracking and chipping of the coating surface in a fretting environment. The differences in the damage mechanisms between the Keronite PEO and anodised coating surfaces are shown in Fig. 18.26.

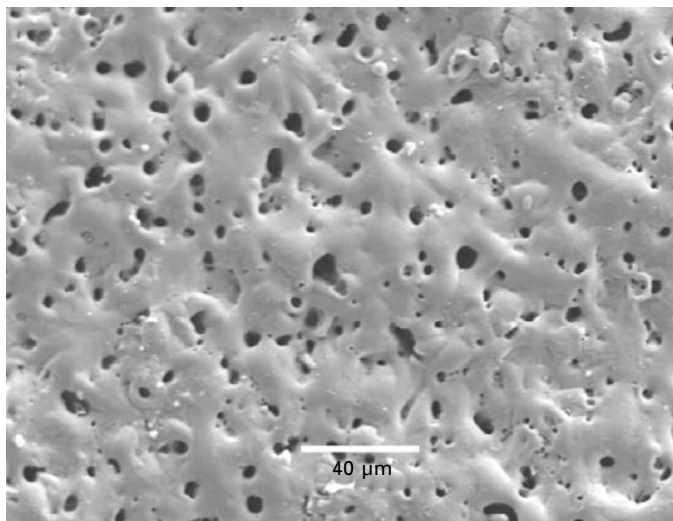
18.7.7 Thermo-optical properties

Spacecraft and scientific instruments usually contain electronic hardware, including sensitive detectors that require good thermal management (see also Section 18.3) Thermal control coatings, thermal blankets and electric heaters are some methods used to control component temperatures in space. The operating temperature of a spacecraft is determined by the direct heat input from the sun, the reflected solar energy from the earth, the background

temperature of space, the internal heat generated by the spacecraft and the emittance and absorptance of spacecraft surfaces. Predicting the operating temperature of the spacecraft therefore requires knowledge of the thermal properties (absorptance and emittance) of the coatings used. In addition to these basic requirements, it is usually necessary to be aware of other spacecraft requirements such as spacecraft charging, and particulate and molecular contamination requirements, in order to choose the proper thermal control coating. It is also important to know how the coating properties will degrade throughout the life of the spacecraft due to exposure to UV, high energy protons and electrons, low energy solar wind protons, and contamination from other parts of the spacecraft. The practice for the selection and application of thermal-control coatings includes data on absorptance and emittance of particular thermal-control materials (Anon., 1995), which are determined and verified by testing in space-simulated environments to various standards, e.g. ECSS-Q-ST-70-09C, 2008.

The colour, surface roughness and the thickness of the coating can have significant effect upon its emittance and absorptance, in addition to its degradation in space conditions. Black anodised coatings prepared by the incorporation of inorganic dyes (Ni acetate/Co acetate) do not have stable thermo-optical properties upon exposure to space environments. Plasma electrolytic oxidation offers unique opportunities to create optically black coatings on a variety of aluminium alloys in relatively benign electrolytes.

Keronite PEO coatings on Cu-containing aluminium alloys, such as 2219 and 7075, are grey black, and these have been extensively studied by ESA as thermal-control coatings. Such coatings have high absorptance ($\alpha \geq 0.8$) and emittance ($\epsilon \geq 0.7$), and these values remain stable after exposure to a variety of simulated space conditions. However, this process is limited to alloys containing high Cu. Recently there has been growing interest within space industries for black-finish coatings on other aluminium alloys. Keronite International Ltd. has recently developed an industrial-scale new PEO process capable of producing a charcoal black finish on most wrought and some cast aluminium alloys. Unlike the standard PEO process, this new process converts the aluminium alloys into a black finish and the resulting surface characteristics and properties are not dependent on the substrate alloy composition or on any post-dyeing. Also, the new black PEO coatings have higher absorptance ($\alpha \geq 0.9$) and emittance ($\epsilon \geq 0.8$). This coating surface also has a very low reflectance of $<0.1\%$. This reflectance value is less than the reported reflectance values for super black Ni-P coating and is significantly less than that for a black sulphuric acid anodised coating and black paints. A typical SEM image of this new black Keronite surface is shown in Fig. 18.27, and some properties of the various PEO coatings and the anodised coatings are shown in Table 18.5.



18.27 SEM image of black Keronite on AA6060 alloy showing coating surface morphology with crater-like porosity.

18.8 PEO applications

Keronite PEO coatings have been extensively evaluated by ESA for spacecraft material applications as thermal-control coatings. Studies have been made also for cryogenic bearing applications (Fig. 18.28) and for satellite optical equipment (Fig. 18.29), with extremely good results. Several other studies for various space and aerospace applications are currently underway on Keronite PEO coated parts including sun sensors (Figures 18.30 and 18.31). Centre National d'Etudes Spatiales (CNES), ESA, University of Southampton and Office National d'Etudes et de Recherches Aérospatiales (ONERA) have participated in a cooperative effort to develop a test-bed called the Material Exposure and Degradation Experiment (MEDET). Keronite coated thermal-control micro-calorimeters are now mounted on the MEDET flight hardware (Fig. 18.32) that is located on the external payload facility of ESA's Columbus Laboratory on the International Space Station (ISS) since February 2008 (Duzellier *et al.*, 2008).

18.9 Summary

PEO technology is already in use for a number of high volume/low cost applications and as a replacement for hard anodising. Also, from the preceding sections in this chapter, it can be seen that this technology does offer unique benefits for high-performance space components and piece parts. In similar applications, hard anodising would not meet similar stringent requirements.

Table 18.5 Characteristics of Keronite PEO and anodised coatings on aluminium alloys

Coating type	Alloy	Colour	T (μm)	S ($\mu\text{m}/\text{min}$)	Ra (μm)	P (%)	XRD	(HV _{0.05})	SS (hrs)	(α_S)	(ϵ_n)	R (%)	UV	VO (TML %)	TSR –196 to +100°C	Other features	Environmental impact
Keronite black Type 1	2219-T6	Grey to charcoal black	max.60	1–2	1–1.6	<5	Mostly crystalline alumina	1200–1550	> 360	0.88–0.89 ¹	0.71–0.75	–	Pass	–	Yes	Easily coatable	None
Keronite black Type 1	7075-T6 /T7351	Grey to charcoal black	max.60	1–2	< 1	<2	Mostly crystalline alumina	1600–1650	> 360	0.81–0.83 ²	0.70–0.72	–	Pass	< 0.1	Yes	Easily coatable	None
Keronite black Type 1	2195	Charcoal	max.50	3.5	<1.2	<5	Mostly crystalline alumina	1300–1590	> 96	0.88–0.89 ³	0.6–0.7	–	Pass	–	Yes	Easily coatable	None
Keronite new black Type 2	6082-T6	Charcoal black	max.25	4	1–1.5	30–50	Mostly amorphous alumina	500–1000	> 10000	0.94 ⁴	0.84	0.1	Pass	–	Yes	Easily coatable and consistent properties with different types of alloys	None
Hard anodising	7075-T6	Light grey	max.60	0.8–1	<1	14–20	Amorphous alumina	400–420	<360	0.84–0.89 ²	0.86–0.88	–	–	–	Yes	Problems with Cu, resulting in high porosity level	Large quantity of strong acids

Black anodising	7075-T6	Charcoal black	max.35	-	-	-	Amorphous alumina	-	0.85-0.97 ⁵	0.5-0.81	-	-	-	-	Problems with Cu, results in extensive cracking and difficult to control	Harmful substances, e.g. nickel acetate and cobalt acetate

SS – ASTM B117; TSR – thermal shock resistance, UV resistance – grey scale rating ≥ 4 , T- thickness; P – porosity; α_s – solar absorptance; ϵ_n – infrared emittance; R – reflectance; VO – Vacuum out-gassing; S – coating speed

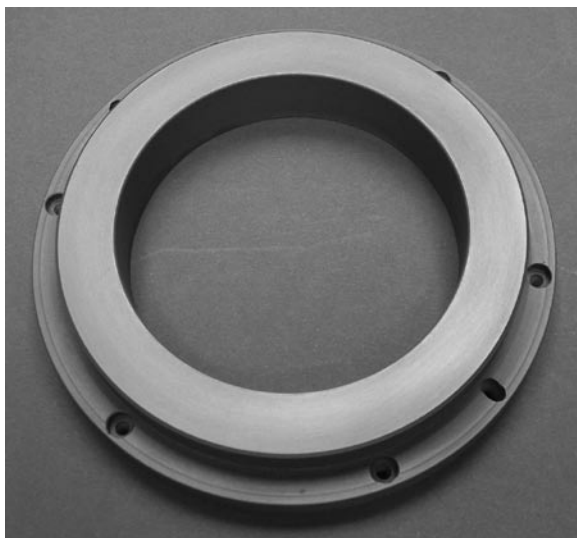
¹ Shrestha *et al.*, 2003

² Shrestha *et al.*, 2006

³ Polsak A, 2008

⁴ Shrestha and Dunn, 2007

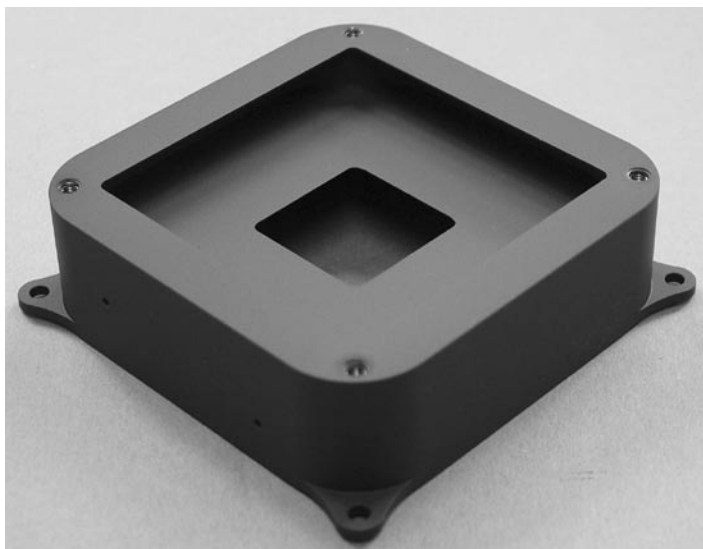
⁵ Corocher and Martin, April 2004



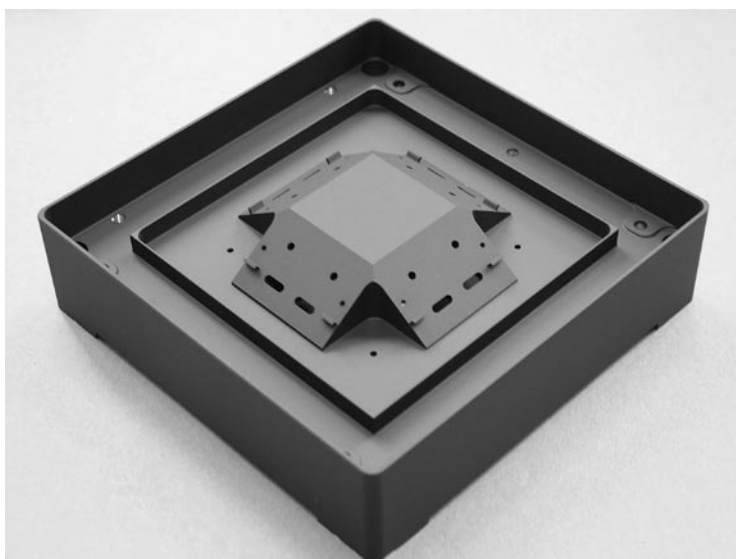
18.28 Keronite composite coating on AA6061 alloy for EMIR GRISM cryostat wheel bearing used for space observation. The coating was extensively evaluated for wear resistance, debris formation, stick-slip behaviour, ultra-low friction.



18.29 Barrel for satellites treated with new black Keronite on AA2618 alloy. The black Keronite coating has recently been extensively tested in humidity, vibration, debris formation, low optical reflectivity tests and as a sub-layer for adhesive bonding.



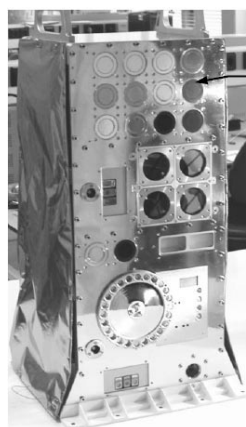
18.30 Fine sun sensor (FSS) baffle treated with black Keronite PEO coating.



18.31 Coarse sun sensor (CSS) housing treated with black Keronite PEO coating.

The growing demand for reduced environmental impact, lower life-cycle cost, recyclability, increased multi-functionality and greater durability will drive forward new technologies such as PEO.

PEO is an emerging surface technology and has increasingly received



Keronite
micro-
calorimeter



18.32 Keronite coated micro-calorimeter part mounted on the MEDET system for the International Space Station.



18.33 Fully automated Keronite PEO production line at Powdertech, Oxford, UK. Machine is set up for coating the three wheels shown.

research and industrial interests in the past decade due to its environmental friendliness, desirable surface properties and suitability for complex components (often unachievable by other line-of-sight coating routes such as plasma spraying). While PEO has become increasingly popular, continued research and industry support will help in optimising the process to suit application requirements and make this novel surface technology economically more viable and globally acceptable.

Industrial-scale PEO systems offered by Keronite International Ltd have been in operation for several years now, with applications involving aerospace and space, automotive, oil and gas, textile, motor sports, electronics and other applications. A fully automated Keronite PEO production plant in the UK is shown in Fig. 18.33.

18.10 References

- Anon. (1995), *Spacecraft Thermal Control Coatings Design and Application*, NASA Practice No. PD-ED-1239, October 1995.
- Anon. (1997), *Aluminium – Semi-finished Products*, Pechiney Rhenalu Publ.
- Barucci M, Risegari L, Olivieri E, Pasca E and Ventura G (2003), 'Aluminium alloys for space applications: Low temperature thermal conductivity of A6061-T6 and A1050', *Proc. of the 8th Conference, Astroparticle, Particle and Space Physics, Detectors and Medical Physics Applications*, doi No: 10.1142/9789812702707_0079, World Scientific Publishing Co.
- Choppy K J, Kovar R F and Cushman B M (2007), *Fretting Wear-resistant Micro-arc Oxidation Coatings for Aluminium and Titanium Alloy Bearings*, AFRL-ML-WP-TP-2007-443.
- Corocher G and Martin G G (2004), 'Evaluation of black anodizing coatings made according to the two processes described in ESA-PSS-703', *Private Communication*, ESA Mat. Report 3931.
- Cramer S D and Covino B S (2005), *Corrosion of Materials*, Volume 13B, ASM Handbook, ASM International.
- Curran J A and Clyne T W (2005), 'Thermo-physical properties of plasma electrolytic oxide coatings on aluminium', *Surf. & Coat. Technology*, 199, 168–176.
- Curran J A and Clyne T W (2006), 'Porosity in plasma electrolytic coatings', *Acta Materialia*, 54, 1985–1993.
- Dahm K L, Black A J, Shrestha S and Dearnley P A (2009), 'Plasma electrolytic oxidation treatment of aluminium alloys for lightweight disc brake rotors', *Proc. of Braking 2009: Institution of Mechanical Engineers (IMEchE) Conference June 2009*, ISBN 1 84334 559 5.
- Davenport A J, Moulinier F A M, Liu B and Morgan P C (2000), 'Surface finishing of aluminium aerospace alloys', *Proc. Aluminium Surface Science and Technology*, UMIST, Manchester, UK.
- Davies J R (1993), *Aluminium and Aluminium Alloys*, ASM Speciality Handbook.
- Dearnley P A, Gummersbach J, Weiss H, Ogwu A A and Davies T J (1999), 'The sliding wear resistance and frictional characteristics of surface modified aluminium alloys under extreme pressure', *Wear*, 225–229, 127–134.
- Dunn B D (1984), 'The corrosion properties of Spacelab structural alloy aluminium 2219-T851', *ESA STR-212*.

- Dunn B D and Stanyon R (1997), 'An inspection of Spacelab hardware', *ESA STR-241*.
- Duzellier S, Dinguirard M, Falguere D, Pons C, Inguibert V, Tighe A P, van Eesbeek M, Durin C, Gabriel S, Goulty D and Roberts G (2008), 'Preliminary Flight Data from the Materials Exposure and Degradation Experiment (MEDET)', *9th Intl. Space Conference on Protection of Materials and Structures from the Space Environment*, ICPMSE-9, Toronto, 20–23 May.
- ECSS-Q-7-71A rev.1, June 2004, *Space Product Assurance – Data for Selection of Space Materials and Processes*, ESA Publications Division, ISSN 1028:396X.
- ECSS-Q-ST-70-03C, July 2008, *Black Anodising of Aluminium with Inorganic Dyes*, ESA Requirements and Standards Division.
- ECSS-Q-ST-70-09C, July 2008, *Space Product Assurance – Measurements of Thermo-optical Properties of Thermal Control Materials*, ESA Requirements and Standards Division.
- Godja N, Wendrinsky J, Löcker C, Kiss N, Schindel A and Nauer G E (2009), 'Spark Anodization as a Successful Method for Surface Treatments', *Surface Modification Technologies, Surface Modifications Technologies XXII*, Ed by T.S. Sudarshan and P. Nylen, Maney Pub. London, ISBN 978-0-9817065-1-1, pp. 101–112.
- Goueffon Y, Arurault L, Mabru C, Tonon C and Guigue P (2009), 'Black anodic coatings for space applications: Study of the process parameters, characteristics and mechanical properties', *Journal of Materials Processing Technology*, 209, 5145–5151.
- Markov G A and Markova G V (1976), *USSR Patent 526 961*, Bul. Inv. 32.
- Merstallinger A, Semerad E and Dunn B D (2003), 'Influence of coatings and alloying on cold welding due to impact and fretting', *Proc. 9th European Space Symposium on Material in a Space Environment*, ESTEC Noordwijk (NL).
- MIL-A-8625 (1993) F, 'Anodic coatings for aluminium and aluminium alloys', *US Military Specification*, September 1993.
- Mistry K, Priest M and Shrestha S (2008), 'The potential of plasma electrolytic oxidised eutectic Al-Si alloy as a cylinder wall surface for lightweight engine blocks', *IMEchE Proceedings, Tribology 2008: Surface Engineering of Automotive Powertrains for Environmentally Friendly Transport*, IMech E, London.
- Monfort F, Berkani A, Matykina E, Skeldon P, Thompson G E, Habazaki H and Shimizu K (2007), 'Development of anodic coatings on aluminium under sparking conditions in silicate electrolyte', *Corrosion Science*, 49, 672–693.
- Monfort F, Berkani A, Matykina E, Skeldon P, Thompson G E, Habazaki H and Shimizu K (2006), 'A tracer study of oxide growth during spark anodizing of aluminium', *Journal of The Electrochemical Society*, 152, 382–387.
- Nebiolo M, Basile L, Suppo A, Cramarossa A, Rossi M F and Laudatao R (2007), 'Cryogenic tanks for launch vehicles', *IAS-04-IAF S.3.10*.
- Pereira A M, Pimenta G and Dunn B D (2008), 'Assessment of chemical conversion coatings for the protection of aluminium alloys – a comparison of Alodine 1200 with chromium-free conversion coating', *ESA STM-276*, ISBN: 978-92-9221-897-2.
- Poeton (2008), Available from: www.poeton.co.uk/w1/a3000.htm
- Rama Krishna L, Sudha Purnima A and Sundararajan G (2006), 'A comparative study of tribological behaviour of microarc oxidation and hard anodised coatings', *Wear*, 261, 1095–1101.
- Rao V D N, Cikanek H A, Boyer B A, Lesnevsky L N, Tchernovsky N M and Tjuri N V (1997), *Friction and Wear Characteristics of Micro-arc Oxidation Coating for Light Weight, Wear Resistant, Powertrain Component Application*, SAE Technical Paper Series 970022.

- Reidenbach F (1994), Volume 05: Surface Engineering', *ASM Handbook*, ASM International.
- Rohr T, Ghidini T, Eesbeek M, Nikulainen M, Meusy N, Dunn B D and Bosma J (2008), *Risk Mitigation of Obsolescence for Materials and Processes as a Consequence of Sustainable Development*, ESA presentation, San Diego, CA.
- Rooij A de (1989), Bimetallic compatible couples, *ESA Journal*, Vol. 13.
- Sharma R (2007), JWST NIRSpec cryogenic light shield mechanism, *Proc. 12th Euro. Space Mechanisms & Tribology Symp. (ESMATS)*, September 2007, Liverpool, UK ESA SP-653.
- Sheasby P G and Pinner R (2001), *The Surface Treatment and Finishing of Aluminium and its Alloys*, Finishing Publications Ltd., Sixth edition. Vol. 2.
- Shrestha S, Merstallinger A, Sickert D and Dunn B D (2003), Some preliminary evaluations of black coating on aluminium AA2219 alloy produced by plasma electrolytic oxidation (PEO) process for space applications, *Proc. 9th Intl. Symposium on Materials in a Space Environment*, 16–20 June, The Netherlands, 57–65.
- Shrestha S, Shashkov P and Dunn B D (2006), Microstructural and thermo-optical properties of black Keronite PEO coating on aluminium alloy AA7075 for spacecraft materials applications, *Proc. 10th Intl. Symposium on Materials in a Space Environment*, Collioure, France, 19–23 June (ESA SP-616).
- Shrestha S and Dunn B D (2007), Advanced plasma electrolytic oxidation treatment for protection of light weight materials and structures in a space environment, *Surface World*, November 2007.
- Shrestha S, Hutchins S, Dunkin O, Curran J and Wagner R (2007), Recent Developments in Black Finish Coatings on Aluminium Alloys by Keronite® Plasma Electrolytic Oxidation, *Proc. of the Global Powertrain Congress, Engine, Transmission, Propulsion & Emission*, Berlin, 39–42, 207–215.
- Suminov I V, Apelfeld A V, Ludin V B, Krit B L and Borisov A M (2005), *Microarc Oxidation – Theory, Technology and Equipment*, Moscow Ecomet 2005, ISBN 5-89594-110-9.
- US Geological Survey (2008), *Minerals Yearbook, Aluminum*, 1950 to 2008.
- Wang H W, Skeldon P, Thompson G E and Stevens K (2000), Hard anodising of aluminium alloys, *Proc. Aluminium Surface Science and Technology*, UMIST, London, 588–593.
- Yerokhin A L, Nie X, Leyland A, Matthews A and Dowey S J (1999), 'Plasma electrolysis for surface engineering', *Surf. & Coat. Technology*, 122, 73–93.
- Yerokhin A L, Shatrov A, Samsonov V, Shashkov P, Leyland A and Matthews A (2004), 'Fatigue properties of Keronite coatings on a magnesium alloy, *Surf. & Coat. Technology*, 182, 78–84.

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