

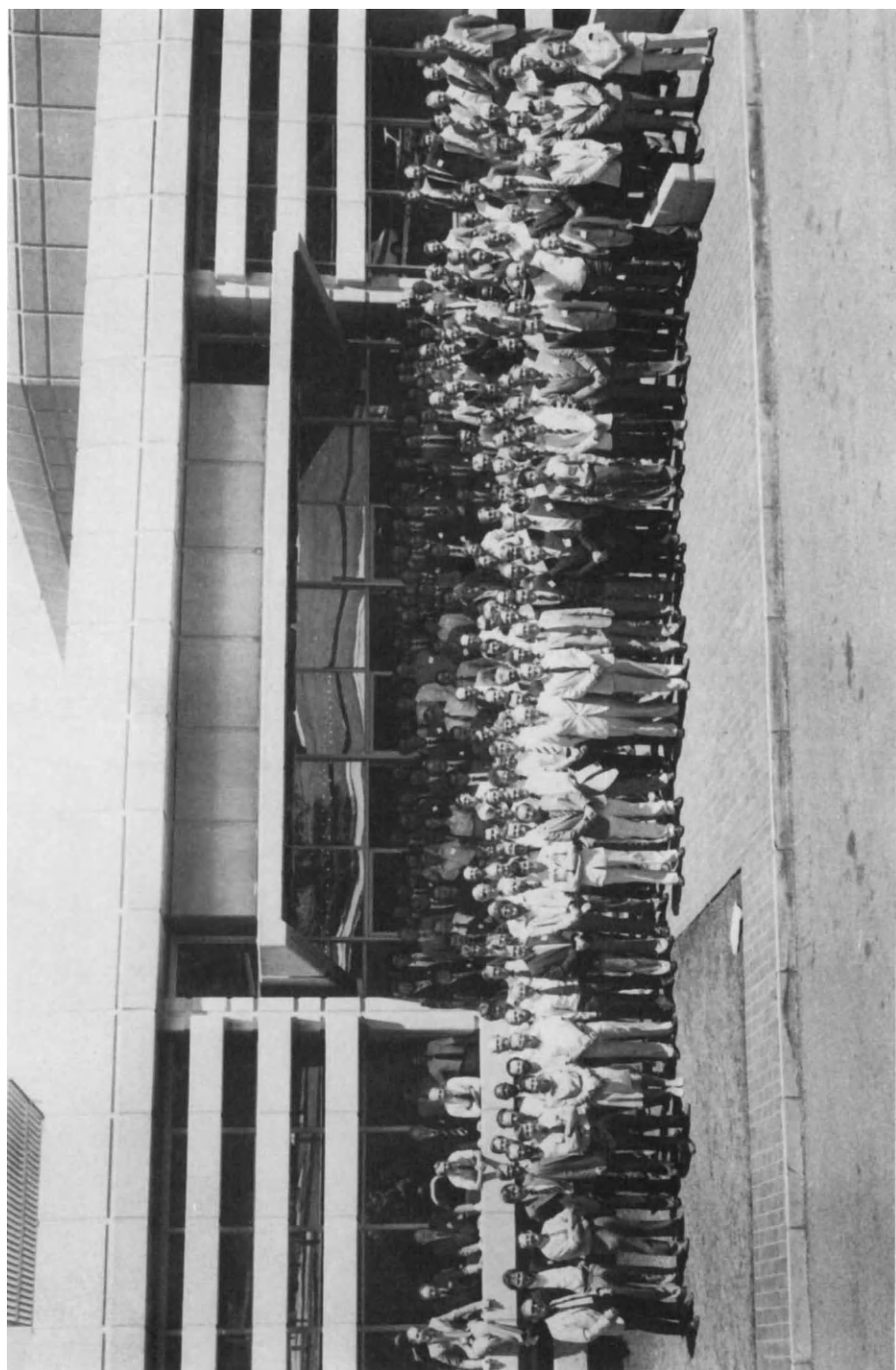
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Specialty Steels and Hard Materials

Proceedings of the International Conference on
Recent Developments in Specialty Steels and Hard Materials
(Materials Development '82)
held in Pretoria, South Africa, 8-12 November 1982

Edited by

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Council for Scientific & Industrial Research, Pretoria, South Africa



PERGAMON PRESS

OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT

U.K.	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
U.S.A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon Press Canada Ltd., Suite 104, 150 Consumers Road, Willowdale, Ontario M2J 1P9, Canada
AUSTRALIA	Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, N.S.W. 2011, Australia
FRANCE	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
FEDERAL REPUBLIC OF GERMANY	Pergamon Press GmbH, Hammerweg 6, D-6242 Kronberg-Taunus, Federal Republic of Germany

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First edition 1983

Library of Congress Cataloging in Publication Data

International Conference on Recent Developments in
Specialty Steels and Hard Materials (1982: Pretoria,
South Africa)

Specialty steels & hard materials.

Includes index.

1. Steel—Congresses. 2. Heat resistant materials—
Congresses. I. Comins, N. R. II. Clark, J. B.
III. Title.

TA472.157 1982 620.1'7 83-2410

British Library Cataloguing in Publication Data

International Conference on Recent Developments
in Specialty Steels and Hard Materials
(1982 Pretoria)

Specialty steels & hard materials.

1. Steel—Congresses

1. Title II. Comins, N.R. III. Clark, J.B.

669'.142 TN730

ISBN 0-08-029358-1

In order to make this volume available as economically and as rapidly as possible the authors' typescripts have been reproduced in their original forms. This method unfortunately has its typographical limitations but it is hoped that they in no way distract the reader.

Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter

Preface

Materials Development '82 took place from 8 - 12 November 1982 in Pretoria, South Africa. This International Conference provided a forum for scientists, engineers and technologists to discuss recent research and development in the fields of specialty steels and hard metals. The Conference was held under the auspices of IUPAP (International Union of Pure and Applied Physics) and the high pressure section was under the sponsorship of AIRAPT (International Association for the Advancement of High Pressure Science and Technology).

South Africa is well known internationally as a major exporter of many important raw materials including chromium, vanadium, manganese, etc., some of which, such as chromium, are now regarded as strategic in many countries. There has been continuing development over the years to market these materials in ever more processed forms, and attention is now focussed on the next step in the 'Materials Life Cycle', viz., engineering materials, including novel ones particularly suited to local production. This conference was the first International meeting of its kind in South Africa and was particularly valuable in illustrating the importance of Materials Science and Engineering. The meeting was attended by some 270 delegates including visitors from Germany, Israel, Japan, Republic of China, Sweden, Switzerland, U.K., U.S.A., Zambia and Zimbabwe.

The programme included thirteen invited plenary lectures and thirty-six contributed research papers, all presented orally. The keynote lecturers were invited by the Organising Committee with the idea of surveying a range of aspects in each topic. The focus was on structure-property relationships with the intention of strengthening the link between the understanding of microstructural detail, alloy design, processing technology and applications, as well as including aspects of economic viability. Presentations on specialty steels included discussion of high-strength low alloy steels, stainless steels, maraging steels, high speed steels and rapid solidification processing as well as consideration of the roles of specific alloying elements. An equally wide variety of topics was to be found in the hard materials section with papers covering tungsten carbide-cobalt hard metals, non-oxide ceramics, CVD processed hard materials and coatings, synthesis of diamonds and sintered polycrystalline ultra-hard materials.

These proceedings are divided into the following categories : plenary papers covering the entire range of materials of interest in the conference, contributed specialty steel papers and contributed hard materials papers. Contributed papers were selected by the Programme Committee and refereed as complete but draft manuscripts before the final versions were prepared.

It is hoped that this volume will provide timely reviews as well as significant research and development contributions in the field of specialty steels and hard materials.

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Pretoria,
South Africa.

Acknowledgements

The sponsorship of the following organisations is gratefully acknowledged:

Boart International Limited
Council for Mineral Technology (MINTEK)
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 Co-operative Scientific Programmes (CSP)
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Appreciation is also due to:

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South African Transport Services
Technical Services Department, CSIR
The Southern Africa Stainless Steel Development Association (SASSDA)

and the following hosts for technical visits during the Conference:

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The Organizers also wish to thank those organizations which supported the Conference by way of purchasing advertising or exhibition space or by sending delegates.

Thanks are due particularly to the members of the various Conference Committees, and above all to the Organizing Committee and Conference Secretariat. For Mrs Cilla Taylor, who ran the Secretariat and was responsible for the conference arrangements and much of the co-ordination, a special vote of thanks. The smooth running and friendly and stimulating atmosphere achieved at this meeting is a tribute to the efforts of all these people.

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In preparing these proceedings, the editors have benefited from the untiring help and support of many people. Mrs Sanny Biagio was responsible for the administrative work on the proceedings, and Mrs Nicolene Basson for much of the language editing of all manuscripts. Many papers required alterations and this would not have been possible without the support of Mrs Susan Stephan, Ms Maureen Taverner, Mrs Fran Obermeyer, Mrs Dottie Visser, Mrs Adele Foreman, Mrs Santie Mörsner and Mrs Irma Uytenbogaardt, who during the Conference, and after, assisted in the Editorial Office. Thanks also to Dr Martin Shaw, Mrs Janet McQueer, Miss Dorothy Park and Mrs Margaret Comins for their assistance.

The authors are thanked for their co-operation throughout the refereeing procedure, for their prompt submission of manuscripts, and where this was not the case, their tolerance of the many telexes. Finally, to the many unnamed referees who ensured that the manuscripts were up to standard, and all the other people involved in making the Conference the success it was, our hearty thanks.

Rapid Solidification Processing and the Control of Structure/Property Relationships

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ABSTRACT

In general, materials processing plays a major role in the structure/property relationships which make materials useful to society. A recent illustration of this dynamic interplay is provided by rapid solidification processing which leads to compositional uniformity and extremely fine dispersions of second-phase precipitates. The fundamental modes of solidification are discussed, particularly from the standpoints of solute partitioning at the solid-liquid interface, solute trapping, and massive (segregationless) solidification. Segregationless solidification can produce unusually high degrees of super-saturation relative to phases which are otherwise difficult to dissolve in the solid matrix. This condition is favoured by supercooling of the solidification process and by high velocity of the solid-liquid interface. An important consequence of such rapid solidification is that the alloy chemistry can be potentially designed to create small second-phase precipitates which are particularly insoluble in the solid matrix and which therefore resist coalescence on subsequent processing at high temperatures. As a result, these dispersions are very effective in pinning grain boundaries and inhibiting grain growth of the matrix phase. Some recent findings are presented dealing with the influence of these microstructural features on structure/property relationships in alloy systems.

KEY WORDS

Rapid solidification; solidification morphology; solute partitioning; interfacial velocity; massive solidification; second-phase dispersions; materials processing/structure/property relationships.

INTRODUCTION

Structure/property relationships in materials constitute the essence of materials science. Here, we try to discern the inner architecture of materials and then to connect this microdomain (through theories, models, or

mechanisms) to the macroworld of observed properties. The interplay is often called "understanding", and is one aspect of elucidating how nature works. But the field of materials becomes more useful to society only when processing is brought into play. This means that in order for materials to perform appropriately in the service of mankind, they have to be produced, fabricated, and quality-controlled on a commercial scale; and all this must be carried out cost-effectively and with reliable results. Accordingly, there are many interactive connections - both obvious and subtle - among the structure, properties, processing, and performance of materials. This complex, multidisciplinary system is modern materials science and engineering (MSE), and is conceptualized in Fig. 1.

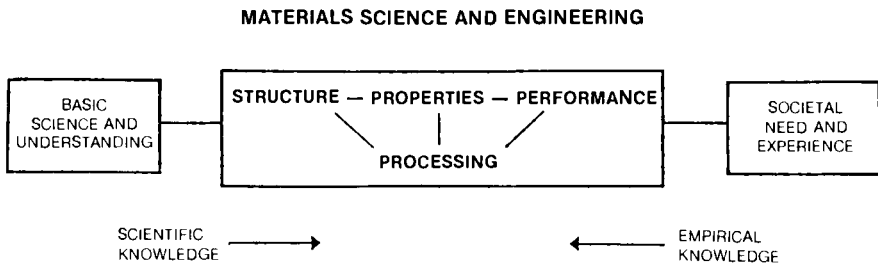


Fig. 1 A model of materials science and engineering, indicating the interplay of processing with structure, properties, and performance of materials, together with the countercurrent flows of scientific and empirical knowledge (Cohen, 1980).

For present purposes, we shall focus on rapid solidification processing (RSP) to illustrate how new processing methods can extend the range of structure/property relationships and thereby lead to further advances in the understanding as well as in the technology of materials. Moreover, we shall concentrate on crystalline materials, rather than on the metallic glasses which have received considerable attention in the field of rapid solidification during the past 20 years, but which are limited to much narrower ranges of compositions than are the crystalline materials.

MODES OF SOLIDIFICATION

Modes of solidification may be classified according to the morphology of growth (i.e., smooth-front, cellular, or dendritic) and compositional changes at the solid-liquid interface (i.e., with or without partitioning of solute atoms between the liquid and solid phases). These variations in solidification behaviour depend primarily on the velocity of the interface under the operative conditions of nucleation (usually heterogeneous) and heat flow. We shall attempt to take these interdependent factors into account in order to deal with the microstructural consequences of rapid solidification.

For present purposes, we first consider the binary phase diagram in Fig. 2, with metastable extensions of the L/ α liquidus and α /L solidus curves. The $T_0^{L/\alpha}$ curve is also shown; this is the locus of temperatures where liquid and α -solid solutions of the same composition have the same free energy per unit volume, or where $\Delta g^{L/\alpha} = 0$. Thus, it is only at temperatures below the $T_0^{L/\alpha}$ curve that $\Delta g^{L/\alpha} < 0$, and there, melts such as C'_0 and C''_0 can solidify spontaneously to the α -phase without any changes in composition. In contrast, alloy C'_0 does not have a $T_0^{L/\alpha}$ temperature, and so in such instances, solidification to the α -phase without compositional partitioning is ruled out thermodynamically.

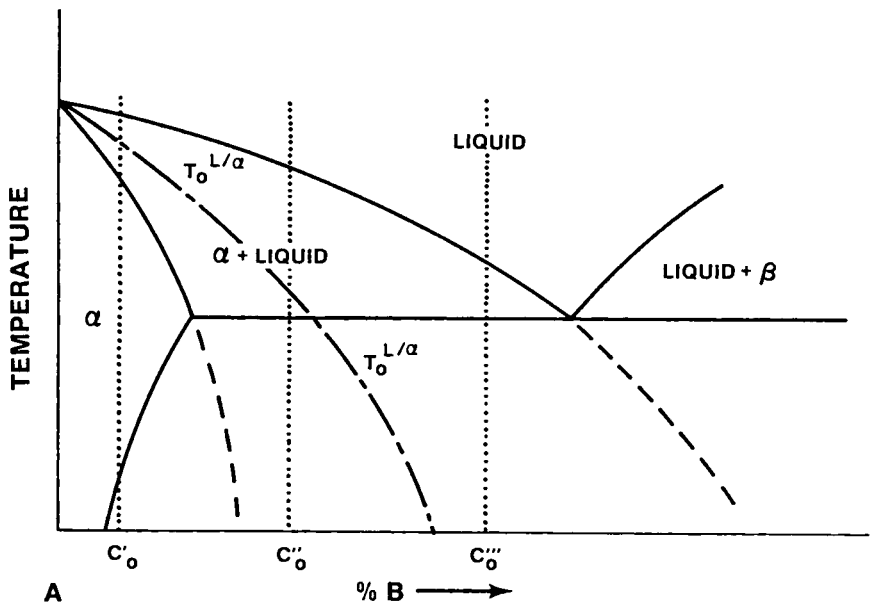


Fig. 2 A schematic binary phase diagram, showing the $T_0^{L/\alpha}$ curve where liquid and α -solid solutions of the same composition have the same free energy. The metastable extensions of the solidus and liquidus lines are also shown. Alloy C'_0 does not have a $T_0^{L/\alpha}$ temperature.

It is evident that one way of achieving partitionless (otherwise called massive) solidification is through supercooling of the melt (a) to avoid equilibrium solidification with solute partitioning along the liquidus and solidus lines, (b) to avoid any degree of partitioning on cooling to below $T_0^{L/\alpha}$, and (c) to avoid formation of other phases (for example, the β -solid

solution) which may exist in the equilibrium diagram. Hence, we are concerned with several metastable aspects of the alloy system under discussion.

As we shall see, massive (segregation-free) solidification may have a profound influence on the final microstructure, leading to compositional uniformity, high-degrees of supersaturation in solid solutions, very fine dispersions of second-phase precipitates when such solid solutions are allowed to decompose, and new variations in the nature of these small precipitates by multi-alloying of the liquid phase beyond the basic phase diagram of the principal components.

Suppression of the solidification modes involving compositional changes is promoted (1) by rapid cooling of the melt through and below the liquidus temperatures, and (2) by minimizing the stimulating role of heterogeneous nucleants on the liquid/solid transformation. Both of these approaches tend to depress the nucleation temperature and so favour the attainment of massive solidification.

Processes for rapid heat extraction from a melt are well known (Mehrabian, Kear and Cohen, 1978; Mehrabian, Kear and Cohen, 1980) and typically depend on geometries having large surface-to-volume ratios as well as on large heat-transfer coefficients between the solidifying system and the cooling medium. Some practical cooling-rate limits are given in Table 1 for three methods of rapid solidification. We shall focus mainly on atomization in this paper as the means for obtaining rapid solidification; this technique is advantageous from our standpoint because (a) the relevant heat-flow analysis has been well worked-out (Levi and Mehrabian, 1982b), and (b) the spherical particles produced by this method are appropriate for consolidation via powder-metallurgy operations into bulk specimens for property testing.

TABLE 1 Cooling-Rate and Interfacial Velocity Limitations in Rapid Solidification processing of 10 μm Specimens of Aluminium, Iron, and Nickel under Conditions of No Supercooling (Mehrabian, 1982)

Method	Atomization with Forced-Convection Cooling	Melt Spinning	Surface Melting and Self-Quenching
Shape of Product	Sphere	Ribbon filament	Thin surface layer
Heat-Transfer Coefficient ($\text{W/m}^2 \cdot \text{K}$)	5×10^4	10^6	Tends to infinity
Maximum Cooling Rate in Melt (K/s)	7×10^6	2.5×10^7	10^8
Maximum Interfacial Velocity (m/s)	0.1 - 0.27	0.6 - 0.75	(Al) 1.5 - 2.3 (Fe, Ni) 0.35 - 0.65
Fraction Solidified- Range	0.1 to 0.95	0.0 to 1.0	0.1 to 1.0

When massive solidification is nucleated by supercooling the melt to a temperature T_N below $T_0^{L/\alpha}$, the solid-liquid interfacial temperature will be raised by evolution of the latent heat of solidification, despite the high rate of heat extraction that may be imposed by the surroundings. Accordingly, if the temperature of the advancing interface reaches $T_0^{L/\alpha}$ due to this recalescence, further massive solidification will no longer be possible. Actually, massive solidification may cease at some lower temperature, T_x , where solute redistribution between the liquid and solid phases begins to set in; T_x will depend on the interfacial velocity, but must lie in the $\alpha+L$ region of the phase diagram between the solidus temperature and $T_0^{L/\alpha}$.

If the interfacial temperature remains below T_x throughout the liquid-to-solid transformation, the entire solidification will then be segregationless; supercooling to this extent is termed hypercooling. In other words, hypercooling can be defined as a degree of supercooling such that

$$\Delta H < \int_{T_N}^{T_x} \kappa_L dT \quad (1)$$

where ΔH = heat evolved per mole of solid formed, and

κ_L = specific heat per mole of liquid.

SOLIDIFICATION WITHOUT SUPERCOOLING

Before analysing the quantitative heat-flow problem (entailing the supercooling of a liquid droplet, the concomitant latent-heat evolution, and the resulting interfacial velocity), it will be helpful to review some fundamentals of solidification when diffusional partitioning does take place, as in the case when compositional equilibrium is maintained locally at the moving interface. Here, it is customary to consider the thermal gradient (G_L) in the melt just ahead of the interface and the interfacial velocity or solid growth rate (R) in relation to each other; this is done in Fig. 3. The slope of the line AB is given by (Flemings, 1974):

$$\frac{G_L}{R} = \frac{m_L C_0 (k_{eq} - 1)}{D_L k_{eq}} \quad (2)$$

where m_L = slope of the liquidus line (negative in Fig. 2) = dT/dC_L ,

k_{eq} = equilibrium partition ratio = C_S/C_L (< 1 in Fig. 2), and

D_L = diffusivity of solute in the liquid.

We see from Fig. 3 that, when G_L/R is greater than the right-hand side of eq.(2), the interface advances on a plane (or smooth) front as heat is withdrawn from the system. Protuberances on the moving interface tend to be smoothed out because of the stabilizing effect of the relatively steep temperature gradient in the liquid (G_L) compared to the interfacial velocity (R). Under such circumstances, there will be no microsegregation of solute atoms behind the advancing front, except possibly for an initial transient and the very last liquid to solidify.

On the other hand, when G_L/R is less than the right-hand side of eq.(2), the interface becomes morphologically unstable, and protuberances tend to grow preferentially inasmuch as there will be combinations of temperature and composition ahead where the melt would otherwise be supercooled (or supersaturated) with respect to the solid phase. This is the well-studied case of constitutional supercooling* (Chalmers, 1959) which results in cellular or dendritic growth morphologies, with solute-enriched microsegregations building-up in the liquid between the cells or dendritic arms. These microsegregations are common in ingots and castings, and are also the regions where other solid phases may precipitate either during or after the solidification process.

AVERAGE COOLING RATE $\dot{T} = G_L R$

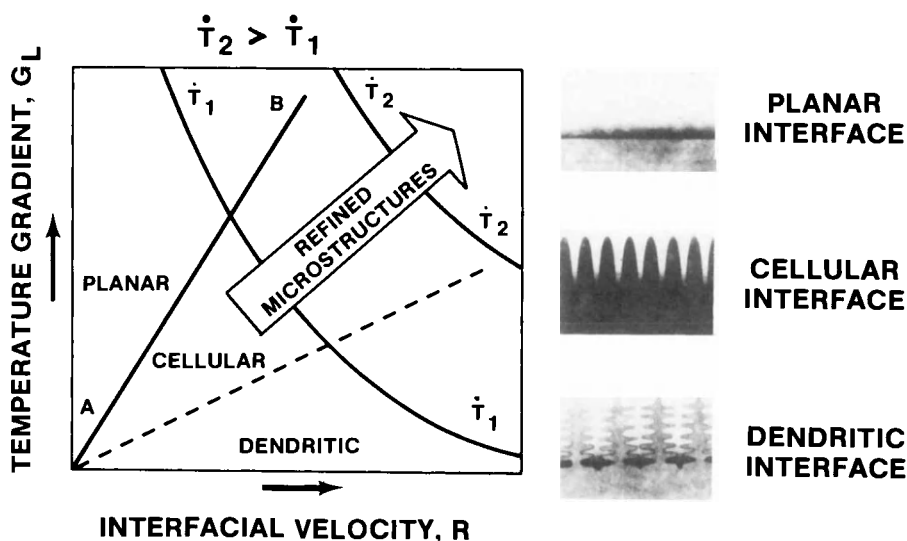


Fig. 3 Mode of solidification as a function of temperature gradient in the liquid (G_L) and the interfacial velocity or growth rate (R). Microstructural refinement due to increasing the cooling rate ($T = G_L R$) is indicated by the arrow (Cohen, Kear, and Mehrabian, 1980). Line AB is given by eq. (2).

As indicated by Fig. 3, increasing R at a given G_L causes the interface to change from planar to cellular to dendritic. For the simple case under discussion, the composition gradient in the liquid at the interface is

$$\frac{R C_0 (k_{eq} - 1)}{D_L k_{eq}} \quad . \quad \text{On comparison with eq.(2), this means that the liquid concen-}$$

tration gradient (which is negative) not only becomes steeper (negatively) with increasing R , but is morphologically destabilizing. In this regime, the intercellular or dendritic-arm spacings become smaller as the solidification time is reduced by faster cooling rates. Since the product $G_L \cdot R$ is

* It should be recognized that constitutional supercooling is not supercooling in the conventional sense; it still assumes compositional equilibrium at the advancing interface.

a measure of the cooling rate, the sloping arrow in Fig. 3 designates the G_L and R combinations which lead to progressively smaller distances between the microsegregated regions in the solidified structure. Thus, rapid cooling under conditions of constitutional supercooling, and with local equilibrium still being substantially maintained at the moving interfaces, can provide increasing degrees of compositional uniformity together with finer dispersions of second-phase precipitates, although not to the extent that can be realized from massive solidification.

There are two assumptions not mentioned yet in this analysis of constitutional supercooling which become important at high interfacial velocities: (1) the spacings between the protuberances on the growth front may become so small at large values of R that surface-tension effects cannot be neglected as a stabilizing influence in helping maintain a smooth interface, and (2) the latent heat evolution at large R also cannot be neglected because it then becomes an important factor in the thermal fields at play. This complex solidification problem has been solved (Coriell and Sekerka, 1980), and some calculated results for an aluminium-copper alloy are represented in Fig. 4 (Coriell and Sekerka, 1980; Cohen, Kear and Mehrabian, 1980).

The line AB in Fig. 4 has the same significance as the line AB in Fig. 3, but the G_L, R regime of cellular and dendritic solidification is now confined to the dome-shaped region in Fig. 4. In other words, smooth-front growth is obtained not only to the left of line AB, as discussed in connection with eq.(2), but also for conditions above and to the right of the dome-shaped region. The right-hand boundary EF corresponds to such high growth rates that morphological stability is re-established due to the aforementioned surface-tension and heat-evolution effects. It is seen that this limiting velocity is relatively insensitive to G_L .

Each $G_L \cdot R$ line in Fig. 4 defines the locus of a given cooling rate ($\dot{T}$), from which we may note that more G_L, R combinations become available for smooth-front solidification with increasing $\dot{T}$. Conversely, the calculations show that the regime of cellular and dendritic solidification expands as a function of the melt composition (C_0), signifying that morphological stability is more difficult to achieve at higher solute contents. It can also be shown that the boundary EF moves to lower interfacial velocities as the solute partition ratio is increased.

In general, the attainment of plane-front solidification at high growth rates does not mean that compositional partitioning and segregation are eliminated. Nevertheless, solute trapping to an increasing extent can be visualized, with the solute partition ratio deviating more and more from its equilibrium value and approaching unity in the limit. The velocity required to obtain such partitionless solidification is that necessary to overtake any compositional gradient in the liquid due to solute partitioning at the interface. An upper bound to this "overtaking velocity" can be approximated as the diffusive velocity or D_L/δ_L , where D_L is the diffusivity of the solute specie in the liquid, and δ_L is the corresponding atomic jump distance. In Fig. 4, the diffusive velocity is indicated at $R \approx 25$ m/s, taking D_L for Cu in liquid Al as 5×10^{-9} m²/s and δ_L as 2×10^{-10} m. However, the effective diffusion distance may be more like $10 \delta_L$, in which case the growth rate necessary for complete solute trapping would be roughly 2.5 m/s. For growth rates between that corresponding to morphological stability and the interfacial velocity for complete trapping, smooth-front solidification would be expected to occur with some solute build-up in the liquid ahead of the interface.

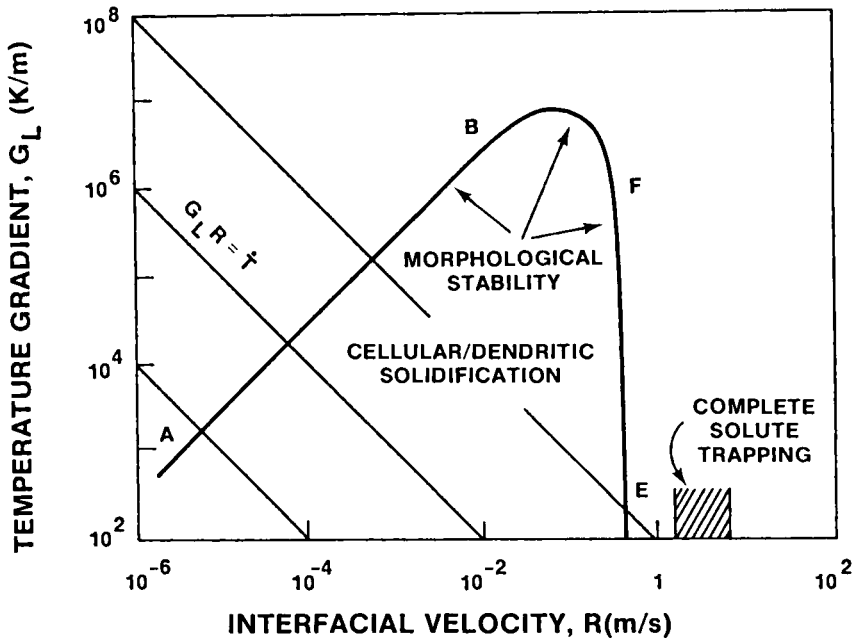


Fig. 4 Regimes of liquid temperature gradient (G_L) and interfacial velocity (R) for smooth-front growth (morphologically stable interface) and for cellular or dendritic growth. The boundary ABFE between these two regimes is calculated for an Al-0.1 w/o Cu alloy, assuming equilibrium partitioning of Cu at the moving interface. (Coriell and Sekerka, 1980; Cohen, Kear, and Mehrabian, 1980). Cross-hatched band indicates estimated interfacial velocity which is fast enough to achieve partitionless solidification.

SOLIDIFICATION WITH SUPERCOOLING

Thus far, in treating the problem of compositional partitioning, we have assumed that nucleation of the solid phase sets in at the liquidus temperature, and that local equilibrium is maintained at the moving interface even at high growth rates approaching the conditions for morphological stability. However, the situation becomes quite different if the melt can be hypercooled so that nucleation and the entire growth process take place in conformity with eq. (1). We shall now discuss some of the associated phenomena in the solidification of atomized spherical droplets, using the enthalpy/temperature description due to Levi and Mehrabian (1982a, 1982b).

The thermal history for the solidification of an aluminium droplet is portrayed in Fig. 5 along three enthalpy/temperature paths. The enthalpy (H) per mole of system can be expressed as a function of temperature and fraction solidified:

$$(H - H_{SM}) = [\Delta H_M + \kappa_L(T - T_M)][1 - g] + \kappa_S(T - T_M)g \quad (3)$$

where H_{SM} = enthalpy of the solid phase at the melting temperature T_M ,
 ΔH_M = latent heat of fusion = $H_{LM} - H_{SM}$,
 κ_L = specific heat of liquid,
 κ_S = specific heat of solid, and
 g = weight fraction of solid.

Eq. (3) is plotted in Fig. 5 with H_{SM} taken as zero at T_M . The two terms on the right-hand side of eq. (3) represent the enthalpies of the liquid and solid fractions, respectively, during the solidification process.

Alternatively, the relationship given by eq. (3) can be expressed in terms of a dimensionless enthalpy ψ and a dimensionless temperature θ , where:

$$\psi = (H - H_{SM})/\Delta H_M \quad (4)$$

$$\theta = \kappa_L(T - T_M)/\Delta H_M \quad (5)$$

These parameters are also shown in Fig. 5. Note that $\theta = 0$ at T_M and is negative below T_M , while $\psi = 0$ for the solid ($g = 1$) at T_M and is negative (for $g = 1$) below T_M . $\psi = 1$ for the liquid ($g = 0$) at T_M . Lines of constant g intersect the vertical T_M line at $\psi = 1 - g$; the lines for $g = 0, 0.5$, and 1 are drawn in Fig. 5.

Path A in Fig. 5 denotes isothermal solidification at T_M ($\theta = 0$); there is no supercooling in this case, and the system is entirely solid ($g = 1$) on cooling below T_M . Path B represents adiabatic solidification; here the liquid ($g = 0$) has supercooled to the extent that the heat extracted from the liquid is just equal to the heat evolved on solidification (ΔH_M). As a result, complete solidification can take place without any further removal of heat from the system. The required nucleation temperature for such adiabatic solidification is given by $\theta_N = -1$, and ΔH_M is just sufficient to raise the temperature from $\theta = -1$ up to 0 . As indicated in Fig. 5, supercooling to $\psi < -1$ is otherwise known as hypercooling.

Path C designates an intermediate situation and, correspondingly, exhibits two solidification regimes. The first is a stage of rapid solidification after supercooling to $\theta_N < 0$; here the heat evolved (recalescence) at the advancing interface is readily absorbed by the supercooled liquid phase, setting up negative temperature gradients in the melt. [This contrasts with the positive temperature gradients encountered in the descriptions of Figs. 3 and 4.] The effect of heat loss to the surroundings is relatively minor during this stage of rapid solidification. There is an almost-adiabatic rise in temperature due to the recalescence and the extent of supercooling is diminished as θ approaches zero. In the latter stage, further solidification proceeds more slowly (almost isothermally near T_M), and its progress depends primarily on the heat flow to the surroundings. It may be noted that the rapid solidification stage along path C translates itself into a shallow negative slope of the ψ - θ curve with pronounced adiabatic character in the supercooling regime, whereas the slow solidification stage translates itself into a steep negative slope with pronounced isothermal character and relatively little supercooling.

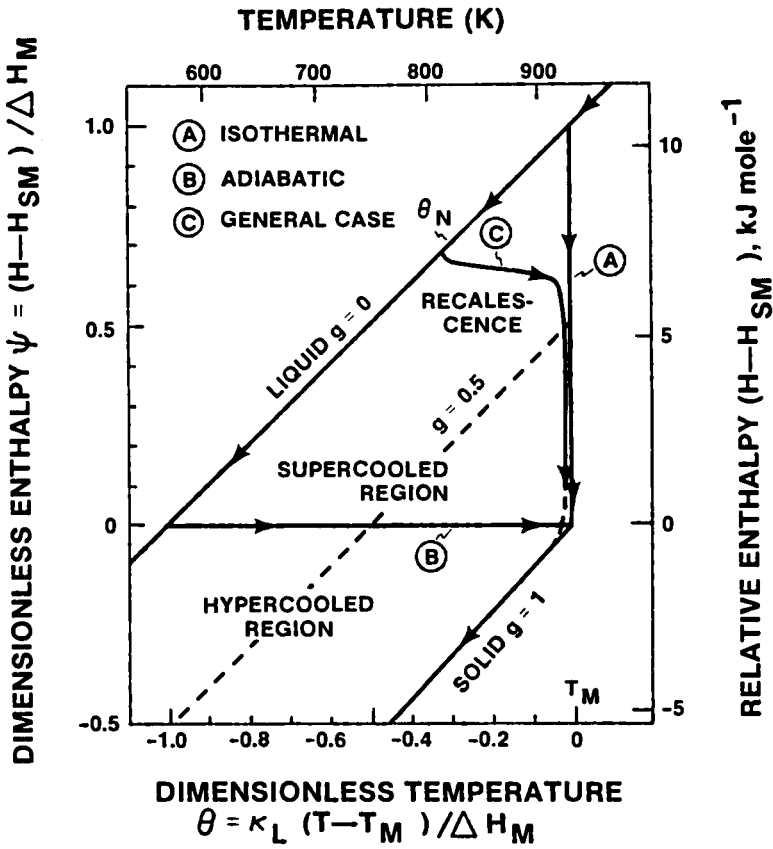


Fig. 5 Enthalpy-temperature diagram for aluminium, showing three solidification paths. In path C, θ_N is the dimensionless nucleation temperature on supercooling. Other symbols are defined in text. (Levi and Mehrabian, 1982b).

Some calculated enthalpy/temperature curves for the solidification of aluminium droplets supercooled to various temperatures (Levi and Mehrabian, 1982b) are shown in Fig. 6 for constant heat-extraction conditions ($K/Bi = 100$). K is a kinetic factor which relates the growth rate to the degree of supercooling, while Bi (the Biot number) $= hr/k_L$, where h = heat-transfer coefficient, r = droplet radius, and k_L = liquid thermal conductivity. As K/Bi decreases, the heat extraction becomes more efficient relative to the solidification-growth kinetics. The selected K/Bi ratio of 100 for the calculations in Fig. 6 corresponds to the fastest achievable cooling conditions for atomized aluminium droplets. Clearly, the adiabatic character of the solidification process becomes more pronounced with increased supercooling. The hypercooling regime is reached when $\theta_N = -1$; then, the dimensionless enthalpy change (ψ) remains negative throughout the solidification process.

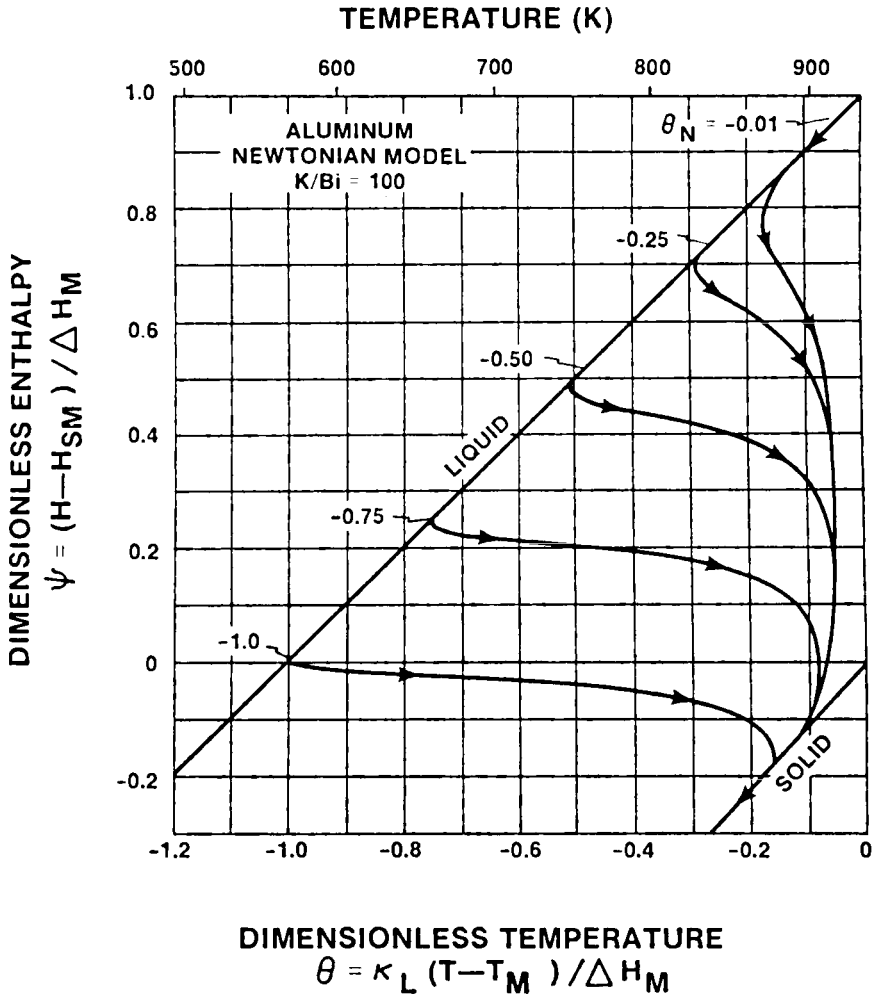


Fig. 6 Calculated enthalpy-temperature curves for the solidification of aluminium droplets after different degrees of supercooling over the range of $\theta_N = -0.01$ to -1.0 . Newtonian heat flow is assumed; the ratio $K/Bi = 100$ corresponds to extremely rapid cooling conditions for atomized aluminium droplets (Levi and Mehrabian, 1982b).

There is evidence that the nucleation of solidification in supercooled droplets starts preferentially at the surface. Calculated interfacial positions and velocities as a function of fraction solidified after such heterogeneous nucleation at $\theta_N = -0.5$ are summarized in Fig. 7 for three droplet sizes (Levi and Mehrabian, 1982b). The growth rate (R) decreases with increasing

q as expected, but remains above ≈ 1 m/s for a significant part of the solidification process under the conditions at hand. Similar calculations for the case of no supercooling ($\theta_N=0$) indicate maximum R values of about 0.1 m/s, and illustrate the importance of supercooling in order to reach interfacial velocities capable of achieving massive solidification.

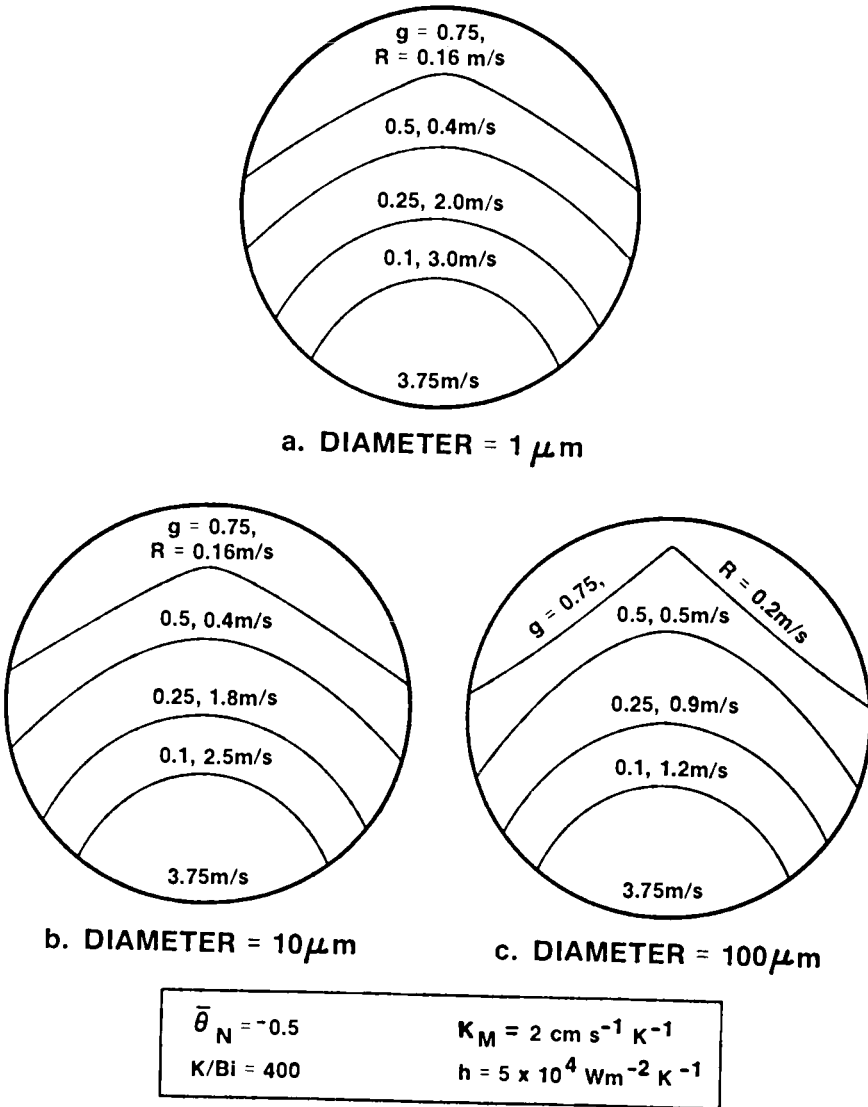


Fig. 7 Interfacial positions and velocities as a function of fraction solidified (q) for three sizes of atomized aluminium droplets, supercooled to $\theta_N = -0.5$. Calculations based on enthalpy (non-Newtonian) heat-flow model. (Levi and Mehrabian, 1982b).

The above concepts have been confirmed experimentally by microstructural observations on very small (0.5-1 μm diameter) atomized Al-6 w/o Si particles, which require no thinning for transmission electron microscopy (Levi and Mehrabian, 1982a). Region A in the electron micrograph of Fig. 8 underwent massive solidification and the resulting supersaturated solid solution then precipitated silicon during further cooling to room temperature. The silicon is deduced to have precipitated from the solid matrix (rather than from the liquid state) in view of the observed crystallographic relationships between the precipitates and the parent solid phase. Region B constitutes a precipitate-free zone, and delineates the growth front at a stage when the interfacial velocity had slowed down sufficiently to allow solute partitioning to set in, with silicon being built-up in the liquid just ahead of the front while being depleted in the solid forming just behind the front. At the same time, it appears that the interface during the solidification of region B must have been moving fast enough to maintain smooth-front growth. In region C, however, further slowing-down of the growth rate, along with the destabilizing effect of an increasing concentration gradient in the liquid (due to less and less solute trapping) then led to morphological instability. Consequently, the rest of the solidification was taken over by cellular growth and a marked segregation of silicon to the cell walls.

CONTROL OF SECOND-PHASE DISPERSIONS

Massive (segregationless) solidification makes it possible to obtain unusually fine dispersions of second-phase precipitates which are very insoluble in the solid matrix. The complete solute trapping that attends massive solidification applies to all of the solutes dissolved in the melt and not just to the main alloying elements. Hence, very stable compounds may be trapped in highly supersaturated solid solutions, thus providing a condition which cannot be realized by conventional solution treatment in the solid state. Precipitation from such supersaturated solid solutions then yields finer and more uniformly distributed dispersions than can be obtained when the precipitation takes place as a part of the solidification process itself, e.g., in the compositional-partitioning types of solidification. As a case in point, MnS precipitates in high-sulphur 303 stainless steel (Fe-17.3Cr-8.7Ni) are in the order of 10 μm in size after regular ingot practice, 0.1 μm after rapid solidification in the cellular/dendritic mode, and 0.01 μm (100 Å) after solidification in the massive mode (Kelly, Cohen and Vander Sande, 1982a). Figure 9 compares the MnS dispersions after cellular and massive solidification.

The second-phase-dispersion feature of rapid solidification plays a significant role in the precipitate pinning of grain boundaries and, hence, in promoting resistance to grain growth at elevated temperatures, whether during the hot consolidation of atomized powders or during subsequent heat treatment. Equation (6), due to Gladman (1966), relates the limiting grain diameter D which comes into interfacial-tension balance with dispersed

precipitates of volume fraction f_v and mean diameter $\bar{d}$:

$$D = \frac{\pi \bar{d}}{6 f_v} \left(\frac{3}{2} - \frac{2}{Z} \right) \quad (6)$$

where Z is a measure of the grain-size contrast between a growing grain and the mean of the surrounding grains. Accordingly, the pinned grain size is

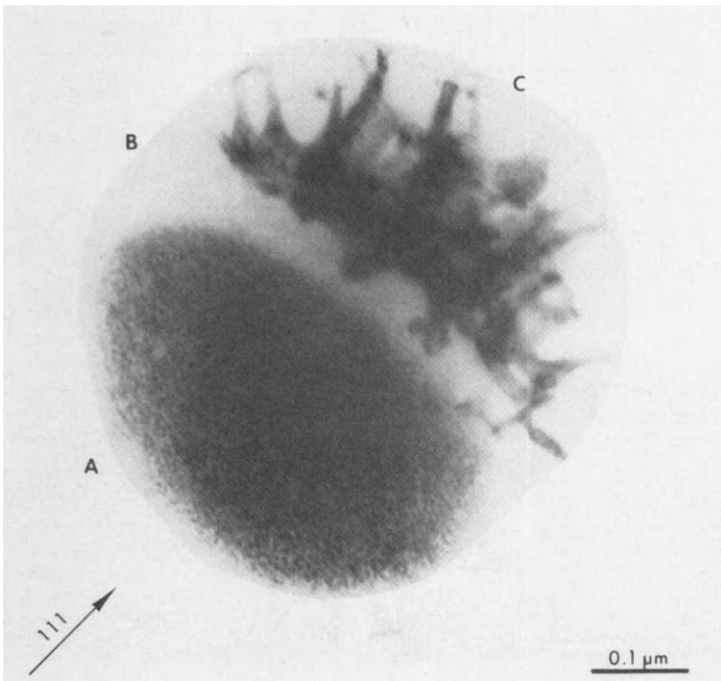


Fig. 8 Transmission electron micrograph of a rapidly solidified Al-6 w/o Si submicron droplet, showing three sequential modes of solidification. Region A has solidified massively and the trapped silicon then precipitated from the supersaturated solid-solution matrix on further cooling; region B continued to solidify with a smooth front, but with solute partitioning; region C has solidified in the cellular mode, indicating the onset of morphological instability and pronounced silicon segregation at the cell walls. (Levi and Mehrabian, 1982a).

smaller, the smaller the precipitate size and the larger its volume fraction, both of which are favoured by rapid solidification, and especially by massive solidification.

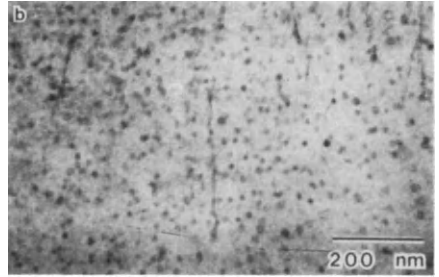
However, for inhibiting grain growth at very high temperatures, the dispersed phase should be designed to resist Ostwald ripening and re-solution in the solid matrix; otherwise, $\bar{d}/f_v$ in eq. (6) will increase and unpinning of grain boundaries will result. The kinetics of Ostwald ripening may be expressed as (Bhattacharyya and Russell, 1972; Olson and others, 1982):

$$\bar{d}^3 - \bar{d}_0^3 = \frac{64D_S C_S}{9 R_g T} \sigma V_p^2 t \quad (7)$$

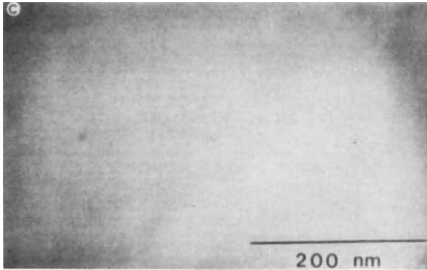
where $\bar{d}_0$ = mean precipitate diameter at zero time,
 D_S = diffusivity (in the solid-solution matrix) of the rate-controlling specie,
 C_S = concentration (in the solid-solution matrix) of the rate-controlling specie,
 R_g = gas constant,
 T = absolute temperature,
 σ = specific interfacial energy,
 V_p = molar volume of the precipitate phase, and
 t = time at temperature T .



(a)



(b)



(c)

Fig. 9 Electron transmission micrographs of centrifugally atomized high-sulphur 303 stainless steel, illustrating (a) cellular, and (b and c) massive solidification. (a) MnS dispersion in fcc matrix; precipitate formed as part of solidification process. Dark-field image. (b) MnS dispersion in bcc matrix; precipitate formed from solid solution after massive solidification. Bright-field image. (c) bcc matrix after massive solidification, but with MnS precipitation suppressed. Bright-field image. (Kelly, Cohen and Vander Sande, 1982a).

It is seen that, in order for $\bar{d}$ to be small, the initial precipitate size $\bar{d}_0$ must also be small, and for $\bar{d}$ to remain small on heating at high temperatures, the product $D_S C_S$ should also be small. If the precipitate phase is designated as MX (e.g., MnS), the precipitate coalescence will be controlled by $D_{S S}^{X X}$ if $D_{S S}^{X X} < D_{S S}^{M M}$, or by $D_{S S}^{M M}$ if $D_{S S}^{M M} < D_{S S}^{X X}$. With a given precipitate stoichiometry, the interrelationships in eqs. (6) and (7) offer alloying guidelines for minimizing $D_S C_S$ in eq. (7) while maximizing f_v in eq. (6). The choice of the precipitate phase, in this context, may be governed by available thermodynamic equations for the appropriate solubility products. A low solubility product (relative to the matrix solid solution) will lead to small C_S values in eq. (7), as well as large f_v values in eq. (6) for a given melt composition. For example, solubility products with respect to an austenitic matrix in steel decrease approximately in the following order of second-phase precipitates: VN, Nb(C,N), TiC, MnS, AlN, TiB₂, TiN (Olsen and others, 1982).

The high-sulphur stainless steel, previously mentioned in connection with MnS dispersions, was rapidly solidified by centrifugal atomizing. Within the distribution of the powder-particle sizes thus produced, it was interesting to find that the larger particles were fcc and nonferromagnetic, with the solidification mode being cellular, whereas the smaller ones were bcc and ferromagnetic, with the solidification mode being massive. Evidently, the smaller droplets in the atomizing run had supercooled sufficiently to solidify into bcc ferrite rather than the expected fcc austenite, and segregationless solidification was achieved by such supercooling. From results of this type, it was possible to derive the data in Table 2, which shows that the heterogeneities which are responsible for the fcc nucleation can be relegated to a vanishingly small fraction (by number) of the atomized droplets if the average droplet size is smaller than about 20 μm , thereby promoting the formation of the bcc phase as a solidification product (Kelly, Cohen and Vander Sande, 1982b). An example of the resistance to austenitic grain growth due to rapid solidification processing is given in Fig. 10.

TABLE 2 Effect of Droplet Size of Centrifugally Atomized Stainless Steel on the Nucleation to FCC Austenite and BCC Ferrite; FCC Nucleants Estimated at 2×10^{12} per Cubic Meter (Kelly, Cohen and Vander Sande, 1982b)

Average Droplet Diameter (μm)	Number Fraction of Solidified Particles	
	FCC	BCC
70	0.5	0.5
20	0.01	0.99
10	0.002	0.998
1	0.000002	0.999998

SOME ILLUSTRATIVE PROPERTIES

The fracture toughness of an experimental martensitic steel is plotted in Fig. 11a and b as a function of austenitizing temperature (Fleyshman, 1982). Whether after conventional or rapid solidification processing (RSP), this alloy exhibits an increase in sharp-crack (K_Q) and blunt-crack (CVN) fracture toughness with increasing austenitizing temperature. However, a

substantial difference in toughness becomes evident when the testing is carried out at subatmospheric temperatures (Fig. 11c). The CVN shelf energy of the RSP steel is maintained to about 100 °C below room temperature, and the mid-way transition temperature is lowered by about 50 °C due to the fine austenitic grain size retained at high austenitizing temperatures.

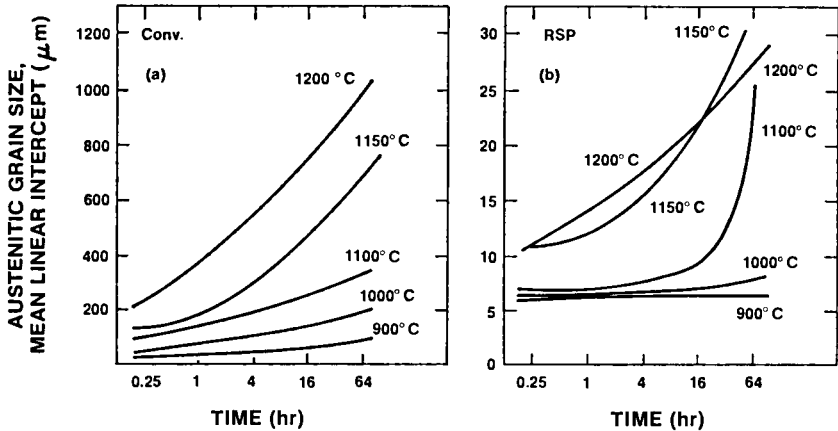


Fig. 10 Grain-growth characteristics of 9Ni-4Co-0.2C steel (a) after conventional processing (normal ingot and hot-rolling practice) and (b) after rapid solidification processing. The latter involved centrifugal atomizing and consolidation by hot extrusion. (Suga and others, 1980).

Another aspect of RSP is illustrated by the creep-strength properties in Fig. 12 (Anderson and others, 1980). Here, a novel class of Ni-Mo-Al superalloys becomes relatively ductile when processed by rapid solidification methods (centrifugal atomizing and hot consolidation at Pratt and Whitney Aircraft). As a consequence of RSP, alloy compositions can be extended into new regimes for enhancing high-temperature strength. A comparison with a state-of-the-art superalloy (Mar M-200 = Ni-9Cr-10Co-5Al-2Ti-12W-1Nb) is given in Fig. 12.

An example of dispersion strengthening resulting from RSP applied to (otherwise extremely brittle) Fe_3Al alloys is shown in Fig. 13 (Adam and others, 1982). Because of the grain refinement due to grain-boundary pinning by the dispersed precipitates, the dispersion strengthening is also accompanied by a significant improvement in ductility.

Such fine second-phase precipitates have also been found to contribute oxidation resistance to high-temperature alloys by strengthening the adherence of protective oxide films. This beneficial effect is demonstrated in Fig. 14 for the RSP Fe_3Al in comparison with a conventionally processed stainless steel (AISI 347) and a cobalt-base heat-resisting alloy (Haynes Alloy 188). The latter two materials lose weight due to film-spalling during the oxidation test, while the RSP alloy displays pronounced resistance to scaling (Adam and others, 1982).

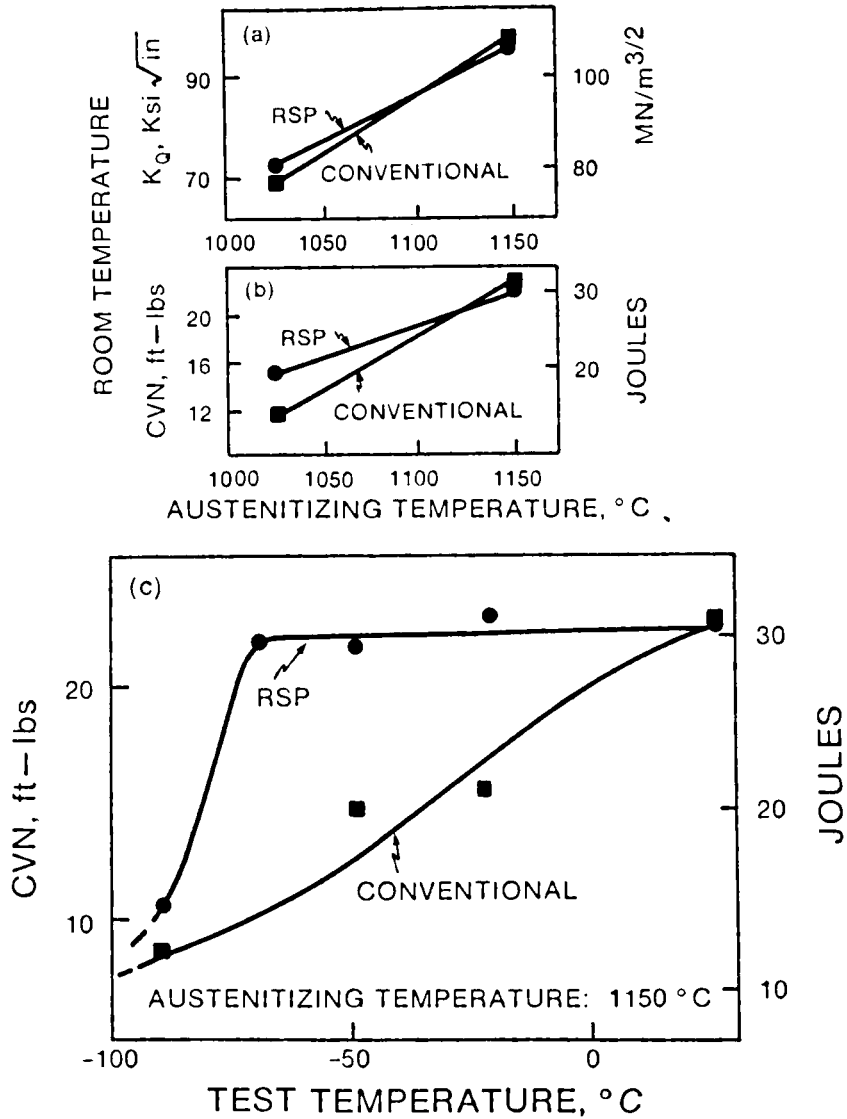


Fig. 11 Fracture-toughness characteristics of conventionally processed and RSP 0.25C-4Mo steel; water quenched from austenitizing temperatures shown and tempered at 150°C for 1 hr. (a) and (b) Effect of austenitizing temperature on room-temperature properties, and (c) effect of test temperature on fracture toughness after austenitizing at 1150°C . K_Q is the plane-strain fracture toughness based on the maximum load vs. crack-opening displacement for a fatigue-precracked specimen in a slow-bend test. (Fleyshman, 1982).

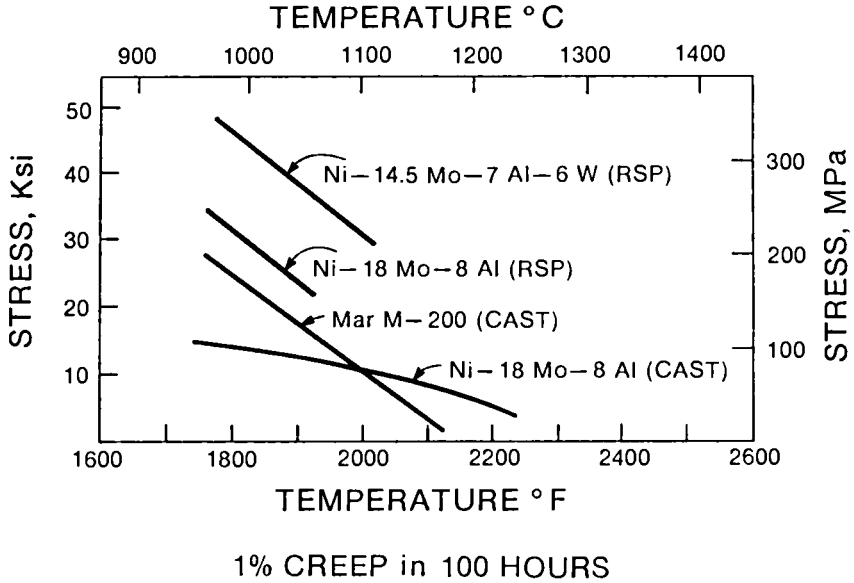


Fig. 12 Creep strength of superalloys, showing some effects of RSP in comparison with cast Mar M-200; see text for composition of Mar M-200. (Anderson and others, 1980.)

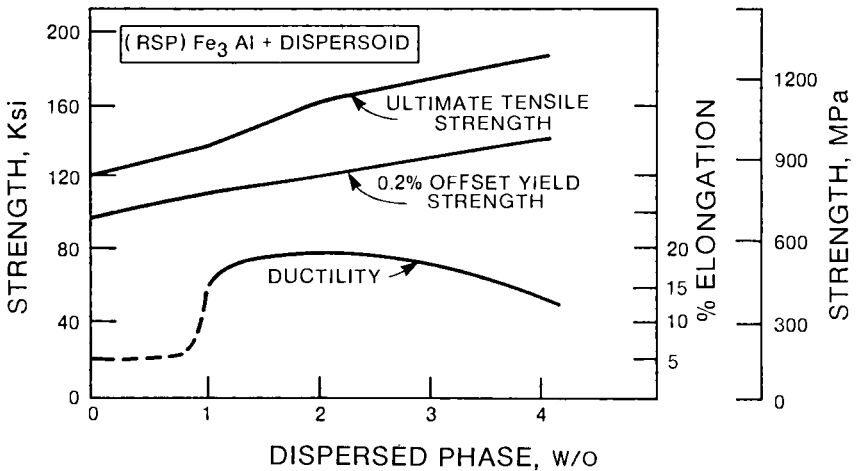


Fig. 13 Effect of RSP and a dispersed second phase on the room-temperature tensile properties of Fe₃Al. (Adam and others, 1982).

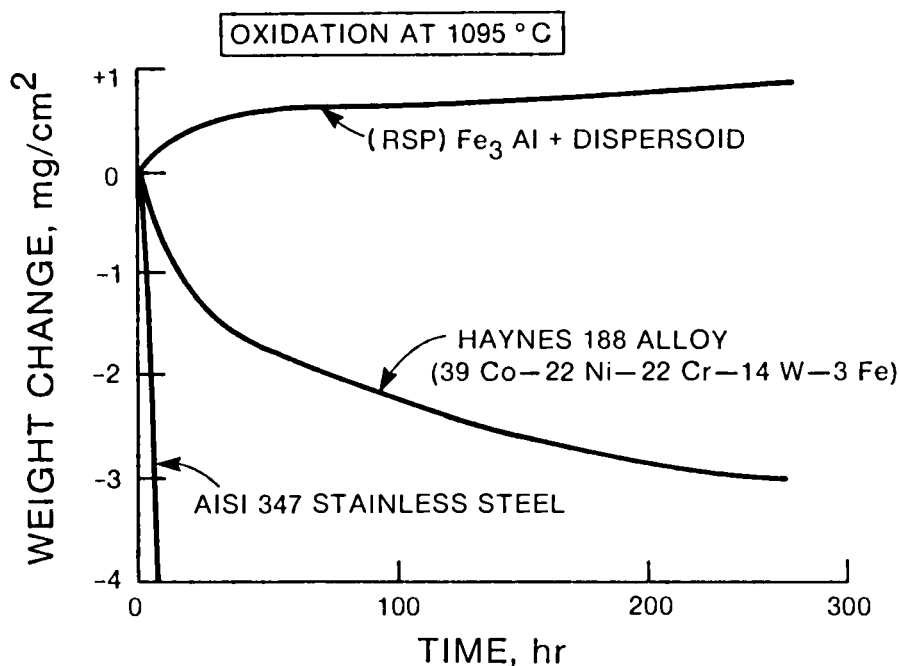


Fig. 14 Effect of RSP and a dispersed phase on cyclic oxidation resistance of Fe₃Al at 1095 °C. (Adam and others, 1982.)

CLOSURE

The advent of rapid solidification processing offers a timely example of the important manner in which materials processing interacts with structure/property relationships. This dynamic interplay has paved the way, not only to new accessible ranges of structure/property relationships in alloy systems, but also to new studies of rapid solidification phenomena (e.g. heat flow, super-cooling, interfacial velocity, etc.) and their influence on the resulting fine structure of materials. Particular attention is drawn to the attainment of massive (segregationless or partitionless) solidification as a route for achieving unusually high degrees of supersaturation relative to second phases which are otherwise difficult to dissolve in the solidified alloy. The solid-state precipitation of such stable phases in extremely fine dispersions then leads to unusual resistance to grain growth, with consequent effects on mechanical and oxidation behaviour.

ACKNOWLEDGEMENTS

The author is particularly grateful to the Office of Naval Research for sponsoring this field of investigation at MIT under Contract No. N00014-81-K-0013; to Dr Robert Mehrabian of the National Bureau of Standards for many

important discussions and ideas in connection with this paper; and to Dr Colin Adam of Pratt and Whitney Aircraft for furnishing some of the illustrative property data.

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Microstructural Design in Low Alloy Steels

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ABSTRACT

The evolution of micro-alloyed steels from plain carbon steels is examined with emphasis on grain size control by use of Nb, Ti and V additions and by the application of controlled rolling. The structural changes during controlled rolling are described as well as the influence of alloying elements on these changes, and on the final microstructure. The achievement of high strength and toughness is discussed including the role of inclusions.

KEYWORDS

Carbide dispersions; controlled alloying; ductile-brittle transition; γ/α interfaces; grain refinement; inclusions; micro-alloying; recrystallization of austenite; solubilities of alloy carbides; sulphide inclusions.

INTRODUCTION

Traditionally carbon has been the most convenient alloying element to use for the strengthening of steel, being both extremely cheap and easily alloyed with iron. Structural steels containing up to 0.3% carbon which have been widely used in engineering mainly as hot finished plates and beams, typically possess yield strengths around 300-350 MNm⁻². However their use in the modern environment is limited because difficulties can arise both in welding and in forming due to the high carbon content. The development of welding as the main fabrication technique has led to serious cracking and distortion problems which can only be eliminated by the use of lower carbon steels. There is also, of course, increasing emphasis on tough steels which resist crack initiation and propagation. The transition from ductile to brittle behaviour is extremely sensitive to increasing carbon content which increases the volume fraction of pearlite in the steel. Fig. 1 shows how the ductile-brittle transition temperature increases dramatically with carbon content; for example a 0.3C steel can behave in a brittle manner at 50°C, whereas similar behaviour in a 0.1C steel will only occur if the temperature is lowered to around -50°C.

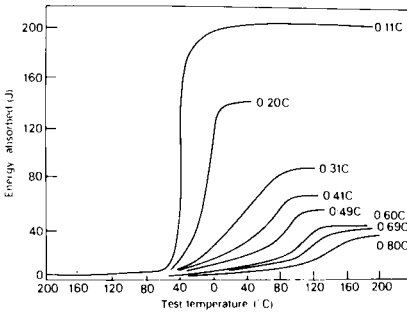


Fig. 1. Effect of carbon on toughness measured by Charpy impact transition temperature (Burns & Pickering)

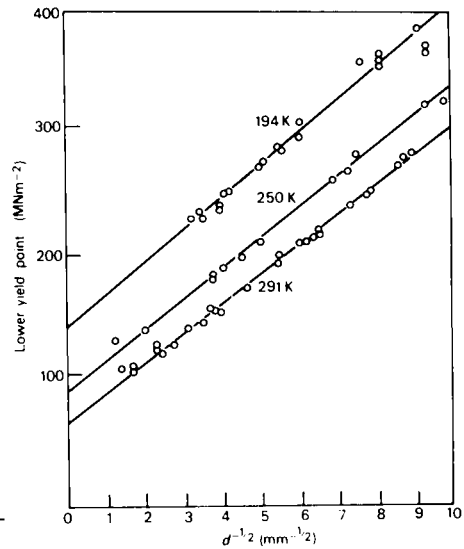


Fig. 2. Dependence of the lower yield stress of mild steel on grain size (Petch)

GRAIN SIZE

The great importance of grain refinement as a major strengthening mechanism derives from the scientific work of Hall and Petch (Hall, 1951; Petch, 1953) on iron and mild steel which related the yield stress σ_y to the grain diameter d thus:

$$\sigma_y = \sigma_0 + k_y d^{-1/2} \quad (1)$$

The linear relationship between σ_y and $d^{-1/2}$ is illustrated in Fig. 2 for mild steel tested at three temperatures, which emphasizes the substantial gains in strength to be obtained by use of finer grain sizes. Typically a coarse grained mild steel with a grain diameter of 0.04 mm ($d^{-1/2} = 5$) would have a yield stress at room temperature of about 200 MNm⁻² (13 t.s.i.); when the grain size is refined to 0.007 mm ($d^{-1/2} = 12$) the yield stress is raised to around 380 MNm⁻² (25 t.s.i.). It is thus not at all surprising that in the last two decades the emphasis has been on the development of processing and suitable steels to achieve very fine grain sizes.

An added bonus of fine grain size is that the toughness of the steel increases with decreasing grain size, other things being equal. It is practically the only method of strengthening which at the same time leads to increased toughness. The transition temperature T_C has been shown to be linearly related to $\ln d^{-1/2}$ as shown in Fig. 3 for a 0.11C steel. Consequently the achievement of fine grain sizes in steels is advantageous not only because strength is improved, but at the same time so is the ductility. One of the main developments over the last twenty years has been the

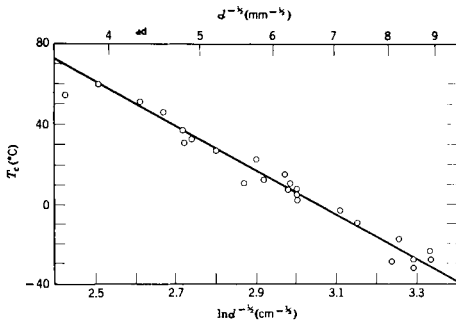


Fig. 3. Dependence of transition temperature on grain size (Petch)

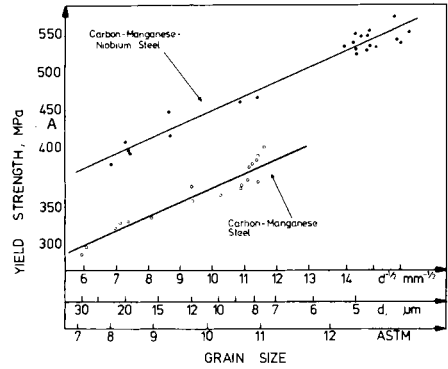


Fig. 4. Effect of grain size on yield stress of a carbon-manganese-niobium steel (Le Bon and Saint Martin)

attainment of fine grain sizes in the range 5-20 μm achieved by the application of controlled rolling techniques together with the effective use of minor alloying additions, for example niobium (Microalloying, 1975). Figure 4 shows how the addition of this element to carbon-manganese steel substantially refines the grain size and consequently raises the overall yield strength.

COMPOSITION CONTROL

The overwhelming need to have constructional steels which could be welded satisfactorily led to the move to lower carbon contents. This trend was accelerated by the realization that the presence of pearlite in the microstructure adversely affects fracture toughness (Pickering & Gladman, 1963). As a result the so-called "pearlite-reduced" steels were produced in which carbon contents less than 0.1 wt% were often achieved (Burgan & Stanistreet, 1967). These steels were largely ferritic with relatively small amounts of pearlite visible in the microstructure. However, in lowering the carbon content, the strength was reduced, consequently the need to refine the grain size and so restore higher strength levels led to the extensive use of controlled rolling.

It was realized at an early stage that small concentrations of certain strong carbide forming elements e.g. <0.1 wt% niobium (Duckworth, Phillips and Chapman, 1965), when added to a steel, made it much easier to achieve fine grain sizes during controlled rolling, although it was some time before the role of these "microalloying" additions was fully understood. When plain carbon steels are rolled in the austenitic condition in the range 1200-1000°C, they are essentially single phase, because the iron carbide visible in microstructures examined at room temperature has completely dissolved in the austenite. Consequently the austenite grain boundaries are not pinned by second phase particles, and grain growth can be very severe, leading to lower strength levels at room temperature.

What is needed is a fine dispersion stable at hot rolling temperatures which

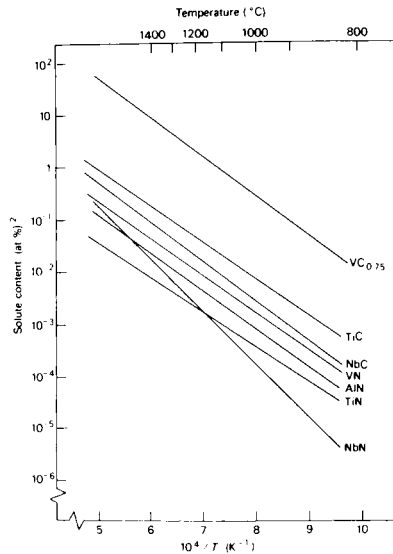


Fig. 5. Solubility products of carbides and nitrides in austenite as a function of temperature (Aronsson)

will not occupy a high volume fraction and so adversely affect room temperature ductility and toughness. The most suitable dispersions are nitrides, carbides and carbo-nitrides formed with several metallic elements, notably aluminium, niobium, titanium and vanadium. The elements are used separately or in combination which leads to a large number of possible compositions. To add to the complexity, the nitride and carbide phases are predominantly of face-centred cubic structure and are mutually soluble in each other, so in many cases the effective dispersion may be a carbo-nitride of one or more metals. Several possibilities are as follows:

AlN Nb(CN) V(CN) (NbV)(CN) TiC TiN Ti(CN)

Data are available for the solubilities of some of the phases in austenite at high temperatures, as shown in Fig. 5. The absolute values are not too important as they will be influenced by inter-solubility effects of, for example, N and C, or of two metallic alloying elements. However, it is helpful to realize that the carbides decrease in solubility in the order $VC \rightarrow TiC \rightarrow NbC$, while at a lower level of solubility the nitrides behave in a similar manner with AlN being slightly less soluble than VN. In this paper there is not space to discuss in detail all the implications of compositional changes, however very fine grain sizes ($<10\mu m$) can be achieved by controlled rolling by making use of most of the phases listed above.

CONTROLLED ROLLING

In contrast to normal hot rolling of steel which is usually carried out between 1250 and 1050°C without very precise control, and leads to relatively coarse grained austenite, in controlled rolling (Irvine and coworkers, 1970; Le Bon & Saint Martin, 1975) several important variables need close attention:

1. temperature at each pass
2. amount of deformation per pass
3. time between passes
4. final rolling temperature
5. rate of cooling after final pass.

Typically normal hot rolling results in ferrite grain sizes in the final structure of between 40 and 200 μm , while on the other hand controlled rolling leads to final grain sizes of less than 10 μm (Micro-alloying, 1975). While plain carbon steels can be treated in this way, high strength levels are much more readily achieved by the use of micro-alloying elements. In such steels a whole series of structural changes take place during rolling which determine the final structure and the mechanical properties of the steel (Micro-alloying, 1975):

1. hot deformation of the steel in the austenitic condition
2. recrystallization of the austenite
3. grain growth of the austenite
4. precipitation of nitrides and carbo-nitrides in austenite
5. transformation of austenite to ferrite ($\gamma \rightarrow \alpha$)
6. precipitation of alloy carbides during the $\gamma \rightarrow \alpha$ transformation
7. precipitation of alloy carbides in ferrite.

The process starts with hot slab either derived from ingots or continuously cast which is rolled from temperatures above 1200°C down to the range 850-700 which can include the γ - α transformation. At the highest temperature the austenite is hot worked and recrystallizes spontaneously during processing (dynamic recrystallization); this occurs repeatedly as the deformation proceeds and results in the replacement of large grains by progressively smaller austenite grains.

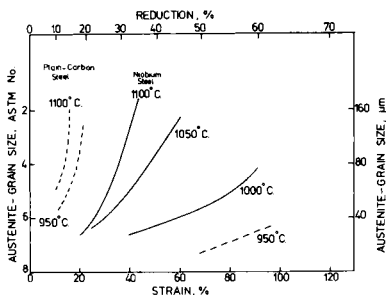


Fig. 6. Critical strain needed to complete recrystallization of austenite as a function of deformation temperature and grain size. Comparison of Nb steel with plain carbon steel (Tanaka et al)

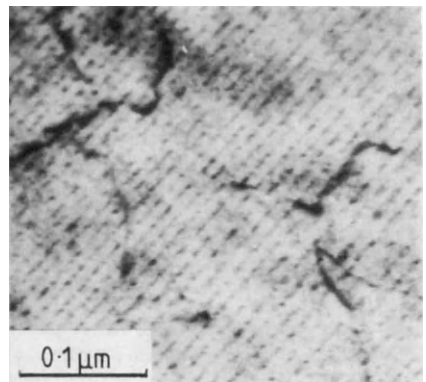


Fig. 7. Fe-0.75V-0.15C transformed at 725°C. Interphase precipitation of VC in ferrite (Batte). Thin-foil EM

In the temperature range 1200-1000°C there is a marked tendency for these grains to coarsen by grain growth, but this is impeded by the presence of second phase particles predominantly nitrides and carbo-nitrides. At the highest temperatures ($\sim 1200^\circ\text{C}$) there are not many particles present, but as the temperature falls during rolling, because of decreasing solubilities, second phase particles are increasingly formed. These particles nucleate preferentially at grain boundaries, consequently pinning them, and thus minimize grain growth. An even more important role of the fine dispersion is that it retards the process of recrystallization, in other words heavier deformations are needed before recrystallization takes place. This is probably due to the stabilization of dislocation networks by the nucleation of fine precipitates on them, which delays the re-organization needed before nucleation of new grains can take place. The recrystallized grain size decreases with increasing deformation, so the final result of retardation is a finer grain size in the austenite.

As the temperature progressively falls, the tendency of the austenite to recrystallize decreases, i.e. it occurs at increasing strains (Fig. 6) as the $\gamma \rightarrow \alpha$ transformation temperature is approached, with the result that the austenite is very fine grained just above the transformation temperature ($\sim 850\text{--}800^\circ\text{C}$) and as a result fine grained ferrite is formed. Alternatively the austenite remains unrecrystallized and ferrite forms in the distorted structure, both at the grain boundaries and at inhomogeneities such as deformation bands within the austenite grains. In both cases fine ferrite grains result, but the formation of ferrite grains within deformed austenite leads to ultra fine grains, particularly if the austenite has received heavy deformation prior to the transformation.

At the lowest rolling temperature (below 850°C) the steel possesses a duplex ($\gamma + \alpha$) structure with the result that the ferrite is also deformed and either develops a dislocation sub-structure or recrystallizes. If the deformation is carried on to too low a temperature the structure is incompletely recrystallized and will possess inferior toughness.

MICROSTRUCTURE OF CONTROL ROLLED STEELS

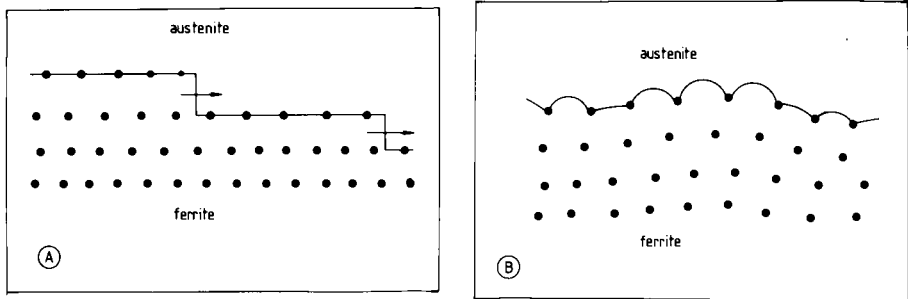
The fine grain sizes obtained by controlled rolling contribute very substantially to the high strength levels obtainable in micro-alloyed steels as illustrated in Fig. 4 for a carbon-manganese-niobium steel, with a yield strength around 550 MNm^{-2} when the grain size is reduced to around $5 \mu\text{m}$. However it should be noted that these properties are not the result of a simple extrapolation of grain size from that of a carbon-manganese steel. As the strength-grain size curve is displaced by $\sim 90 \text{ MNm}^{-2}$ above that of the carbon-manganese steel, it is clear that some other strengthening action is also taking place. This is due to precipitation of alloy carbides, e.g. NbC, VC, TiC during the γ/α transformation, or just subsequent to the transformation. The solubility of these alloy carbides is substantially lower in ferrite than in austenite, so in normal circumstances, precipitation of carbides would be expected.

This precipitation is on an extremely fine scale and can only be effectively studied using transmission electron microscopy. It takes two forms (Honeycombe, 1981):

1. banded precipitation during the transformation (interphase precipitation)
2. subsequent precipitation on dislocations generated during the transformation.

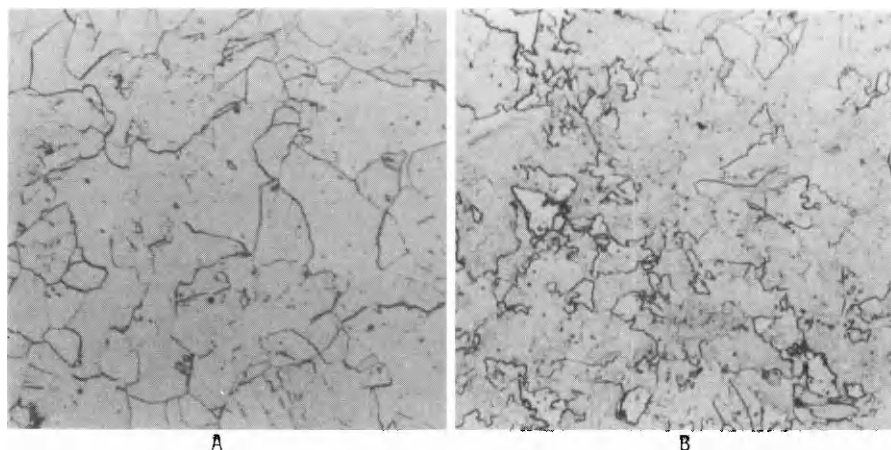
Interphase precipitation has been observed in numerous micro-alloyed and other alloy steels, and is characterized by its banded appearance (Fig. 7). All the familiar carbides in steels and particularly NbC, TiC, VC as well as the nitrides and carbo-nitrides exhibit this striking morphology which has now been identified with the moving γ/α interfaces.

It is now well established (Honeycombe, 1980) that the phase interfaces move in many cases by the migration of small mobile steps along less mobile planar interfaces (Fig. 8A). As the interface is created by the step movement, precipitation takes place on the new planar surface (Fig. 8A), but not normally on the step because it is migrating rapidly. This process is repeated many times building up sheets of precipitate parallel to each other, and with a spacing equal to the height of the steps on the interface which is frequently in the range 5-50nm for NbC, VC and TiC. In the electron microscope the precipitates are usually seen as linear arrays, but by tilting the specimen it can be shown that the precipitates are really in sheets. The γ/α interfaces are often planar for energetic reasons, but frequently curved interfaces form, which do not move by step migration. Nevertheless precipitation still occurs at these curved interfaces and pins them in position until sections of the interface escape by bowing between the particles, and eventually they unzip the interface which is subsequently pinned again to form another array of precipitates (Fig. 8B).



Figs. 8A&B. Models for the movement of the γ/α interface (A) by step migration (B) by bowing around precipitates

Interphase precipitation is normally associated with more or less equi-axed ferrite grains which form at high transformation temperatures, e.g. in the range 850-750°C, and which frequently grow by movement of planar interfaces. When the transformation temperature is somewhat lower (750-650°C), achieved by more rapid cooling, the ferrite becomes more lath shaped and is more heavily dislocated (Figs. 9A&B). This arises from a change in growth mechanism when the driving force is higher, but the diffusivity is less than at higher transformation temperatures. The dislocations originate from two possible sources: firstly as an integral part of the transformation, and secondly, as a result of stresses set up by the volume change in going from γ to α . As the γ/α reaction proceeds more rapidly at these temperatures which are in the vicinity of the nose of the TTT curve, there is less opportunity for interphase precipitation, so the precipitation occurs shortly after the phase transformation, and is predominantly nucleated on these dislocations.



Figs. 9A&B. A 0.08C 0.4Mn 0.21Ti steel solution treated at 1200°C then transformed at (A) 800°C, (B) 650°C. Optical micrographs x 200 (G M Smith)

CONTROL OF MECHANICAL PROPERTIES

It has been shown that grain size refinement during controlled rolling is a major strengthening mechanism. It also provides improvement in toughness, and quantitative work has shown that the transition temperature is reduced by 11.5°C for each unit increment in d^{-2} in the case of carbon-manganese steels. The same unit increment brings about a yield stress increase of about 15 MNmm⁻² excluding the effects of precipitation hardening, but unfortunately an increase in yield strength due to the latter brings about an increase in transition temperature. The real art of alloy design is to reach the required strength level by a balance of grain size control and precipitation such that the toughness is still at an adequate level.

Of the several micro-alloying additions available, Al, Nb, V, Ti, Zr, Mo, perhaps the most effective for control of grain size is niobium, stemming from the relatively low solubility of NbC in austenite. Al, V and Ti are effective in steels with high nitrogen levels, Al because it forms only a nitride, V and Ti because their carbides are more soluble than NbC, so it is sensible to form a carbo-nitride which is less soluble in austenite than a straight carbide, i.e. V(CN) and Ti(CN) rather than VC and TiC, if maximum pinning of austenite grain boundaries is to be achieved. Of course, more complex compositions involving Nb and V, Nb and Ti, or V and Ti have some advantages by bringing about appropriate changes in solubility and in the stability of the carbide dispersion.

Turning to the question of raising the yield strength by precipitation, it is clearly more effective to use a more soluble carbide which could provide a larger volume fraction of precipitate. For example VC is much more soluble in austenite than NbC, so that on subsequent transformation of austenite to ferrite a larger increment in strength can be achieved if vanadium is used. If Nb and V are used in combination, then the NbC can be relied on to provide adequate grain refinement during controlled rolling, while the VC by

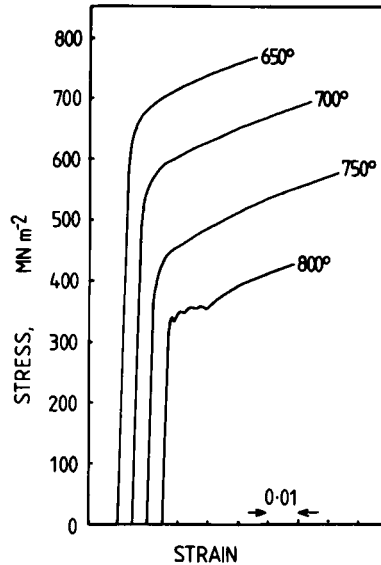


Fig. 10. Stress-strain curves at RT of an 0.08C-0.21Ti-0.4Mn steel isothermally transformed between 800 & 650°C (G M Smith)

precipitating during the γ/α transformation also raises the yield stress.

The carbon level of most micro-alloyed steels is below 0.1 wt% which makes them readily weldable, and it also limits the occurrence of pearlite as previously mentioned. Ideally the carbide forming element should be present in just sufficient quantity to utilize effectively all the carbon present both as carbide particles in the austenite, and as a fine dispersion in the ferrite. Any pearlite formed is unnecessary, and will adversely affect toughness, the ideal structure being a ferritic matrix with a grain size well below $10\mu\text{m}$ containing a fine carbide dispersion with few coarse carbide particles which may remain from the melt.

The nature of the ferrite phase has also some important effects on mechanical properties. Equi-axed ferrite (polygonal) formed at higher temperatures (850-750°C) can lead to a sharp yield point (Fig. 10) particularly in steels where there is insufficient alloying element to combine with all the carbon present (Tither & Lavite, 1975). However a similar steel transformed at lower temperatures (750-650°C) contains lath ferrite ("acicular") which has a high dislocation population and gives a continuous stress-strain curve. This absence of a yield point arises because there is insufficient carbon to lock completely the dislocations, so unlocked segments can lead to dislocation movement without the sudden generation of free dislocations which produces a yield point. The smooth stress-strain curve is preferred in many applications where the rolled material is to be formed accurately on site, e.g. in the building of some pipe lines.

In practice an overall lath ferrite structure is achieved by adding alloying elements which lower the temperature of the $\gamma \rightarrow \alpha$ transformation sufficiently to suppress the formation of both polygonal ferrite and pearlite. For example, if the manganese content of a steel containing 0.03-0.10% Nb is raised to 1.6-2.2%, and 0.25-0.40% Mo is also present, the resulting micro-structure is entirely lath ferrite after air cooling following controlled rolling. The absence of a yield point leads to a substantial degree of work hardening during fabrication, for example, of line pipe, and a net increase in the yield strength of the finished pipe results.

INCLUSIONS

The mechanical properties of micro-alloyed steels can be adversely affected by the presence of inclusions which can reduce the ductility and toughness depending on their shape, distribution and volume fraction. The elongation of some of the inclusions into long ribbons by the controlled rolling leads in many cases to large planar inclusions which cause marked anisotropy of mechanical properties such as ductility. Sulphides provide the biggest problem because of their ability to be deformed at high temperatures, but which become brittle at low temperatures.

The morphology of MnS inclusions is very dependent on the oxygen content of the steel. Type 1 sulphides are isolated globular particles common when oxygen is present in the melt, whereas Type 2 interdendritic eutectic forms are familiar in killed steels. The latter deform more readily with the result that as a result of rolling they form elongated localized co-planar arrays which are particularly harmful to transverse ductility (Baker & Charles, 1972).

Fortunately additions can be made, for example, zirconium, which enters the manganese sulphide inclusions and makes them more brittle at rolling temperatures. This means that the inclusions remain globular and do not deform to flat drawn out stringers during rolling. Rare-earth additions are also made which readily form separate sulphides replacing manganese sulphide, and these also are not deformable. While these measures may minimize directionality of properties and provide ductility for working operations, there is a risk that the fracture toughness will be adversely affected by the presence in the steels of brittle phases.

Steels for line pipe must have adequate toughness with a ductile-brittle transition temperature below the minimum temperature encountered in service so that the pipe will not fail in a brittle manner. Additionally the energy shelf revealed in impact testing should be sufficiently high that the steel absorbs enough energy during ductile failure to avoid running fractures (Paxton, 1981). Ductile failure initiates at inclusions, consequently the morphology and size distribution of inclusions is a vital concern. The really damaging particles are usually greater than $1\mu\text{m}$ diameter, and particles below this limit are relatively harmless. In practice Arctic pipe line specifications call for shelf energies around 95J (70 ft.lb.) at -180°C , and a ductile-brittle transition temperature below this temperature, together with a yield stress of 480 MNm^{-2} (70 k.s.i.).

FURTHER DEVELOPMENTS IN MICRO-ALLOYED STEELS

The logic of the role of carbon is to approach more closely stoichiometric compositions where the carbon is all combined as a fine alloy carbide dis-

persion, and not present in the form of pearlite or coarse carbide particles, both of which are detrimental to ductility. This means a movement to lower carbon levels to around 0.03 wt% (Rothwell & Cooke, 1981), the increased oxygen contents being controlled by vacuum degassing. Such changes inevitably involve even closer control of the steel making process and the introduction of specialized decarburizing methods.

The metallic micro-alloying additions have probably not yet been optimized particularly in lower carbon steels, and the important role that nitrogen can play in controlling the solubilities of the carbide phases has not been fully exploited. More attention should be paid to the effect of metallic alloying elements on the kinetics of the γ/α transformation which determines in practical terms the hardenability. While it is not anticipated that martensitic structures will be aimed for after controlled rolling (for these would require tempering) it is desirable to encourage the formation of lath ferrite rather than equi-axed ferrite, and this is more readily achieved if the γ/α transformation is slowed down.

The bainitic structures offer an alternative route to higher strength (Micro-alloying, 1975; Rothwell & Cooke, 1981) low alloy steels, however the upper bainitic structure contains a dispersion of iron carbide particles which results in inadequate toughness. To overcome this difficulty, carbon levels will have to be lowered to about 0.02%, and sufficient alloying element provided to suppress the ferrite reaction, for example about 0.5%Mo together with small additions of nickel or copper. Normal micro-alloyed steels contain 1-2% manganese primarily to lower the temperature of the γ/α transformation and thus reduce the resultant ferrite grain size, but the metal also has a substantial solid solution hardening effect and reduces the tendency to form pearlite. At the higher levels (1.5-2%) manganese encourages the formation of lath ferrite and bainite. Increasing the Mn content above 2% will thus help in the formation of bainite.

Another approach to higher strength levels is to lower the finishing temperature of controlled rolling through the γ/α transformation into the ferritic field. This poses no threat of excessive mill loads because these do not increase continuously with falling temperature. Ferrite in the range 850-750°C has a similar strength and workability to austenite in the range 1050-950°C, and indeed commercial rolling has been carried out down to 600°C. However if too low a temperature is reached, the ferrite grains will be elongated and possess a preferred orientation with {100} planes parallel to the rolling plane. Such structures give characteristic flat sheared ligaments which are associated with an impaired energy transition (Paxton, 1981) in fracture tests.

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Maraging Steels — Structure, Properties and Applications

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ABSTRACT

Maraging steels are high strength steels containing a very low percentage of carbon. The strengthening effect is achieved by precipitation of substitutional alloying elements in the iron-nickel martensite, which occurs during the aging process.

The metallurgical behaviour of these steels is associated with the thermal hysteresis between the formation of martensite and its reversion to austenite in the Fe-Ni alloys. Maraging steels show some excellent properties in the annealed and the fully heat-treated conditions such as high strength-to-weight ratio, superior toughness at high strength levels, good resistance to hydrogen embrittlement and to stress corrosion cracking. A steep rise in the price of cobalt which is also a strategic material stimulated development of a new cobalt-free maraging steel which possesses strength and ductility properties very similar to 18Ni(250) maraging steel but lower toughness.

KEYWORDS

Maraging steels, high strength-to-weight ratio, superior toughness at high strength levels, good resistance to hydrogen embrittlement and to stress corrosion cracking, good weldability.

INTRODUCTION

Maraging steels are high-strength steels containing a very low percentage of carbon. The strengthening effect during the aging of these steels is caused by precipitation processes of substitutional alloying elements in the iron-nickel martensite. The term "maraging" is an abbreviation of "martensite age hardening".

The metallurgical behaviour of these steels is associated with the thermal hysteresis between the formation of martensite on cooling and its reversion to austenite on heating in the Fe-Ni alloys (see Fig. 1) (Jones and Pumphrey, 1949).

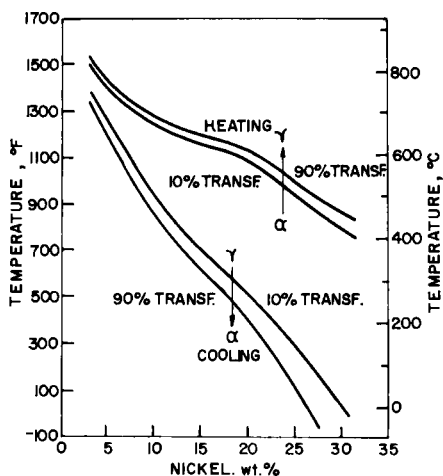


Fig. 1. Metastable Iron-Nickel Phase Diagram.

The first maraging steels that were developed in the 1950's contained 20% to 25% Ni and a combination of small amounts of Al, Ti and Nb (0.3% Al, 1.4% Ti, 0.4% Nb). After formation of the martensitic structure upon cooling, hardening was achieved by aging in the temperature range, 430 °C to 510 °C. The process resulted in high hardness (~65 R_C) and high strength. Toughness however was low at the high strength levels. For that reason steels of the above composition were abandoned and replaced by a new generation of maraging steels, viz. the 18 Ni-Co-Mo type. Their hardening during aging was brought about by the combined effects of cobalt and molybdenum. Titanium present in these steels plays the role of supplementary hardener in addition to being a refining element of the residual carbon.

Later more specialized maraging steels were developed for particular applications, e.g. steels exhibiting greater resistance to austenite reversion, cast alloys etc.

A typical heat treatment of maraging steels consists of solution annealing for 1 hour at 815 °C, although other temperatures or multiple annealing heat treatments may be used in certain cases; followed by cooling in air to room temperature. During cooling the alloys are transformed to martensite. Due to the generally high nickel content and the absence of carbon, the hardenability after annealing is independent of the cooling rate, and the alloys are therefore cooled in air. In the post-annealing condition their hardness is from 30 R_C to 35 R_C , permitting relatively easy further mechanical processing.

Hardening of maraging steels is achieved by aging for 3 to 6 hours at temperatures of $\sim 480^{\circ}\text{C}$. The aging process causes only very slight dimensional changes, and it can therefore be introduced in the final stages of production. Commercial maraging steels are designed to provide a specific level of yield strength, from $1\,375\text{ MN/m}^2$ - $3\,450\text{ MN/m}^2$ (200 ksi to 500 ksi). The lower strength levels (grades 200, 250, 300) depend primarily on the combination of cobalt and molybdenum in the steel. For higher strength levels (grade 350) the Ti content is increased. For grades 400 and 500, nickel, cobalt and molybdenum are still the principal alloying elements, but the Ni content is considerably reduced, while the cobalt and molybdenum contents are increased.

Maraging steels show some excellent properties in the annealed and the fully heat treated conditions. The main properties which have made them so interesting as constructional steels are the high strength-to-weight ratio and their superior toughness at high strength levels. They also show a better resistance to hydrogen embrittlement and to stress corrosion cracking than most of the conventional alloyed steels. They can be welded in any thermal condition (annealed and maraged) without preheating. These properties have led to the use of maraging steels in many demanding applications.

ALLOYING ELEMENTS IN MARAGING STEELS

The main alloying element in maraging steels is nickel. Its presence ensures formation of martensite, thus increasing the strength of the matrix; and it reduces the solubility of other alloying elements in the matrix. In addition, Ni reduces the resistance to dislocation motion in the lattice and the energy of interaction between the dislocations and the interstitials and it promotes stress relaxation which in turn decreases the proneness to brittle fracture (Perkas, 1970). The martensite favours uniform nucleation and growth of precipitating phases. This homogeneous precipitation promotes good plastic properties and high ductility.

The hardening effects associated with the precipitation processes during aging depend on the nickel content of the steel, of the other alloying elements, and on the interaction between some of them, e.g. molybdenum and cobalt (Perkas and Snitsar, 1964). Qualitatively the alloying elements may be divided into three groups: strong hardeners (Be, Ti); moderate hardeners (Al, Nb, Mn, Mo, Si, Ta, V and W) and weak hardeners (Co, Cu, Zr).

The main hardening elements are titanium, molybdenum and cobalt, in various combinations. Titanium, apart from being a hardener, refines the steel by forming carbonitrides with the residual carbon, usually precipitating in the austenitic grain boundaries which, however, leads to some anisotropic effects and reduction of the steel's ductility (Legendre and Castagne, 1968).

Molybdenum may have a double effect: a) its segregation during solidification induces anisotropic properties, b) by lowering the diffusion coefficients of some of the alloying elements it reduces preferential precipitation of secondary phases during aging, increasing the ductility of the steel in the post-aging conditions.

Aluminium has some hardening effect on martensite, but it impairs the ductility in both the pre- and the post-aging conditions.

Silicon at concentrations above 0.1 wt% and especially above 0.3 wt%, reduces plasticity.

Some elements (viz. Si, Cr, Co) influence the hardening process in maraging steels by lowering the solubility of the hardening components, such as molybdenum, tungsten and titanium.

The effect of a decrease in solubility on the hardening process can be expressed in the following ways:

- a) reduction of work of formation of a nucleus which results in an increase in the number of nuclei capable of growth, thereby reducing the distance between the precipitating particles;
- b) increase in the volume fraction of the precipitates.

Cobalt also reduces the resistance of the lattice to dislocation motion and the energy of interaction between the dislocations and the interstitials. An increase in the cobalt raises the M_s temperature, while chromium improves corrosion resistance and enhances the strain hardening of martensite (Perkas, 1970).

MARTENSITE FORMATION

The formation of martensite in maraging steel can be directly related to the iron-rich end of the Fe-Ni phase diagram (Owen and Liu, 1949). The low-temperature equilibrium phases in the iron-rich alloys are either ferrite (at concentrations < 10 wt% Ni) or ferrite and austenite (at concentrations > 10 wt% Ni).

It appears that in alloys containing between ~10 wt% Ni and ~25 wt% Ni, on cooling from the austenitic region of the phase diagram, the austenite is not transformed into the phases predicted by the equilibrium diagram (ferrite and austenite) but to BCC martensite. The temperature of the martensitic transformation (M_s) depends on the Ni content - the higher the latter, the lower the M_s temperature. Above ~33 wt% Ni, only the γ -phase is present at room temperature (Jones and Pumphrey, 1949). According to later studies (Mihalisin, 1968; Gilbert and Owen, 1966; Swanson and Parr, 1964) a variety of transformations can take place in these alloys in the range of Ni concentrations between 0 wt% Ni and 33 wt% Ni.

From 0 wt% Ni to 5 wt% Ni, and independent of the cooling rate, a $\gamma \rightarrow \alpha_{\text{BCC}}$ transformation occurs. In the range, 5 wt% Ni to 10 wt% Ni, and at slow cooling rates, a $\gamma \rightarrow \alpha_{\text{BCC}}$ transformation takes place; but at high cooling rates the transformation becomes $\gamma \rightarrow$ martensite. The increase in the Ni content lowers the cooling rate required to form martensite, and at about 10 wt% Ni a fully martensitic structure is obtained even at very low cooling rates. A typical martensitic morphology characteristic for the Ni range between 10 wt% Ni and 25 wt% Ni is the so-called lath (massive) martensite. Above 25 wt% Ni the martensitic reaction occurs below room temperature and the morphology obtained is called "twinned martensite".

The precise conditions that determine whether lath or twinned martensite is formed are still uncertain, but two factors seem to play a dominant role, viz. the M_s temperature and the stacking-fault energy (SFE). A decrease

in the M_s temperature and an increase in the SFE favour the formation of twinned martensite. The M_s temperature can be modified either by changes in the composition of the alloy or by plastic deformation, while the SFE varies only as a result of alloying. Sometimes the effects of M_s and of SFE may counteract each other.

Alloying elements used in maraging steels generally lower the M_s temperature; but the effect of any individual element depends on the total composition of the alloy (Owen and Wilson, 1965; Tuffnell and Cairns, 1968; Yeo, 1963; Hammond, 1964; Manenc, Thivellier and Thomas, 1971). Figure 2 shows the effect of solute element content on the M_s and A_s temperatures in iron-base alloys. As can be seen, almost all alloying additions lower the M_s temperature. One exception is cobalt, additions of which up to ~8 wt% increase the M_s temperature in iron-nickel alloys. This effect of cobalt on the M_s temperature is very helpful in ensuring the formation of lath martensite even at higher concentrations of other alloying elements.

The orientation relationship between the martensitic platelets and the austenite matrix is believed to be Kurdjumov-Sachs

$$(111)_\gamma \parallel (011)_\alpha ; [\bar{1}\bar{1}0]_\gamma \parallel [\bar{1}\bar{1}1]_\alpha \quad [K-S]$$

The simultaneous existence of the Kurdjumov-Sachs and the Nishiyama-Wasserman orientation relationships has recently been reported (Atsmon and Rosen, 1981).

$$(111)_\gamma \parallel (011)_\alpha ; [100]_\gamma \parallel [100]_\alpha \quad [N-W]$$

Lath martensite is characterized by a high density of uniformly distributed dislocations which are predominantly of the screw type and have a tendency to orient themselves in the $\langle 111 \rangle_\alpha$ directions (Patterson and Wayman, 1966). The high density of the dislocations and their relatively uniform distribution in the martensite provide a large number of potential nucleation sites and guarantee higher diffusion rates, thus ensuring the uniformity of fine precipitates during the age-hardening process.

The substructure of the twinned martensite consists of fine transformation twins, which may coexist with a network of dislocations (Oka and Wayman, 1966; Kelly and Nutting, 1960). The mode of twinning in twinned martensite was reported to be of the $\{112\}_m$ type (Kelly and Nutting, 1960), but in certain iron alloys it was also observed (Oka and Wayman, 1966) to be of the $\{100\}_m$ mode.

In maraging steels the direct contribution of the martensitic transformation to the strength of the alloy is relatively small. The solid-solution-strengthening by Ni is the major contributor to the hardening effect ($> 70\%$ of the overall value of the yield stress, σ_y) in Fe-Ni alloys containing less than 30% Ni.

The work hardening processes, temperature and strain-rate dependences of the yield stress, derived activation values, and energies for the deformation of lath martensite are all similar to the same properties observed in cold worked iron and low alloy steels (Floreen, 1968). The one basic difference is the ductility. Lath martensite of maraging steel (18 wt% Ni) shows a much higher ductility than iron even when tested at very low temperatures (liquid hydrogen) (Floreen, 1964). The reason probably lies in the fact that the number of mobile dislocations in the lath martensite is much higher than in iron. The availability of mobile dislocations in the structure improves the ductility and minimises the cleavage.

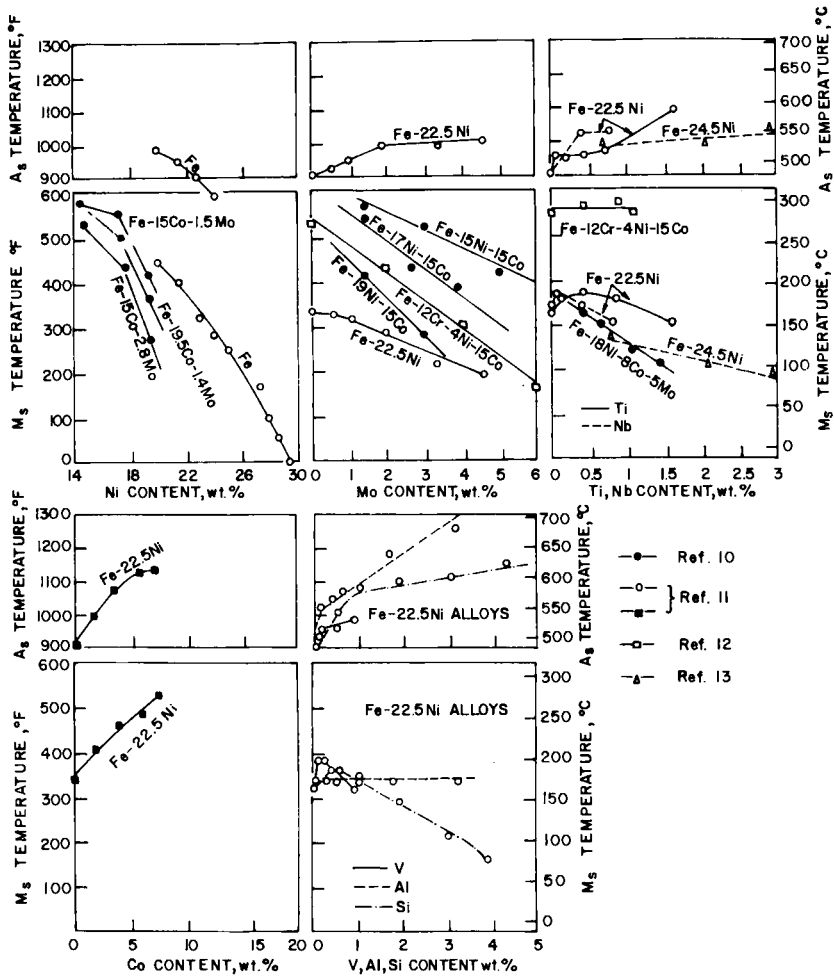


Fig. 2. Effect of solute element contents on M_s and A_s temperatures of iron base alloys.

After tempering, lath martensite exhibits a higher toughness than twinned martensite, a fact attributed to the presence of the microtwins in the latter (Das and Thomas, 1969).

AGING

After transformation to martensite most maraging steels are aged for 3 to 5 hours in the temperature range 480 °C - 500 °C. Two main processes leading to hardening may occur during aging:

- a) precipitation of various intermetallic compounds, sometimes preceded by the formation of thermodynamically metastable intermediate phases;
- b) ordering in the cobalt-containing solid solution.

The total extent of strengthening due to aging will always depend on the combined effect of simultaneously occurring processes of softening and hardening.

Possible softening factors are:

- i) coalescence of fine precipitates,
- ii) changes in the substructure of martensite such as dislocation rearrangements and decreases in their density,
- iii) isothermal formation of austenite.

The precipitation reactions in the maraging process have been objects of many investigations, which were primarily directed towards the identification of the precipitated phases and determination of their shapes, sizes and distribution. Table I lists the results of such identifications.

TABLE I: Data of Phases Precipitating in Maraging Steels in the Course of Aging.

Precipitating phase	Crystallographic Structure	Lattice Parameters (Å)				Remarks
		a	b	c	a/c	
Ni ₃ Mo	Orthorhombic Cu ₃ Ti-type	5.06	4.22	4.45	-	Refs. (a)
Fe ₂ Ti	Hexagonal C14-type	4.81	-	7.85	1.63	Ref. (b)
Fe ₂ Mo	Hexagonal C14-type	4.74	-	7.73	0.61	Refs. (c)
μ-Ni ₃ Ti	DO ₂₄ ordered hexagonal	2.55	-	8.31	3.26	Refs. (d)
σ-FeMo	Tetragonal	9.22	-	4.81	0.52	Refs. (e)
σ-FeTi	Cubic CsCl-type	2.98	-	-	-	Ref. (f)
μ-Fe ₇ Mo ₆	Hexagonal	4.75	-	25.78	5.43	Refs. (g)

(a) (Chilton & Barton, 1967; Shimizu & Okamoto, 1971)

(b) (Reisdorf, 1963)

(c) (Miller & Mitchell, 1965; Marcus, Schwartz & Fine, 1966; Pinard-Legry 1969; Drapier & co-workers, 1971)

(d) (Miller & Mitchell, 1965; Shimizu & Okamoto, 1971; Pinard-Legry, 1969; Garwood & Jones, 1966)

(e) (Bandi, Lutz & Melnick, 1969; Pinard-Legry, 1969; Drapier & co-workers, 1971; Banerjee & Hauser, 1968; Lambert & co-workers, 1970)

(f) (Chilton & Barton, 1967)

(g) (Drapier & co-workers, 1971; Lambert & co-workers, 1970; Boesch & Cowan, 1968).

The precipitates were found to be of different geometrical shapes, such as needles (Chilton and Barton, 1967; Miller and Mitchell, 1965; Garwood and Jones, 1966), disks (Pitler and Ansell, 1964), ribbons (Chilton and Barton, 1967; Baker and Swann, 1964) and spherical (Das and Thomas, 1969; Reisdorf, 1963; Garwood and Jones, 1966; Pitler and Ansell, 1964). The most often reported intermetallic is Ni_3Mo with a rod-shape morphology, which precipitates in parallel to the $\langle 111 \rangle$ directions of the martensitic matrix (Shimizu and Okamoto, 1971). The orientation relationship with the matrix was suggested to be (Shimizu and Okamoto, 1971)

$$(010)_p \parallel (011)_\alpha : [100]_p \parallel [\bar{1}\bar{1}\bar{1}]_\alpha$$

In the initial stages of aging the Ni_3Mo metastable precipitation is favoured because of the low lattice misfit between the precipitate and the matrix. Aging for longer times, however, or at higher temperatures ($>480^\circ\text{C}$) leads to a gradual increase in coherency stresses and the Ni_3Mo is therefore replaced by a more stable Mo-containing precipitate, such as Fe_2Mo or σ -phase (FeMo).

The titanium-containing intermetallic most often found to precipitate during aging is $\mu\text{-Ni}_3\text{Ti}$, but the presence of the $\sigma(\text{FeTi})$ -phase has also been reported occasionally. It is possible that some more complex intermetallics, such as $\text{Ni}_3(\text{MoTi})$ are also formed in the process of aging.

According to the analysis carried out on precipitates extracted from the steel, their compositions are much more complex than that given in Table I. They usually contain additions of iron and other alloying elements (Reisdorf, 1963), which is probably also one of the reasons for the discrepancies in the reported experimental results.

The mechanisms of the different precipitation processes are not fully understood. There is some evidence that one or the other of these processes is preceded by GP zone formation and by ordering reactions (Garwood and Jones, 1966; Miller and Mitchell, 1965).

The nucleation of the precipitates during aging generally occurs on dislocations and lath boundaries. Because of the high density and uniformity of dislocations in lath martensite the precipitates are homogeneously distributed unless a preferred orientation of the dislocations exists when the precipitates may also tend to be oriented (Garwood and Jones, 1966; Miller and Mitchell, 1965). Ordering reactions in cobalt-containing solid solutions, too, contribute to the hardening of maraging steel during aging (Pinard-Legry, 1969; Miller and Mitchell, 1965; Mihalisin, 1966; Spooner, Rack and Kalish, 1971). Ordering is known to occur in BCC Fe-Co alloys over a wide range of solid solution compositions. Both long-range and short-range orders have been reported in maraging steels after aging (Mihalisin, 1966; Spooner, Rack and Kalish, 1971). Except for the direct contribution of the ordering processes to the strengthening, the short range order may affect the precipitation processes of Mo-Ni and Ti-Ni intermetallics, especially in the nickel-rich regions (Rack and Kalish, 1971). This, in combination with the inhibited diffusion of iron towards these regions caused by Co-Fe attraction, may control the overall process of precipitation (Marcus, Schwartz and Fine, 1966; Rack and Kalish, 1971).

One of the most important contributions to the strengthening of maraging steels is the synergistic effect of cobalt and molybdenum. The hardening obtained due to the presence of Co and Mo together is much greater than the

superposition of strength increments of these elements when added individually (Floreen and Speich, 1964; Banerjee, Hauser and Capenos, 1968).

Electron microscopy studies have suggested that the presence of cobalt in molybdenum-bearing maraging steels results in a finer dispersion of molybdenum-containing precipitates (Banerjee and Hauser, 1966). This seems to be associated with two effects:

- a) cobalt decreases the solubility of molybdenum in the martensitic matrix favouring precipitation of molybdenum-containing precipitates (Lambert and co-workers, 1970; Miller and Mitchell, 1965; Floreen and Speich, 1964);
- b) cobalt probably alters the dislocation structure of martensite, providing more nucleation sites for subsequent precipitation (Lambert and co-worker, 1970; Banerjee and Hauser, 1966).

Electrical resistivity measurements have confirmed that the presence of cobalt increases the total amount of precipitated molybdenum (Peters and Cupp, 1966). Cobalt also refines the austenite grains, and the resulting martensite structure is therefore much finer (Lambert and co-workers, 1970).

Although all these effects are known and possible, cobalt shows a strong hardening effect only in the presence of molybdenum. Hardening with other elements is rather minimal.

The precipitation hardening processes in most maraging steels are generally rapid, and changes in hardness and electrical resistivity can already be noted after aging times of less than 1 minute (Floreen and Decker, 1962). The incubation time for age hardening is zero for all practical purposes (Peters and Cupp, 1966; Miner, Jackson and Gibbons, 1966).

The above results suggest that the maraging kinetics are primarily controlled by the martensite structure of the matrix: the absence of an incubation period is associated with the very high supersaturation and precipitation at dislocations (Peters and Cupp, 1966), while the low values of the activation energy are due to the pipe diffusion through the dislocations present at high density in the lath martensite matrix (Tokunaga and Okita, 1971).

It has to be mentioned that some maraging alloys do have incubation times and a much higher activation energy (~ 250 kJ/mol) which is comparable to the values characteristic for substitutional element diffusion in ferrite (Peters and Floreen, 1969; Marcus, Peistrup and Fine, 1965). This would rather question the dominant role of the martensite matrix structure in maraging kinetics. It was therefore also suggested (Floreen, 1968) that the absence of incubation time may be associated with the high tendency to form A_3B precipitates in alloys with a higher nickel content.

In some maraging steels (e.g. 18Ni-8Co-5Mo) a discontinuity in the aging kinetics curves can be observed at certain aging temperatures. This is probably associated with two precipitation processes which may occur simultaneously. The first takes place within the matrix and is predominant at aging temperatures below 450°C ; the second takes place on the dislocations and dominates above 450°C . This complex precipitation process could be identified by electrical resistivity measurements (Peters, 1967).

AUSTENITE REVERSION

The Fe-Ni martensitic matrix, obtained as a result of cooling from the γ -region (see Fig. 1), is metastable and decomposes to austenite and ferrite after prolonged holding at temperatures below A_S . The austenite thus formed may be so rich in Ni, its M_S temperature lying below ambient, that the austenite will be part of the microstructure of the alloy after the post-aqe cooling.

The rate of austenite formation is composition-dependent. Increasing the nickel content generally accelerates austenite formation (Peters, 1968). Other alloying elements, too, may influence the reversion reaction. The effect of individual elements will partly depend on whether the element is an austenite or a ferrite stabilizer (Servant and Cizeron, 1969); but it seems that the changes in matrix composition accompanying precipitation have a much stronger influence on the reversion. For example, elements whose precipitation lowers the Ni content of the matrix will retard the reversion (Ti-formation of Ni_3Ti), while elements which, by a combined process of dissolution and precipitation enrich the Ni content of the matrix, will favour the reversion process (Mo -dissolution of metastable Ni_3Mo and formation of more stable Fe_2Mo).

It was found (Servant and Cizeron, 1969) that in binary alloys (Fe-Ni) the reversion from martensite to austenite is a one-step process, while in more complex alloys two successive steps were observed. First, the martensite decomposes into two distinct phases with different nickel contents, viz. the austenitic nickel-rich γ_r -phase and the low-nickel ferritic α_p -phase.

In the next step the low-nickel ferritic phase is transformed either into a single nickel-depleted austenitic γ_p -phase (Fe-Ni-Mo, Fe-Ni-Co-Mo alloys) or into two phases with different nickel contents: an austenitic one higher in nickel γ_p' -phase and a ferritic phase lower in nickel α_p' -phase (Fe-Ni-Co alloys).

Austenite generally starts to form at the boundaries of the martensite platelets. The austenite produced as a result of reversion is stable and cannot be transformed into martensite by freezing; but the transformation is possible when the steel is subjected to cold working (Koppi and Sadowski, 1967).

The presence of austenite reduces the strength but improves the plastic properties of the steel (Legendre, 1965; Ward, Miller and Bridges, 1971). In addition it has been reported that the reverted austenite increases the resistance of the alloy to stress corrosion (Pinard-Legry, 1969). It has also been established that the reverted austenite affects the magnetic properties such as saturation, magnetization, coercive force, and Curie temperature.

Austenite can also be formed by heating the martensite above the A_S temperature. In this case the transformation from martensite to austenite is by shear, and the resultant austenite has the same chemical composition as the initial martensite. Crystallographically this transformation is similar to the austenite-to-martensite transformation.

At low heating rates some diffusion-controlled reversion of martensite to austenite and ferrite may occur. The reversion may influence the shear reaction of the martensite to austenite transformation by stabilizing the martensite and raising the A_5 temperature. In the presence of additional alloying elements the reactions involved may be very complex, but the general trend is that the decrease in the heating rate raises the A_5 temperature (Goldberg and O'Connor, 1967).

PROPERTIES AND APPLICATIONS

Strength and Toughness vs. Chemistry and Structure

The chief property making maraging steels so interesting as a constructional material is their excellent combination of strength and toughness.

Basically, the strength of a maraging steel is controlled in the post-aging state by properties of the lath martensite formed from austenite by the diffusionless shear reaction, and by the size and dispersion of precipitated particles formed during aging. The martensitic reaction by itself does not guarantee high strength; rather some structural effects associated with this reaction contribute to the improvement of strength. In the case of maraging steels the main contributing factor is probably a drastic change in the dislocation density and distribution.

In addition a considerable improvement in mechanical properties can be achieved by varying the chemical composition of the steel through the addition of elements such as nickel, cobalt, molybdenum, and titanium. This is due to the optimization of certain structural effects. A nickel content of 18% guarantees best mechanical properties, while additions of molybdenum raise the strength and improve impact performance.

An increase in the cobalt content within certain limits (from 12 wt% to 20 wt%) continuously raises the strength. Increasing the cobalt content from 8 wt% to 15 wt% while simultaneously reducing molybdenum from 5 wt% to 3 wt% and titanium from 0.4 to 0.1 wt% reduces the tendency to microsegregation and significantly improves the tensile and impact properties (Floreen, 1969).

The reasons for the superior toughness of a maraging steel are not fully understood. Some beneficial effects may be due to the presence or absence of certain elements, e.g. it is known that elimination of carbon as well as some other impurity elements improves toughness. Molybdenum apparently minimizes the embrittlement of the grain boundaries of the previous austenite, preventing low-energy intergranular fractures (Floreen and Speich, 1964).

The role of nickel is not fully defined - it probably contributes to the minimization of hydrogen embrittlement, but experimental evidence is lacking to prove that nickel is helpful in preventing, or improving resistance to, fracture by the mechanism of void formation and coalescence that is characteristic for maraging steels. It should be mentioned that although all these structural factors are characteristic for all maraging steels, superior toughness is primarily a characteristic of 18 Ni (250) grade steel. For other grades with comparable strength levels the toughness is lower. Since molybdenum is the primary hardener in 18 Ni (250) grade steel, it has been suggested (Floreen, 1968) that the precipitation of the metastable

Mo-rich intermetallic (Ni_3Mo) is responsible for this phenomenon. The precipitate, because of its metastability, probably begins to dissolve during aging, which eventually results in a structure consisting in part of Ni_3Mo particles with adjoining austenite. Such a structural configuration may be effective in preventing void formation at the precipitates, thus delaying fracture. Table II shows the room temperature mechanical properties of the 18 Ni maraging steels in the post-age condition.

The results shown for maraging steels can be strongly affected by the presence of some impurities, in particular sulphur, nitrogen and carbon. The recommended carbon limit for optimum toughness is $<0.01\%$, while that of sulphur and nitrogen is $<0.005\%$. Silicon and manganese must also be kept at levels lower than 0.1% in order to assure high toughness.

The maraging temperature, maraging time, and degree of cold work, may also have an essential influence on the strength-to-fracture toughness ratio. The strength-and-toughness of the ultra-high-strength maraging steels 18 Ni (350) and 13 Ni (400) are dependant on a number of parameters such as production procedure, cold working, heat treatments, etc. For each combination of the parameters mentioned above there is a separate set of properties. Table III presents some experimental results obtained at room temperature.

High and Low Temperature Properties

Maraging steels possess reasonably good mechanical properties at elevated, as well as at low temperatures. Although the fracture toughness values (K_{IC}) sometimes decrease by $\sim 60\%$ when the temperature is lowered from room temperature to -194°C , the combination of strength with toughness is still rather good over a wide range of low temperatures which makes the steels highly attractive for cryogenic applications.

The effect of the test temperature on some mechanical properties of the 18 Ni (350) grade steel is shown in Fig. 3.

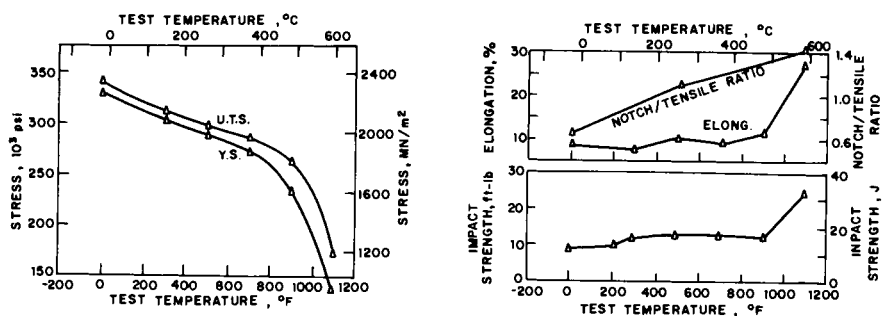


Fig. 3. Temperature dependance of tensile and impact strength of 18 Ni (350) grade maraging steel (Tuffnel and Cairns, 1968).

TABLE II. Room Temperature Mechanical Properties of the 18 Ni Conventional Maraging Steels in the Post-Aging Conditions

Grade	0.2% Y.P. MN/m ²	U.T.S. MN/m ²	Elongation %	Reduction of Area %	Charpy Impact Strength J	Hardness RC	Fracture Toughness KIC MNm ^{-3/2}	Modulus of Elas- ticity GN/m ²	Poisson's Ratio	Refer- ence
18Ni (200)*	1310-1550	1345-1585	6-12	35-67	35-68	44-48	110-176	181	0.26	a)
18Ni (250)*	1655-1825	1690-1860	6-10	35-60	24-45	48-50	99-165	186	0.3	a)
18Ni (300)*	1790-2070	1825-2105	5-10	30-50	16-26	51-55	88-143	190	0.3	a)
Cast Grade	** 1635	1718	10	40	20	-	-	-	-	b)
P/M	*** 1918	1946	10	54	31	52	-	-	-	c)

a) 18% Nickel Maraging Steels: Summary Data, the International Nickel Co. Inc., 1965.

b) Koppi and Sadowski, 1967.

c) Abrahamson, 1973.

* Annealed for 1 hour at 815 °C, aged for 3 hours at 480 °C.

** Homogenization for 4 hours at 980 °C, overaging for 4 hours at 595 °C, annealing for 1 hour at 815 °C, and aging for 3 hours at 480 °C.

*** Rotating electrode processed 18Ni (300) powder extruded at 900 °C, water quenched, and aged for 3 hours at 480 °C.

TABLE III. Room Temperature Mechanical Properties of Ultra-High-Strength Maraging Steels

Material and Form	0.2% Y.P., MN/m ²	U.T.S., MN/m ²	Elongation %	Reduction of Area %	Charpy Impact Strength J	Hardness RC	Fracture Toughness K _{IC} MNm ^{-3/2}	Condition	Reference
0.5 in. plate (Long.) 18Ni (350)	2282	2379	9	37	9.8	58	-	(815 °C-1h) + (510 °C-3h)	a)
1 in. bar 18Ni (350)	2427	2468	8	43	16.3	-	-	(815 °C-1h) + (480 °C-3h)	b)
3/4 in. (vac. m) 18Ni (350)	2179	2268	6	24	9.5*	-	-	(815 °C-1h) + (480 °C-3h)	a)
3/4 in. (air m) 18Ni (350)	2124	2206	8	38	13.6*	-	-	"	
0.5 in. bar 13Ni (400)	2620	2689	5	27	-	59	-	(980 °C-1h) + (480 °C-4h)	c)
9/16 in. plate 13Ni (400)	2417	2417	0.63	0.7	-	63	48.7	(980 °C-1h) + (480 °C-4h)	d)

a) Rack and Kalish, 1971.

b) Tuffnell and Cairns, 1968.

c) Boesch and Cowan, 1968.

d) Magnee and co-workers, 1973.

* Impact tested at - 40 °C.

The high-temperature capability of this steel, however, is limited to 480 °C (900 °F). Above that temperature there is a drastic drop in strength due to the processes of overaging and reversion to austenite, a fact which makes the steel practically useless. The temperature capability of 18 Ni (400) grade steel is even lower, the limit lying near 425 °C (800 °F).

A decrease in the slope of the strength vs. temperature curves can be achieved by prior holding of the steel at the test temperature for 200 hours. This effect was observed in both 18 Ni (350) and 18 Ni (400) grades.

Fatigue Properties

The endurance limit of any maraging steel can be directly related to its tensile strength: the higher the tensile strength the higher the endurance limit. The fatigue properties of the low-grade maraging steels can be improved by lowering the annealing temperature to ~760 °C and by thermochemical (nitriding) and mechanical (shot peening) surface processes. The fatigue properties of these steels are generally comparable to those of high-strength alloyed steels of the same strength levels. The high-cycle fatigue of some maraging steels can also be improved by ausforming or marforming.

Stress Corrosion and Hydrogen Embrittlement

18 Ni maraging steels generally offer better threshold plane strain stress intensity values (K_{ISCC}) than other high-strength steels. In terms of critical crack size, maraging steels can tolerate larger flaws without experiencing crack propagation.

Limiting the concentrations of impurity elements can play a considerable part in improving stress corrosion resistance. When sulphur content, for example, is reduced to a level below 30 ppm, a substantial improvement is obtained in the stress corrosion resistance.

The effect of heat treatment is not consistent, neither is that of the grain size. In certain cases and certain environments a lowering of the homogenization temperature has resulted in remarkable improvements in the stress corrosion resistance. The optimal stress corrosion resistance of maraging steels is obtained by adhering to the recommended sequence of heat treatments.

Tests performed in 3.5% NaCl solution with three grades of maraging steels having different Ti contents showed the dependence of stress corrosion susceptibility on the yield strength. Generally it can be said that 18 Ni maraging steels may be used at high stress levels in non-corrosive atmospheres (moist air) or at medium stress levels in natural saline atmospheres (pH = 7.5). In more acidic saline atmospheres (pH = 3.5) they should not be subjected to stresses higher than 60% of their yield point.

As regards behaviour in certain solutions (e.g. natural seawater) maraging steels generally show excellent stress corrosion resistance even at stresses close to the yield strength.

Studies carried out on maraging steels precharged with hydrogen or directly tested in hydrogen gas show that they are susceptible to hydrogen embrittlement, but that they can tolerate higher quantities of hydrogen than other high-strength steels for a given loss of ductility or a given susceptibility

to delayed fracture. They also recover their original ductility much faster than other steels upon low-temperature annealing (at $\sim 150^{\circ}\text{C}$).

Applications

A number of valuable properties make these steels very attractive in a wide range of engineering applications. Such properties are: combination of high fracture toughness, resistance to hydrogen embrittlement and stress corrosion, easy welding without preheating in both the annealed and the fully heat treated conditions, and easy machining and forming.

The full strength of the steel, in addition to the good combination of mechanical properties in air and some corrosive environments, is obtained by aging at $\sim 480^{\circ}\text{C}$ and air-cooling. Such heat treatment prevents practically any dimensional distortion and cracking even in large parts of complicated shapes.

The uses of conventional 18% Ni maraging steels (grades 200, 250, 300) can be arranged in three groups (Hall and Slunder, 1968):

- a) Hydrospace, aeronautical, and aerospace applications,
- b) structural and machine components,
- c) tools.

A number of very important parts for hydrospace, aeronautics and aerospace are produced from the above steels. These parts include: large rocket motor cases with diameters up to about 6 m including the load cells capable of measuring the engine thrust, torsion-bar suspensions for space vehicles, parts of missile engines, flexible drive shafts for helicopters, aircraft landing gear components, hinges for swing-wing planes, parts of hydrofoil ships, submergence marine vehicles for great depths, etc.

As far as terrestrial structural components are concerned, maraging steels are used for the production of, among others, pressure vessels, bolts, fasteners, and springs, barrels for rapid-firing guns, parts of fuel injection pumps, parts operating at cryogenic temperatures, index plates for machine tools, etc.

Tools, too, are manufactured from maraging steels: diecasting dies, moulds for the plastics industry, some cold-forming dies, rams for extension processes, etc.

The higher grades of maraging steels, 18 Ni (350) and 18 Ni (400), are primarily used as materials for tools, tool fixtures, fasteners, etc. The hardness and elevated-temperature capabilities of these two grades make them suitable for use in bearings.

NEW DEVELOPMENTS

In 1980 a new grade of maraging steel was developed with mechanical properties essentially equivalent to standard 18 Ni (250) grade. The original impetus for this development was the steep rise in the price of cobalt, which is also a strategic material. In many countries, including the USA, the

supply of cobalt is dependant on foreign sources, so that a cobalt-free grade would not only be economically attractive but also strategically advantageous.

The primary goal of this development was an alloy with strength levels comparable to the standard 18 Ni (250) maraging steel. Elimination of cobalt from maraging steel would be sure to lead to lower fracture toughness; but for many applications optimal toughness is not essential.

The new maraging steel was developed in joint research by the Teledyne Vasco, and International Nickel companies and is designated Vasco Max T-250. Table IV gives the chemical analysis of the new steel as well as that of the standard 18 Ni (250) grade, for comparison.

TABLE IV: Nominal Analyses of Vasco Max T-250 and 18 Ni (250) Maraging Steels

	Ni %	Co %	Mo %	Ti %	Remarks*
Standard 18 Ni (250)	18.5	7.5	4.8	0.4	Fe balance
Vasco Max T - 250	18.5	None	3.0	1.4	Fe balance

*The balance of elements other than Fe, such as Al, C, P, S, is the same in both steels.

Vasco Max T-250 also contains less molybdenum - another strategic material.

The heat treatment applied to the T-250 steel is the conventional maraging heat treatment of annealing at 815 °C, air cooling and aging for three hours at 482 °C. The mechanical properties of the, as yet, semi-commercial heat appear to be excellent. Table V lists some room-temperature mechanical properties of the two steels compared in Table IV after the maraging heat treatment.

The data summarized in Table V show that the strength and ductility properties of both steels are very similar to each other. The toughness values of the new steel are lower but should be acceptable for many applications. The fracture mechanism was found to be void formation followed by coalescence, which is typical also for the conventional maraging steels.

The preliminary microstructure investigations confirmed the presence of lath martensite after annealing and air cooling. The hardening is apparently caused by the precipitation of the Ni₃Ti intermetallic. Molybdenum does not precipitate during aging because without cobalt in the alloy the solubility of molybdenum is fairly high.

In some respects, the new steel may even have properties superior to those of the conventional maraging steels. Hardening due to Ti-containing precipitation shows greater resistance to overaging and austenite reversion than alloys hardened primarily by cobalt. The new steel may also be more resis-

TABLE V. Room Temperature Mechanical Properties of Vasco Max T-250 and 18Ni (250) Maraging Steels

Material	0.2% Y.P. MN/m ²	U.T.S. MN/m ²	Elongation %	Reduction of Area %	Charpy Impact Strength J	Hardness R _C	Fracture Toughness, K _{IC} MNm ^{-3/2}
Vasco Max T-250 - longitudinal	1747	1788	10.5	56.1	24	50.8	79.5
Vasco Max T-250 - transverse	1746	1788	8.9	45.8	22	50.1	74.5
18Ni (250) - longitudinal	1694	1729	10.0	46.7	30	50.8	110
18Ni 250 - transverse	1692	1721	8.1	30.3	-	50.3	-

tant to softening during exposure at temperatures of 500 °-600 °C. Another potential advantage of the present composition is its resistance to the so-called C-curve embrittlement, which is caused by the precipitation of a continuous film of TiC on the austenitic grain boundaries. Because of the higher Ti content the carbon solubility at elevated temperatures is lessened, and consequently the amount of carbon available for forming the grain boundary film is reduced. This should ease the requirements for hot working and minimize a potential source of trouble.

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Design of Strong, Ductile, Duplex Low Alloy Steels

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ABSTRACT

Strength, toughness, and ductility are undoubtedly the most important properties specified for structural steels unless the application involves aggressive environments. The major difficulty in optimising these properties comes from the fact that strength is usually inversely related to toughness and ductility; the increase in the former is achieved at the expense of the latter and vice versa. This is true in the majority of cases when relatively inexpensive alloying and processing are sought for a practical alloy development.

This paper is aimed at summarising our current alloy design programmes at Berkeley which utilise the concept of two-phase steels as a means of optimising these mutually exclusive properties. The underlying principle here is to utilise composites whereby the advantages of the second phase are optimised while the less desirable features of this phase are simultaneously mitigated by the presence of the other constituent phase. The size, distribution, shape and volume fraction of the second phase critically control the mechanical behaviour of the dual phase systems. As a consequence, these structures offer a degree of metallurgical flexibility that is absent in single phase structures or in many precipitation strengthened systems, for attaining optimum sets of mechanical properties.

Examples are presented here of martensite/austenite (~ 2-5%) mixtures designed for optimum combinations of high strength, toughness, and wear properties in medium carbon steels, e.g. for mining and agricultural applications, and martensite/ferrite (~ 80%) structure for high strength, good formability and improved low temperature ductility in low carbon steels. Applications to sheet, line pipe, and wires will be demonstrated for the latter class of steels.

KEYWORDS

alloy design; low alloy steels, high strength and toughness; good wear and corrosion resistance; dual-phase structures.

INTRODUCTION

There are current needs to optimise and conserve raw materials and energy, such that physical metallurgists and engineers are challenged to improve the mechanical properties of engineering alloys, in particular steels, and also to minimise high capital costs of new processing facilities. This concept has been the basis for the alloy design programme for nearly two decades now at Berkeley, a programme which optimises ranges of mechanical properties through the characterisation and subsequent manipulation of the microstructure and chemical composition. Three different classes of steels have been utilised in the programme, representing three of some of the most important uses of steel in industry today:

- i) Structural steels as used in mining and agricultural industries, and in defence applications.
- ii) Steels used in the transportation industries, and
- iii) Steels used as rods, tensile wires and pipelines

These categories require high-strength for load-bearing, and high toughness and ductility to resist the propagation of cracks through the material and to ensure good formability. For mining and agricultural applications, wear and corrosion resistance are significant properties also.

Conventional manipulation of mechanical properties through microstructural control has shown that high strength and high toughness are often conflicting requirements, as an increase in strength is often accompanied by a reduction in the ductility and fracture toughness. Typical microstructural effects that show this trend are solute strengthening, precipitation hardening and dislocation hardening. Nevertheless, two methods of microstructural control are available that can result in an increase in both properties--grain refinement and phase transformation through heat treatment. The principles of composites (viz mixing ductile and hard but tough phases with coherent interfaces) have formed the basis for the alloy design programmes we have developed. The careful selection of heat-treatment temperature, time and path has led to the development of the different classes of steel; these steels exhibit high strength and toughness as a result of a refined microstructure that is a composite of a hard, strong phase and a softer, tough phase. In the case of the structural steels, the steels are medium carbon alloys with a composite microstructure of austenite and martensite (or bainite), the major phase, whereas in the case of the steels used in transportation, rods, wires and in pipelines, they are lean, low-carbon steels with a composite microstructure of ferrite (major phase) and martensite (or bainite).

STRUCTURE-PROPERTIES

Strong, Tough, Wear-Resistant Medium Carbon Structural Steels

High strength structural steels are used extensively for components such as aircraft landing gear, missiles, rocket casing, armour plate and other defence applications. Moreover, where such steels have high hardness and consequently good abrasive resistance, they are used in mining and agricultural operations e.g. as buckets and in comminution and mineral-processing operations. The limiting factors in the use of high strength steels is their fracture toughness, and in wet environments, their corrosion and wear.

As mentioned above, high-strength structural steels also require toughness and ductility to resist crack propagation and to ensure good formability for ease of fabrication. All too often, steels in use today have arrived on the commercial market through a process of trial and error. Almost all such steels could benefit from increased levels of toughness.

With this object in mind, a systematic study of the relation between martensite microstructures and mechanical properties utilising a series of Fe-C-X high purity, vacuum-melted experimental alloys (where X is the substitutional solute) has been under way at Berkeley since 1964 (see Rao and Thomas, 1980; Thomas, 1978 for review). These steels have been termed "Qua-tough" steels. The martensite transformation, if controlled so that the inhomogeneous shear component occurs by slip rather than by twinning, is the most efficient method of producing a high density of dislocations, uniformly distributed, in a fine-grained microstructure (Thomas, 1977). The dislocations are a necessary component for both strength and toughness. Whether twinned or dislocated slip martensite occurs is determined mainly by the composition of the steel, in particular the carbon content through its effect in the transformation start temperature, M_s and on the strength of the martensite. The composition must be regulated to maintain $M_s > 200^\circ\text{C}$; this sets the carbon limit to about 0.3wt%. As a result of detailed analyses by electron microscopy and diffraction, retained austenite has been detected, although its presence was not expected. In addition it has been found that this retained austenite, if stable, promotes toughness. Consequently, the microstructure which appears to result in optimum mechanical properties, is a duplex austenite-martensite structure in which martensite laths are surrounded by thin films of retained austenite, see Fig. 1.

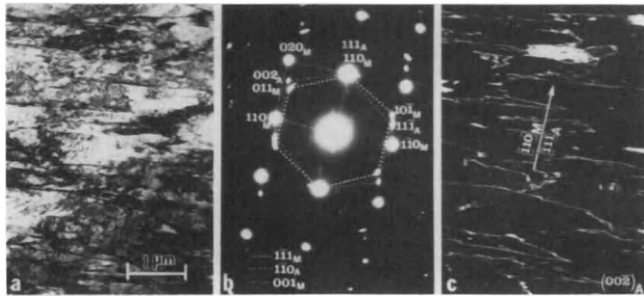
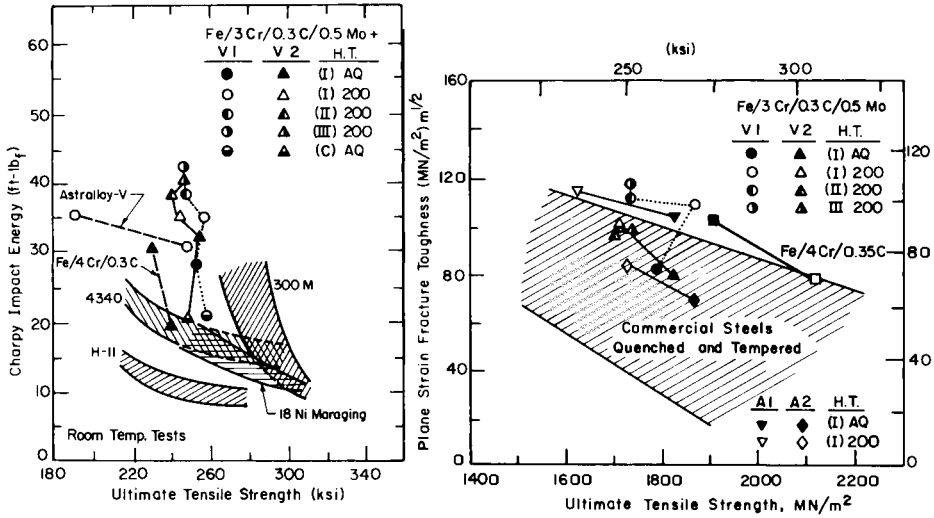


Fig. 1 - Bright-field (a) and dark-field (c) TEM micrographs of Fe-3Cr-2Mn-0.3C steel in the as-quenched condition revealing the general appearance of laths and retained austenite. (b) Shows the selected area electron diffraction pattern (After Sarikaya and Thomas (1981), courtesy of A.S.M.)

The excellent combinations of strength and toughness exhibited by the qua-tough steels can be seen even in the untempered condition, as shown in Figs. 2-3. Tempering in the 300-400°C temperature range leads to tempered martensite embrittlement (TME), and the drop in toughness is associated with the decomposition of the retained austenite to interlath carbide. Recent studies (Jhingan, 1982; Sarikaya and others, 1981; Thomas and Sarikaya, 1981) have shown that the retained austenite is remarkably stable, the activation energy for austenite decomposition being ~ 74 kcal/mole, however the way in which austenite stabilisation occurs is not uniquely known. In an attempt to clarify the importance of chemical stabilisation of the austenite, the local chemical composition of the region adjacent to the austenite/martensite interface has been examined. Using transmission electron microscopy (lattice imaging and convergent beam microdiffraction), and atom-probe spectroscopy, it has been possible to show that the austenite is substantially enriched in carbon with a large peak in the carbon concentration found at the austenite/martensite interface even in the as-quenched condition (see Fig. 4). Carbon depletion has occurred in the martensite matrix, although the distribution is non-uniform due to autotempering. Although chemical stabilisation is obviously a factor in austenite stabilisation, mechanical stabilisation

and the size effect (Easterling and Tholen, 1980), i.e. the retained austenite exists as thin films 50-250 Å thick, also play important roles.



Figs. 2 and 3 - Mechanical properties summary showing toughness to strength relationship in the experimental 0.3%C alloys and equivalent commercial alloys: Fig. 2: CVN impact energy vs. tensile strength; Fig. 3: Plane strain fracture toughness (K_{1C}) vs. tensile strength (After Sarikaya, Rao and Thomas)

In addition to the microscopy experiments described above, in-situ fracture studies have been performed using thin foils of quenched, and quenched and tempered steels, in a high voltage electron microscope equipped with a tensile stage (Thomas and others, 1981). Fracture appears to occur exclusively within the martensite laths (depleted with respect to carbon). In the tough condition, fracture is preceded by localised dislocation slip, work-hardening, thinning down (necking) and hole formation. Packets of laths unfavourably oriented, do not participate in fracture initiation. In the tempered condition, slip and failure depends on carbide morphology. It is suggested that the fracture process depends primarily on the plastic deformation characteristics of the martensite laths, which in turn are affected by the microstructure.

With the increasing potential application for structural steels in a "dynamic" structure (where the resistance to fatigue plays an important role), such as machinery in the mining industry, the fatigue properties of the experimental qua-tough steels have been analysed to avoid the possibility that an increase in toughness is obtained at the expense of fatigue properties. The results have shown that variations in fracture toughness (K_{1C}) from 65 MPam^{1/2} to 198 MPam^{1/2} (induced by varying Mn alloying element and by 200°C tempering), appear to have little effect on the "mid-range" of crack growth rates exceeding 5×10^{-8} nm/cycles. In addition, the experimental steels have better fatigue resistance in the medium crack growth range than commercial steels AISI 4340 and 300M for the same heat-treatment conditions such as as-quenched and 200°C tempering (Kung and Thomas, unpublished).

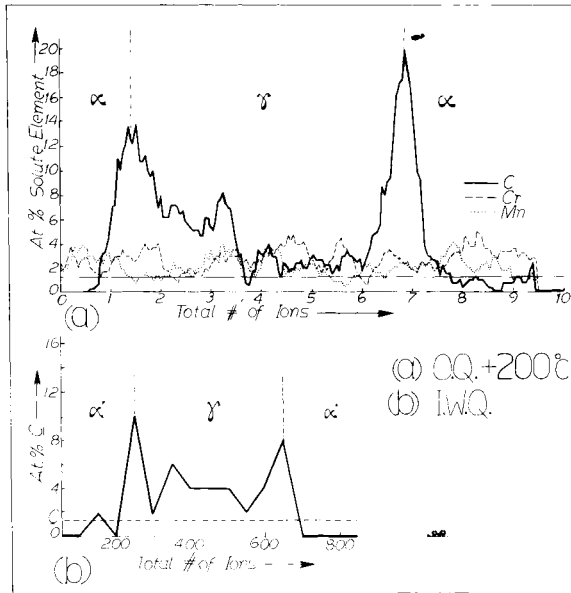
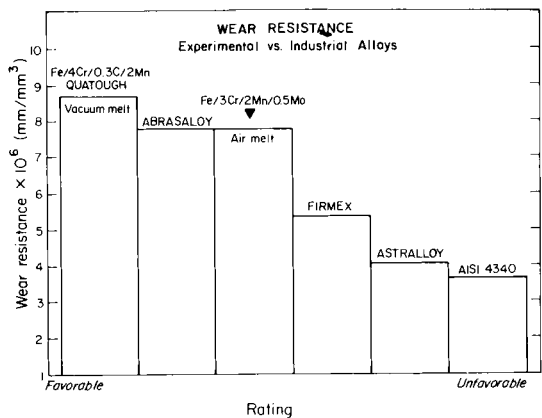
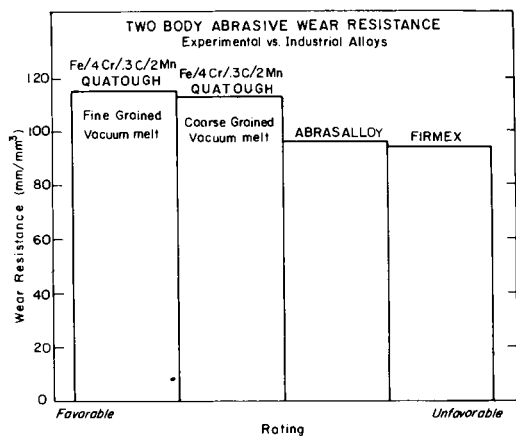


Fig. 4 - (a) Field ion-atom probe analysis of C, Cr and Mn of Fe-3Cr-2Mn-0.5Mo-0.3C after tempering at 200°C for 1 hr; (b) Atom probe analysis of C in Fe-4Cr-0.34C alloy following quenching 0.5mm dia. sample in iced water. (After Sarikaya and others, 1981)

Many of the uses of structural steels require not only good strength-toughness characteristics, but also good wear-corrosion-resistance. As part of the alloy design programme, both sliding and abrasive wear behaviour have been examined and measured for the qua-tough steels (Kwok, 1982; Salesky and Thomas, 1981). The results show that the duplex martensite/austenite microstructure of these steels exhibits good wear-resistance in both categories of wear, and are superior to many, commercial alloys that are described as wear-resistant alloys (see Fig. 5). Sliding wear behaviour was found to be beneficially affected by tensile strength, hardness, fracture toughness, and grain-refinement, whereas abrasive wear was found to be positively affected by only the first two factors. More recently, the sliding wear behaviour of these steels has been further enhanced by laser surface hardening. Using a 500 watt, continuous CO_2 laser, localised, rapid heating and quenching can be confined to the surface of the alloys, producing a hard, grain-refined microstructure to depths of 500 microns. In addition to these studies, a more fundamental study has been carried out into the mechanisms of wear, specifically sliding wear (Salesky, 1982). The results suggest for several iron-based materials, tested in air, wear particles are formed by crack initiation and propagation along the boundary of dislocation cells present in a deformed region found adjacent to the wear surface (see Fig. 6). Oxidation then occurs during separation of the platelet from the parent material. Consequently materials with a fine-scale microstructure and a high yield strength, in the absence of large undeformable particles, appear to be the most wear-resistant.



(a)



(b)

Fig. 5 - Histograms of relative wear resistance of experimental and commercial alloys: (a) sliding wear resistance; (b) two-body abrasive wear resistance. (Courtesy of W. J. Salesky and S. Kwok)

Finally, the corrosion properties of some of the experimental steels have been examined and compared to commercial alloys as well as the dual phase steels discussed in the following section. The data obtained are shown in Table 1. The 4wt% chromium steels give good corrosion resistance as the table shows, and have greater corrosion resistance than 4340, a structural steel of similar properties (data obtained at Battelle, Northwest). Once again the qua-tough steels show superior mechanical properties over equivalent commercial alloys.

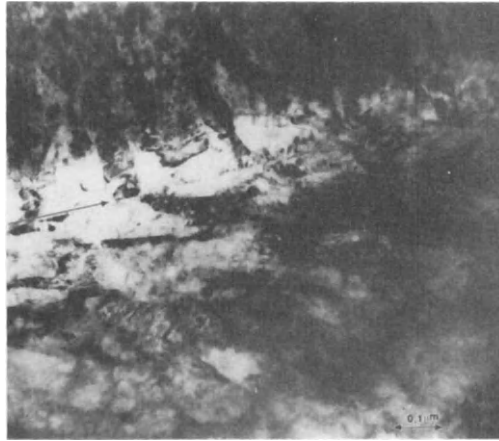


Fig. 6 - Electron micrograph showing abrasive worn quatough steel (below arrow). The martensite laths follow the wear direction. The arrow shows the interface above which nickel has been plated to preserve the worn surface. (Courtesy of W. J. Salesky)

Table 1

CORROSION* DATA FOR LOW CARBON QUA-TOUGH AND
AND SOME COMMERCIAL STEELS

<u>Specimen</u>	<u>Condition</u>	<u>Weight Loss</u>	<u>MmPY</u>
		<u>Mg/Decimeter²</u>	<u>Mm Per</u> <u>Year</u>
Fe-2Si-0.1C	As-received	2091.6	1.70
	Duplex Ferrite- Martensite	1956.4	1.59
AISI 1010	As-received	2077.2	1.68
	Duplex Ferrite- Martensite	1946.9	1.58
Fe-4Cr-0.3C-2Mn	As-quenched	1173.5	0.95
	200°C Tempered	988.5	0.80
Fe-4Cr-0.3C-5Ni	As-quenched (Coarse grained)	926.1	0.75
	As-quenched (Grain refined)	774.5	0.63
AISI 4340	As-received	--	2.79.
AISI 410 (Stainless steel)	As-received	--	3.05

* 15% NaCl, 100 ppm CO₂ (pH 4.4) at 250°C
(Courtesy of Battelle Northwest and R. Clark).

Dual-Phase, Low-Carbon Steels

During the past several years, dual-phase ferrite-martensite steels have received increasing attention (Davenport, 1981; Kot and Morris, 1979; Kot and Bramfitt, 1981), through their possession of characteristic microstructural features which combine high strength and ductility with excellent formability. The strengthening principle of the dual-phase structure involves the incorporation of inherently strong martensite, as the load-carrying constituent, in a soft, ferrite matrix, which supplies the system with the essential ductility. Thus these alloys can be considered equivalent to fibre composites, with the advantage of producing coherent phases by solid-state phase transformation (Fig. 7a). The alloy design principles followed at Berkeley have been described in detail by Thomas and Koo (1979) and will not be repeated here. However, it is emphasised that the properties of dual-phase steels are largely dependent upon three factors:

- (i) morphology--size, shape and distribution of both the ferrite and martensite, (e.g. Fig. 7b).
- (ii) the properties of the two phases, and
- (iii) the volume fraction of martensite (or bainite).

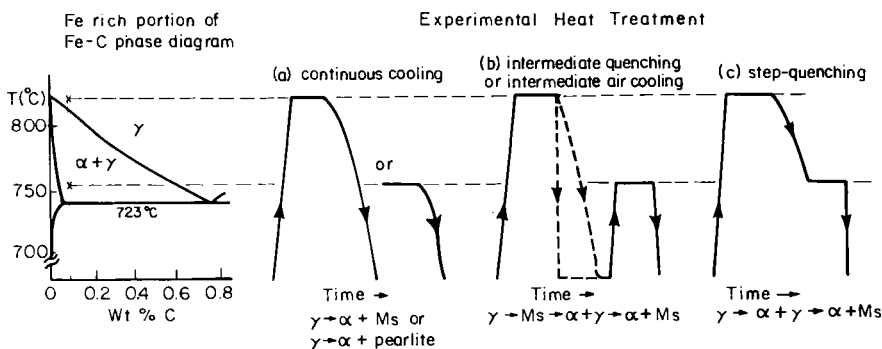


Fig. 7a - Sketches to show principles of dual phase steels. The volume fractions of ferrite and austenite (and ultimately martensite or bainite) depend on carbon content and intercritical annealing temperature. Several transformation paths are indicated.

Of these factors, morphology plays the most important role in controlling ductility (Kim and Thomas, 1981). It has been shown that a coarse dual-phase structure has very poor tensile elongation ductility. This is due to cleavage crack initiation and propagation within the ferrite matrix where the maximum stress concentration takes place (Fig. 8). However, when the microstructure is refined, the degree of stress concentration decreases, and fracture is initiated by void nucleation and growth around the ferrite/martensite interfaces. These voids, once initiated, propagate within the ferrite matrix without fracture occurring within the martensite (Fig. 9). The flow strength, on the other hand, appears to be less sensitive to morphology, and depends approximately, and in an empirical fashion, on the "law of mixtures" given below.

$$\sigma_c = \sigma_M V_M + \sigma_\alpha (1 - V_M)$$

where σ_M and σ_α are the strengths of martensite and ferrite respectively, and V_M and $(1 - V_M)$ are their corresponding volume fractions. In general, there is a linear increase in strength as a function of volume fraction of martensite. However, in some alloy systems (Hoel and Thomas, 1981) which contain carbide-forming elements such as Nb and Mo, the strength decreases or remains constant with increasing martensite

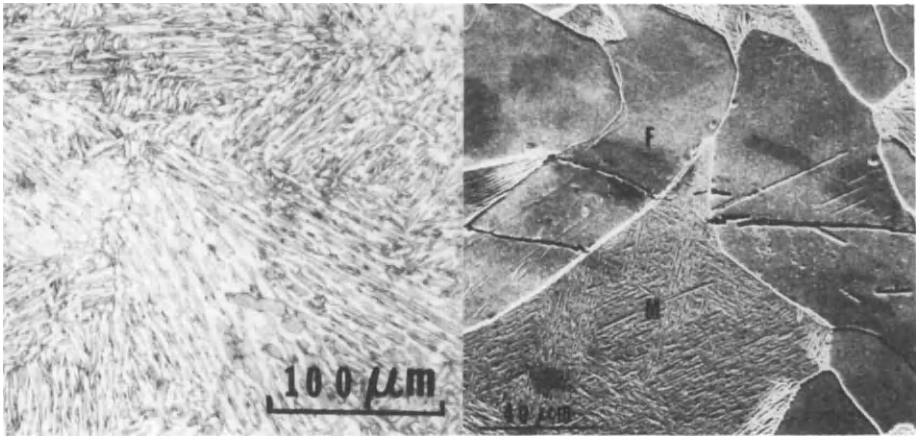


Fig. 7b - Optical micrograph showing the fibrous ferrite-martensite composite microstructure with prior austenite grains in a dual-phase Fe-Si-0.1C steel. (After Thomas and Koo (1979), courtesy of A.I.M.E.)

Fig. 8 - Scanning electron micrograph of step-quenched coarse dual-phase structure showing the cleavage cracks developed in ferrite. M: martensite; F: ferrite. The stress axis is normal to the micrograph. (After Kim and Thomas (1981), courtesy of A.I.M.E.)

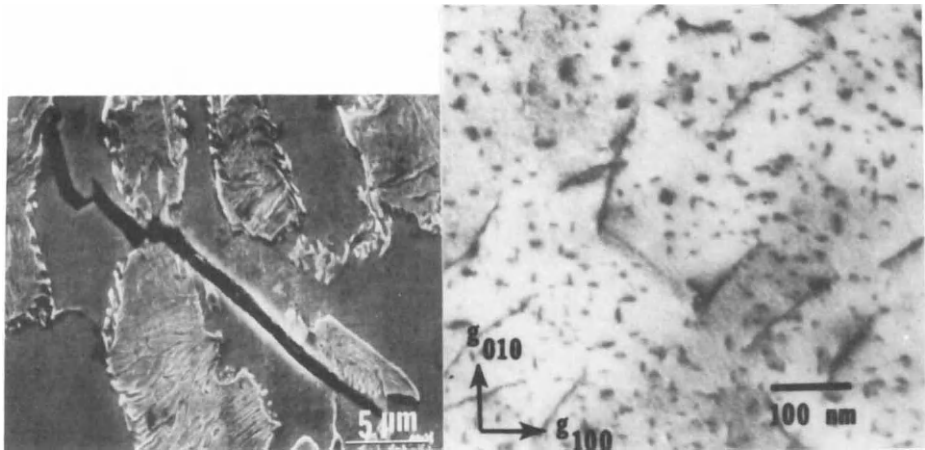


Fig. 9 - Scanning electron micrograph of intercritically annealed fine globular structure showing crack propagation in the ferrite matrix. The stress axis is normal to the micrograph. (After Kim and Thomas (1981), courtesy of A.I.M.E.)

Fig. 10 - Transmission electron micrograph showing the presence of fine homogeneously nucleated precipitates in the ferrite phase of a Mo-bearing dual-phase steel. These precipitates strengthen the ferrite phase. (After Hoel and Thomas (1981), courtesy of Scripta Met.)

volume fraction; this represents an anomaly in the usual "law of mixtures" behaviour. If the volume fraction of martensite has been increased by raising the annealing temperature within the ($\alpha + \gamma$) field, then two ways are possible wherein the strength of the steel can be reduced. The first is by a decrease in the carbon content of the ferrite, which leads to a decrease in the density of carbide precipitation in the ferrite (Fig. 10), and the second is by a decrease in the carbon content of the martensite, thus lowering its strength. The overall effect, which depends on the relative magnitude of these factors, can result in a negative slope in the "law-of-mixtures" equation (Eq. 1), if the strength of the ferrite changes significantly. (For more details, see Thomas and Koo 1979.) Thus, the complex interactions of parameters such as morphology, properties and volume fraction of constituent phases must all be controlled when designing dual-phase alloys. When this is achieved, excellent mechanical properties can be realised, with high strengths attainable for relatively low carbon alloys (see Fig. 11). Moreover, the alloy compositions are quite simple, with no need for microalloying elements, and are therefore inexpensive, and by controlling the composition, considerable flexibility (i.e. strict heat treatment is not needed) in intercritical annealing temperature is possible (Thomas and Koo, 1979).

The main principles of alloy development for high formability as used in sheet, rods, wire, etc. can be summarised as follows:

- (1) The ferrite should contain mobile dislocations, and should therefore be 'clean' and free from extensive pinning.
- (2) The percentage of carbon in the martensite should not exceed 0.3wt%, in order to obtain a strong, tough martensite (as illustrated for the 0.3C steels in the previous section).
- (3) A fine distribution of martensite (or bainite) particles should be present in the ferrite matrix; the optimum volume fraction for good ductility and formability is ~20% martensite, but for high strength, without the high formability requirements, a greater percentage of martensite can be used. Thus the properties of a dual-phase steel can be "tailor-made" to suit the need, by the appropriate heat-treatment (Fig. 7a).

Utilising these principles several ranges of alloys have been developed, starting with a simple Fe/Si/C alloy, which has the fibrous structure shown in Fig. 7b, and has excellent properties (Fig. 11). The figure summarises our data in comparison with data for some high strength low-alloy (HSLA) steels that contain expensive microalloying additions. Although interest in dual-phase steels has been generated largely by the recent fuel crisis and its impact on the need for weight savings in transportation systems, i.e. for flat sheet products, the potential application for dual-phase alloys are broad indeed. These alloys form a new class of strong, ductile steels for applications requiring tensile strength levels of ~100ksi for pipeline, and up to 400ksi for tensile wires, rods and bars. These properties can be obtained by cold wire drawing without the necessity for intermediate patenting heat treatments (Nakagawa (1982). Strengths up to 400ksi are indeed remarkable for such simple steels with less than 0.1wt% carbon.

Steels used for pipeline must have high strength as well as high toughness (low ductile-to-brittle transition temperature). The alloy design principle for pipeline application is that high toughness can be obtained primarily by grain size control, while maintaining a dual-phase structure to simultaneously obtain high strength. Controlled rolling of an Fe/1.5Mn/0.06C alloy, followed by direct quenching produces a duplex microstructure in which upper bainite particles are uniformly distributed within the fine, ferrite matrix (Kim and Thomas, 1982). The mechanical properties of this ferrite-bainite steel, in the as-hot-rolled condition, far exceed the property specifications for arctic pipeline. A further advantage of this ferrite-bainite steel is that there is an abrupt increase in strength during pipe-forming due to its high work-hardening rate. This clearly demonstrates the potential use of dual-phase ferrite-bainite structures in

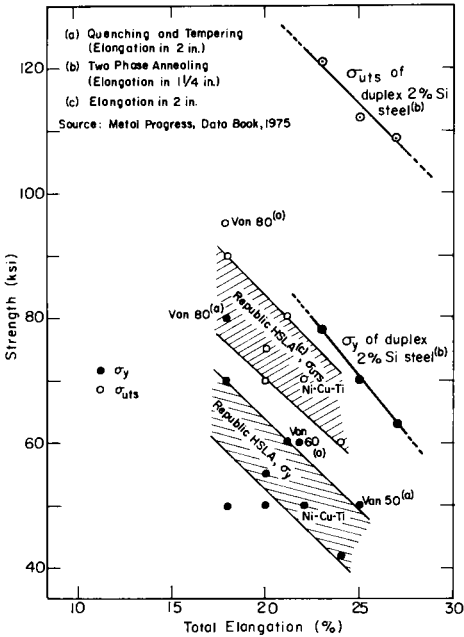


Fig. 11 - strength vs. tensile ductility for Fe-2Si-0.06C dual phase steel compared to HSLA steels. Notice the superior properties and higher tensile to yield ratios (high formability) typical for low carbon dual phase steels (After Thomas and Koo (1979), courtesy of A.I.M.E.)

Table 2
PROPERTY SPECIFICATIONS FOR ARCTIC PIPELINE AND TYPICAL MECHANICAL PROPERTIES OF THE AS-HOT-ROLLED Fe/1.5Mn/.06C STEEL WITH AND WITHOUT COLD WORKING

	UTS MN.m ⁻²	Charpy shelf energy	
		Transverse	Longitudinal
Arctic Pipeline	585.7	92 J. at -60°C	136 - 170 J. at -60°C
Fe/1.5Mn/.06C (as hot-rolled)	642.2	149 J. up to -100°C	183 J. up to -100°C
Fe/1.5Mn/.06C (with 2% cold reduction)	649.0	129 J. up to -100°C	170 J. up to -150°C

pipeline applications (Table 2).

In conclusion, from the standpoint of their superior properties, and simplicity in composition and processing, dual-phase steels show great promise, not only for the transportation industry, but for general structural applications, e.g., pipeline, wires, rods and bars. Their advantages include economy of material and enormous flexibility wherein a single alloy can be manipulated to provide a wide range of products and properties. The main limitations of low carbon dual phase steels for general applications are material dimensions, i.e. sufficient hardenability must be achieved (~ 0.5 in thickness/diameter) to obtain martensite/bainite on quenching from the ($\alpha + \gamma$) field, and problems of microstructure control if welding must be done after the dual phase treatment.

ACKNOWLEDGEMENTS

The author would like to acknowledge the graduate students, research fellows and staff of the Department of Materials Science and Mineral Engineering, University of California, Berkeley, who contributed to the alloy design programme. Especial thanks are due to Drs. J. Rayment and N. J. Kim for their help with this manuscript. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. In addition, industrial support in alloy preparation is acknowledged--Daido Steel Company and Japan Steel Works, Japan; Republic Steel Corporation, U.S.A.; Climax Molybdenum, U.S.A.

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A Review of Worldwide Developments in Stainless Steels

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ABSTRACT

New refining techniques for stainless steels, widely adopted during the 1970's, have facilitated the production of common grades of stainless steel and greatly expanded the composition range for commercially feasible austenitic, ferritic, and duplex stainless steels. A representative selection of these newer grades is characterized according to crevice corrosion resistance, stress corrosion cracking resistance, and field application experience.

KEYWORDS

Stainless steels: austenitic, ferritic, duplex; stainless steel refining methods; pitting; crevice corrosion; stress corrosion cracking; seawater corrosion; molybdenum.

INTRODUCTION

Stainless steels are iron-base alloys containing sufficient chromium, a minimum of about 10.5 percent, to form a "passive film" of surface-associated oxygen. This film, responsible for the superior corrosion resistance of the stainless steels, is transient in nature. Its formation and stability are subject to change through further alloying of the steel and through variations in the exposure environment. The 1970's witnessed the widespread adoption of new steelmaking techniques that have substantially expanded the ranges of composition for stainless steels commonly available in commercial production. It is useful to briefly review the roles of various alloying elements in stainless steels as a basis for discussion of the interrelated developments of stainless steel technology, commercial production practice, and practical applications.

Chromium contents above the minimum level efficiently increase the ease of formation and stability of the passive film. But chromium can have severe detrimental effects on mechanical properties, particularly the toughness of ferritic stainless steels of higher carbon levels and the hot rolling characteristics of the austenitic stainless steels. Therefore, in the early 1970's, most commercial stainless steels contained 18% Cr or less. Carbon is a desirable alloying element in the martensitic stainless steels where

it is necessary for the transformation behaviour. However, carbon is detrimental to stainless steels because the formation of chromium carbide reduces the effective chromium level. Under certain conditions, this precipitation can cause susceptibility to localized attack at chromium-depleted regions. Carbon also has a deleterious effect on toughness, especially in the ferritic grades. Except for the martensitic grades, it is desirable to reduce the carbon content as low as possible consistent with economic and technical limitations. Nickel has a strong favourable effect on the rate of formation of the passive film. When added in sufficient concentration, nickel stabilizes the austenitic or face-centered cubic crystal structure. Austenite is tougher than ferrite, and because of the high solubility of carbon in austenite, the austenitic grades more easily tolerate higher levels of carbon. Molybdenum acts to stabilize the passive film, especially at higher chromium levels. Increasing molybdenum to improve corrosion resistance is substantially less detrimental to mechanical properties than achieving the same level of corrosion resistance by the simple addition of chromium. Nitrogen, frequently in combination with manganese, is used for stabilizing the austenitic structure, for strengthening, and most recently for retarding formation of intermetallic phases. Copper is added to enhance resistance to sulphuric acid and related environments. Titanium and niobium may be added to remove carbon from solution as carbides, but may also form oxides, nitrides, or sulphides. Other elements may be used to improve machinability (sulphur, lead, selenium), oxidation resistance (aluminium, silicon), and mechanical or processing characteristics (vanadium, zirconium, rare earth metals, boron).

STAINLESS STEELMAKING TECHNOLOGY

Commercial production of stainless steels is guided by the needs of the end-user market and the limitations of stainless steelmaking equipment. In the early 1970's, production was dominated by the austenitic grades, primarily AISI Type 304 and its various corresponding national standards. This grade readily tolerated the level of carbon economically achievable while providing a particularly useful combination of corrosion resistance, mechanical properties, and fabricability. Higher levels of corrosion resistance were obtained by adding molybdenum for AISI Type 316 (2-3% Mo) and AISI Type 317 (3-4% Mo). However, difficulty in control of tramp elements made these higher alloyed steels increasingly susceptible to defects in hot rolling and problems in welding so that the increased cost of these steels was disproportionately higher than the added cost of the alloy elements. Higher alloy proprietary austenitic grades were available from a few mills, but these grades were not widely produced. The practical difficulties of lowering carbon content limited the ferritic stainless steels in alloy content, AISI Type 430 (17% Cr) and AISI Type 434 (17% Cr-1% Mo), and in product form, light gauge sheet not generally intended for welding. An exception was AISI Type 446 (26% Cr) used for furnace equipment where high oxidation resistance was required and low room temperature impact toughness was acceptable. There were a few grades of duplex stainless steels at the 18% and 26% Cr levels, utilizing about 5% Ni to produce a mixed ferrite-austenite structure to achieve some of the corrosion resistance characteristics of the ferritic grades while retaining some of the mechanical characteristics of the austenitic grades.

The development of stainless steelmaking technology took a revolutionary leap in the early 1970's with the rapid commercial adoption of new refining techniques. Most important was the installation of the argon-oxygen decarburization (AOD) process (Krivsky, 1966, 1974). The AOD and related processes, involving different gas injection or partial pressure systems (Weymueller, 1971), facilitate the removal of carbon without excessive loss

of chromium. The primary incentive for adoption of these systems was the ability to use a much less expensive, higher-carbon ferrochromium in the furnace charge. Almost incidentally, the AOD¹ opened new ranges of alloy composition to commercial development. Not only could carbon content be readily reduced to much lower levels, major alloying elements could be controlled much more precisely, nitrogen became an easily controlled intentional alloy element, and tramp elements severely detrimental to hot rolling could be substantially reduced in common practice (Netoskie, Heckel and Wiencek, 1977). In this same period, the use of vacuum melting and refining of stainless steels, particularly the higher alloy ferritic grades, complemented the advances in conventional production technology in expanding the range of stainless steels commercially available (Harrington and Palmer, 1970; Oppenheim and Laddach, 1971).

AUSTENITIC STAINLESS STEELS

Because of the past and continuing commercial importance of the austenitic grades, it is appropriate to begin a discussion of new developments by examining the impact of the new production technology on the most common grades. First and foremost, the AOD has restrained the escalation of alloy cost by permitting the customary use of high carbon charge chromium, class II nickel, and molybdenum oxide in the alloy charge. Because these major elements can be controlled with precision, steels are now typically produced very near the minimums of the specified alloy ranges. Product uniformity is improved, but the lowered alloy content may necessitate upgrading to achieve satisfactory performance in marginal applications. The ease of carbon removal has facilitated production of the "L-grades", austenitic grades with a maximum of 0.030% C intended to permit welding without sensitization to intergranular corrosion. Consequently, the relative share of these low-carbon grades in total stainless steel production has grown. The ability to control nitrogen as an alloy element, obtained by "blowing-in" nitrogen in the AOD, has permitted further alloy cost reduction through the use of nitrogen with or without manganese to replace a portion of the nickel addition. The ASTM has limited nitrogen to 0.10% maximum in the basic austenitic grades and the corresponding low-carbon grades and has established a series of corresponding nitrogen grades with 0.10-0.16% N designated by an "N" appended to the customary AISI notation. It is now well documented (Netoskie, Heckel and Wiencek, 1977; Aggen, 1977) that the AOD, through superior control of tramp elements such as sulphur, lead, tin and bismuth, reduces the tendency to defects of hot rolling. Prior to the AOD, Type 317 was considered to be a steel difficult to produce with a good mill yield. Now Type 317 is produced with comparative ease, and substantially higher alloyed austenitic grades can be produced by conventional practice.

The logical extension of the improvements in common grades is the commercial development of proprietary grades of substantially increased alloy content with correspondingly improved corrosion resistance². As shown in Table 1,

¹In this discussion, references to "the AOD" should be taken to represent broadly the whole group of advanced stainless steel melting and refining techniques.

²A discussion of advances in stainless steels necessarily involves citing proprietary grades as examples of particular effects. The grades listed in Table 1 and cited in the text are intended only as examples and not as an encyclopedic listing. The authors extend their apologies for their omission of many undoubtedly superior proprietary grades because of the space limitations of this article. Trademarks and commonly used names of the proprietary grades are attributed to producers in Table 1, but not in the text.

upgrading has occurred by stepwise increases of molybdenum up to more than 6%, the possible use of nitrogen up to as much as 0.25%, and some increase in the level of chromium. The technology of these new grades will now be examined in the context of their resistance to pitting and crevice corrosion, their resistance to chloride stress corrosion cracking, and the role of austenitizing elements.

TABLE 1 Common Names and Nominal Compositions for Selected Austenitic, Ferritic, and Duplex Stainless Steels

Common Name	UNS	Nominal Composition (wt %)			
	Number	Cr	Mo	Ni	Other ¹
I. Austenitic Grades					
AISI Type 304	S30400	18-20	-	8-10.5	0.08C, 0.10N
AISI Type 304L	S30403	18-20	-	8-12	0.030C, 0.10N
AISI Type 304N	S30451	18-20	-	8-10.5	0.08C, 0.10-0.16N
AISI Type 304LN	S30453	18-20	-	8-12	0.030C, 0.10-0.16N
AISI Type 316	S31600	16-18	2-3	10-14	0.08C, 0.10N
AISI Type 316L	S31603	16-18	2-3	10-14	0.030C, 0.10N
AISI Type 316N	S31651	16-18	2-3	10-14	0.08C, 0.1-0.16N
AISI Type 316LN	S31653	16-18	2-3	10-14	0.030C, 0.10-0.16N
AISI Type 317	S31700	18-20	3-4	11-15	0.08C, 0.10N
AISI Type 317L	S31703	18-20	3-4	11-15	0.030C, 0.10N
"Type 317LM" ²	-	18-20	4-5	12-18	0.030C
Alloy 904L ³	N08904	19-23	4-5	23-28	0.020C, 1.0-2.0Cu
AL-6X ⁴	N08366	20-22	6-7	23.5-25.5	0.030C
254 SMO ⁵	S31254	19.5-20.5	6-6.5	17.5-18.5	0.020C, 0.180-0.220N, 0.5-1.0Cu
20Mo-6 ⁶	-	22-26	5-6.7	33-37	0.030C, 2-4Cu
II. Ferritic Grades					
AISI Type 409	S40900	10.5-11.75	-	-	0.08C, Ti:(6XC)-0.75
3CR12 ⁷	-	11-12	-	-	0.03C, 0.03N, Ti:4 (C+N) min.
AISI Type 430	S43000	16-18	-	-	0.12C
AISI Type 434	S43400	16-18	0.75-1.25	-	0.12C
"Type 439" ⁸	S43035	17-19	-	-	0.07C, Ti: (0.20+4 (C+N)) -1.10
AISI Type 444	S44400	17.5-19.5	1.75-2.5	-	0.025C, 0.035N, (Ti+Nb) : (0.20+4 (C+N)) -0.80
AISI Type 446	S44600	23-27	-	-	0.20C, 0.25N
E-BRITE ⁴	S44626	25-27	0.75-1.5	-	0.010C, 0.015N, Nb:0.05 -0.20
SEA-CURE ⁹	S44660	25-27	2.5-3.5	1.5-3.5	0.025C, 0.035N, (Ti+Nb) : (0.20+4 (C+N)) -0.80
MONIT ¹⁰	S44635	24.5-26	3.5-4.5	3.5-4.5	0.025C, 0.035N, (Ti+Nb) : (0.20+4 (C+N)) -0.80
SUPERFERRIT ¹¹	-	27-29	1.8-2.5	3.0-3.5	0.020C, Nb>12 (C+N)
AL 29-4C ⁴	S44735	28-30	3.5-4.2	-	0.025C, 0.035N, (Ti+Nb) : (0.20+4 (C+N)) -0.80
AL 29-4 ⁴	S44700	28-30	3.5-4.2	-	0.010C, 0.020N
AL 29-4-2 ⁴	S44800	28-30	3.5-4.2	2-2.5	0.010C, 0.020N

(Continued)

TABLE 1 Common Names and Nominal Compositions for Selected Austenitic, Ferritic, and Duplex Stainless Steels

Common Name	UNS Number	Nominal Composition (wt %)			
		Cr	Mo	Ni	Other ¹
III. Duplex Grades					
3RE60 ¹²	S31500	18-19	2.5-3	4.25-5.25	0.030C
SAF 2205 ¹² , AF22 ¹³	S31803	21-23	2.5-3.5	4.5-6.5	0.030C, 0.08-0.20N
AISI Type 329	S32900	23-28	1-2	2.5-5	0.08C
Ferrallium 255 ¹⁴	S32550	24-27	2-4	4.5-6.5	0.040C, 1.5-2.5Cu, 0.1-0.25N
DP-3 ¹⁵	-	24-26	2.5-3.5	5.5-7.5	0.030C, 0.2-0.8Cu, 0.1-0.5W, 0.10-0.20N

¹Maximum unless otherwise specified.²Common name frequently attributed to Eastern Stainless Steel.³Common name frequently attributed to Nyby-Uddeholm.⁴Trademark of Allegheny-Ludlum Steel.⁵Trademark of Avesta Jernwerks.⁶Trademark of Carpenter Technology.⁷Trademark of Southern Cross Steel.⁸Common name frequently attributed to Allegheny-Ludlum Steel.⁹Trademark of Trent Tube Division, Colt Ind.¹⁰Trademark of Nyby-Uddeholm.¹¹Trademark of Thyssen Edelstahlwerke.¹²Trademark of Sandvik.¹³Trademark of Mannesmann.¹⁴Trademark of Langley Alloys.¹⁵Trademark of Sumitomo.

Resistance to Pitting and Crevice Corrosion

Laboratory evaluation of the pitting and crevice corrosion resistance of stainless steels has been greatly facilitated by the work of Brigham and co-workers (Brigham, 1974a, 1974b; Brigham and Tozer, 1974). They demonstrated that for a particular aggressive corrosion environment such as 10% FeCl₃·6H₂O solution, there are critical temperatures for the initiation of pitting and crevice corrosion, respectively, for the various grades of stainless steel. Because the critical temperature for crevice corrosion is consistently below the critical temperature for pitting, and because it is practically impossible to avoid crevices in construction and operation of processing equipment, the critical crevice temperature (CCT) is of greater engineering importance. The time for initiation of attack at temperatures above the CCT is short enough to make determination of the CCT a practical task in the laboratory. Brigham found that the CCT was dependent on the geometry of the crevice (and possibly the crevice material) but that the CCT for a particular geometry was reproducible. A specimen geometry utilizing a rubber band with teflon spacers has proved convenient and reproducible (ASTM, 1981). More recently, the "multiple crevice assembly", comprised of serrated nonmetallic washers pressed on the surface of a coupon by a nonmetallic or electrically-isolated

bolt, has provided an effective method of dealing statistically with the problem of initiation of attack on highly resistant grades (Anderson, 1976).

Tables 2 and 3 (Bond and co-workers, 1977; Bond, Bertoli and Dundas, 1980) demonstrate the improved crevice corrosion resistance obtained with the higher alloyed austenitic grades. Especially notable is the improved performance in seawater. Experience prior to the 1970's had demonstrated that AISI Type 316 could be used in seawater only when high flow rates and the absence of natural and artificial crevices could be assured. Therefore, only with extreme care in design and rigorous cleaning practices could stainless steels be used in brackish water or seawater. The 4.5% Mo grades, such as Alloy 904L, represent a significant improvement over Type 316, yet these grades are still susceptible to crevice corrosion at artificial crevices and natural biofouling sites (Bernhardsson, Mellstrom and Tynell, 1980). So these grades provide only partial relief from risk and maintenance requirements. However, the development of AL-6X with the first field trials beginning in 1970, provided a stainless steel resistant to corrosion even under severe biofouling conditions (Maurer, 1980). Perseverance in developing this grade has resulted in over eight million meters of tubing in regular service in over twenty full-size seawater cooled power plant condensers in North America. The success of this tubing over the wide range of service conditions encountered provides a basis for acceptance of stainless steel condenser tubing even by the highly conservative materials practices of national electric power authorities. The United States experience is now being used as a basis for rapid commercial development in Europe. The first full-size units employing 254 SMO (an austenitic grade with Cr and Mo levels similar to those of AL-6X) stainless steel tubing are being installed after field tests of one year (Wallen, Liljas and Olsson, 1982). Such grades are advanced only to the point of field tests in Japan.

TABLE 2 Critical Crevice Temperature for Exposure
In 10% Ferric Chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (pH = 1, 24 hours)

Grade	Temperature for No Crevice Corrosion		Temperature for Slight Crevice Corrosion	
	$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C}$	$^{\circ}\text{F}$
AISI Type 304	-	-	-2.5, -2.5	27.5, 27.5
AISI Type 316	-2.5	27.5	-2.5, 0	27.5, 32
AISI Type 317	-2.5, 0	27.5, 32	0, 2.5	32, 36.5
Type 317LM	-2.5, 0	27.5, 32	0, 2.5	32, 36.5
Alloy 904L	-2.5, 0	27.5, 32	0, 2.5	32, 36.5
AL-6X	17.5, 20	63.5, 68	20, 22.5	68, 72.5
254 SMO	40, 40	104, 104	42.5, 42.5	108.5, 108.5
AISI Type 444	-	-	0, 0	32, 32
E-BRITE	20, 22.5	68, 72.5	22.5, 25	72.5, 77
SEA-CURE	42.5, 42.5	108.5, 108.5	45, 45	113, 113
AL 29-4	47.5, 50	117.5, 122	50, 52.5	122, 126.5
AL 29-4-2	37.5, 40	99.5, 104	40, 42.5	104, 108.5
AL 29-4C	52.5, 52.5	126, 126	55, 55	131, 131
AISI Type 329	5, 5	41, 41	7.5, 7.5	45.4, 45.5

TABLE 3 Crevice Corrosion Resistance of Stainless Steels
In Low Velocity Seawater at Ambient Temperature^a

	Probability of Initiation of Corrosion At Artificial Crevice - %			Maximum Depth Of Attack - mm		
	61 days	272 days	752 days	61 days	272 days	752 days
AISI Type 304	10.5	NT ^b	NT	1.47 ^c	NT	NT
AISI Type 316	7.2	NT	NT	0.23	NT	NT
AISI Type 317	8.0	NT	NT	0.10	NT	NT
Type 317 LM	NT	10.8	3.2	NT	0.17 (0.12) ^d	0.04 (0.09) ^d
Alloy 904L	0	1.7	0.8	0	0.06	0.05 (0.08) ^d
AL-6X	-	0.8	0.8	0	0.01 (0.02) ^d	0.02
254 SMO	NT	0 ^e	0	NT	0 ^e	0
AISI Type 444	13	NT	NT	0.64 ^c	NT	NT
E-BRITE	3	NT	NT	0.43	NT	NT
SEA-CURE	NT	0 ^e	0	NT	0 ^e	0
MONIT	0	0	0	0	0	0
AL 29-4	0	0	0	0	0	0
AL 29-4-2	1.4	0	0	<0.02	0	0
AISI Type 329	18	NT	NT	0.15	NT	NT

^aFor the 61-day test, the temperature range was 15.6-25 °C.

For the 272-day and 752-day tests, the temperature range was 5-31 °C.

^bNT = Not Tested.

^cPerforated Specimen.

^dAttack at fouling sites.

^e186 day exposure.

One application making extensive use of higher alloyed austenitic stainless steels in recent years has been the construction of flue gas desulphurization scrubbers (Lizlovs, 1977; Lizlovs, 1978; AISI, 1978; INCO, 1980; Anderson, 1981; Wallen, Liljas and Olsson, 1982). Although many designs have been used or proposed, the limestone slurry scrubber has been the most common approach for North American coal-fired power plants. Early in the 1970's, it was found that grades with 2.75-4.0% Mo were satisfactory; however, more recent designs have utilized increased slurry recirculation to minimize total water requirements and sludge production. The resultant chloride (and sometimes fluoride as well) build up and increased temperature, along with the presence of sulphurous and sulphuric acids, has necessitated the use of the proprietary austenitic stainless grades for the primary construction of the scrubber, with highly-alloyed nickel-base materials being utilized in critical sections. As shown in Table 4, extremely severe laboratory tests are being used to rank and assess the use of these grades for new scrubber designs. Although these higher alloyed materials pose a very high initial capital investment, their reliability in longer term performance and resistance to transient conditions that are severely damaging to lesser alloys and nonmetallic coatings have

repeatedly justified the higher alloy approach. Similarly, the "closing-up" of paper mills with respect to pollution effluents now mandated for North America and Europe is necessitating an upgrading of the materials of construction of the processing equipment. As indicated by the industry-sponsored field tests still in progress, increased temperatures and more corrosive chemical environments require use of the higher alloyed austenitic grades (Tuthill, 1980, 1982).

TABLE 4 Evaluation of Stainless Steels
In Simulated Flue Gas Scrubber Environments¹

<u>Alloy Type</u>	<u>Corrosion Rate mg/dm²/day</u>	<u>Maximum Pit Depth, mm</u>	<u>Visual Observations</u>
AISI Type 316	1.6, 2470	0.26	large pits, severe general corrosion
AISI Type 317	0.9, 273	0.017	small pits, general corrosion
Alloy 904L	1.2, 600	0.064	large pits, severe general corrosion
SEA-CURE	12, 17	0.076	attack at crevices
Ferralium 255	12, 30	0.12	attack at crevices
MONIT	0, 0.4	0.03	attack at crevices
20Mo-6	0, 0.5	0.004	few pits at crevices
254 SMO	0, 0	0	no visible corrosion

¹Simulation of transient condition of calcium carbonate interruption in limestone slurry scrubber resulting in dilute hydrochloric acid under oxidizing conditions. Multiple crevice assembly; 30 000 ppm Cl⁻ as CaCl₂, initial pH 3, continuous bubbling of SO₂ and O₂; 2 days at 60 C (140 F); final pH < 1.

Resistance to Stress Corrosion Cracking

The highly alloyed austenitic grades offer a possible solution to the problem of chloride stress corrosion cracking (SCC) long associated with the use of the common grades of austenitic stainless steel in heat transfer service. As shown in Table 5, none of the austenitic stainless steels passes the boiling 42% MgCl laboratory test when stressed beyond yielding. However, this test is thought to be overly severe because it predicts failures for grades such as Carpenter 20Cb-3 and Incoloy 800 which have proved resistant to SCC in years of service (Dana, 1956). It is true that the boiling 42% MgCl₂ test can be made to discriminate among austenitic stainless steels by either time to failure for loading to yielding, or by determination of the critical stress (frequently reported as percentage of yield stress) required for SCC, as shown in Fig. 1. While the ranking is accurate, the information may not be sufficient. It is unlikely that tubing will be installed without introducing some region of high residual stresses, whether by bending for U-tubes, by seal welding, or by roller or hydraulic expansion during installation. Of greater practical significance, it has been demonstrated that laboratory tests based on fully yielded specimens and NaCl solutions, whether boiling 25% solution or the "wick test" as shown in Figure 2, are representative of field conditions not actually involving magnesium chloride environments (Dana, 1956; Dundas and Bond, 1980). It has been shown (Dundas and Bond, 1980) that austenitic stainless steels with less than about 0.08% N and with alloy content above about 18% Cr and about 3.5% Mo will not suffer SCC in boiling NaCl or the wick test. The use of nitrogen, almost always in association with a reduced level of nickel in commercial practice, raised the level of

molybdenum required to pass the NaCl SCC tests. The precise relationship has not been determined, but it is observed that even at the high level of nitrogen present in 254 SMO, this 6% Mo steel passes the boiling 25% NaCl and wick tests. Based on the results of the NaCl tests, it appears that the higher alloyed austenitics may be utilized in a wide range of applications from which concern for the possibility of SCC has excluded the common austenitic grades.

TABLE 5 Stress Corrosion Cracking Resistance of Stainless Steels

Grade	Stress Corrosion Cracking Test ^a		
	Boiling 42% MgCl ₂	Wick Test	Boiling 25% NaCl
AISI Type 304	F ^b	F	F
AISI Type 316	F	F	F
AISI Type 317	F	(P ^c or F) ^d	(P or F)
Type 317 LM	F	(P or F)	(P or F)
Alloy 904L	F	(P or F)	(P or F)
AL-6X	F	P	P
254 SMO	F	P	P
20Mo-6	F	P	P
AISI Type 409	P	P	P
Type 439	P	P	P
AISI Type 444	P	P	P
E-BRITE	P	P	P
SEA-CURE	F	P	P
MONIT	F	P	P
AL 29-4	P	P	P
AL 29-4-2	F	P	P
AL 29-4C	NT ^e	P	P
3RE60	F	NT	NT
SAF 2205, AF 22	F	NT	(P or F) ^f
Ferralium	F	NT	(P or F) ^f

^aU-bend tests, stressed beyond yielding.

^bF - Fails, cracking observed.

^cP - Passes, no cracking observed.

^dSusceptibility of grade to SCC determined by variation of composition within specified range.

^eNot tested.

^fSusceptibility of grade to SCC determined by variation of thermal history.

Use of Nitrogen in Austenitic Stainless Steels

Nitrogen, an inexpensive alloying element easily controlled by the AOD, represents more than an opportunity to save on the cost of the nickel addition (Sakamoto and co-workers, 1980). Nitrogen provides improved pitting resistance for molybdenum-containing grades and increased strength for all austenitic grades, and its previously discussed negative effect, direct or indirect, on SCC resistance can be avoided. The substitution of nitrogen for nickel has important effects on processing requirements and corrosion resistance through its influence on the precipitation of sigma phase. The high chromium and molybdenum levels required for corrosion resistance increase the tendency toward formation of sigma phase, and the correspondingly high level of nickel

required to stabilize the austenitic structure seems to accelerate the precipitation of sigma phase. For these reasons AL-6X is available only in very light gauges, and welded tubing is produced under conditions controlled to achieve only brief high temperature exposure (Aggen, 1977). On the other hand, 254 SMO having essentially similar chromium and molybdenum contents but a partial substitution of nitrogen for nickel, is processed and field welded in plate sections up to 50 mm without significant degradation by sigma phase (Wallen, Liljas and Olsson, 1982). This observation suggests that nitrogen may be used to advantage in solving corrosion problems of the common austenitic grades where sigma phase precipitation may occur on a more subtle but still deleterious scale. Furthermore, stabilization of the austenitic structure with respect to intermetallic phase precipitation may permit the development of new austenitic stainless steels at high levels of chromium. The synergy of the chromium-molybdenum interaction is enhanced at higher chromium levels, offering high corrosion resistance and economy of alloy cost. Such grades represent an area attractive for new alloy development in the 1980's.

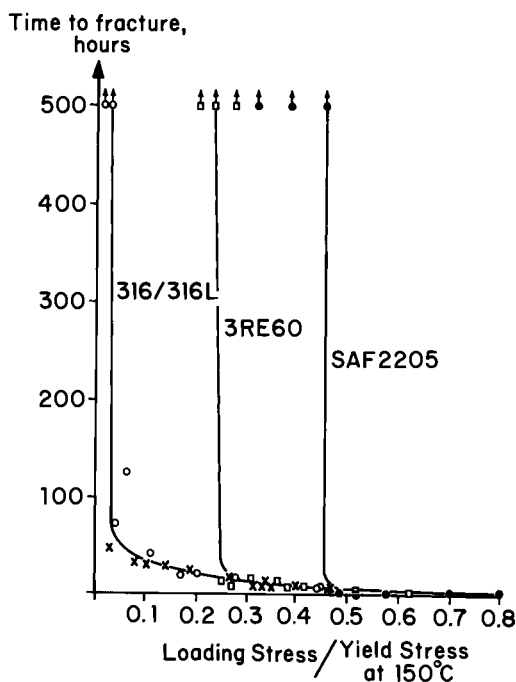


Fig. 1 SCC-tests on tensile specimens exposed to aerated 45% MgCl_2 at 150 °C.

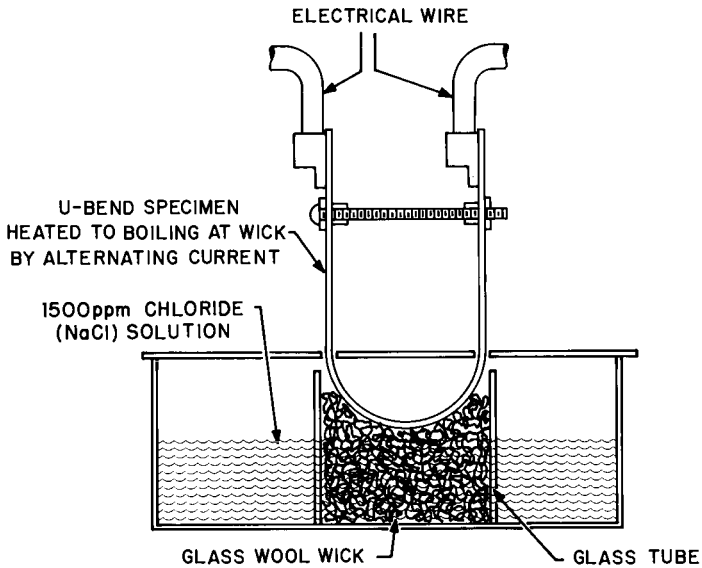


Fig. 2 Experimental apparatus for Wick test.

FERRITIC STAINLESS STEELS

If the problems of toughness and weldability can be overcome by controlling interstitial elements, especially carbon but also nitrogen, then chromium and molybdenum can be used in highly efficient combinations to achieve ferritic stainless steels exhibiting excellent corrosion resistance (Binder and Spendlow, 1951). Ferritic grades are especially useful because of their practical immunity to chloride stress corrosion cracking. However, before the AOD became available, the cost of low interstitial charge material and the difficulty of preserving low interstitial levels through processing made the higher alloy ferritic grades noncompetitive commercially. The advent of the AOD and its vacuum enhanced variations such as vacuum-oxygen-decarburization (VOD) and the increased use of vacuum induction melting (VIM) made a full range of chromium and molybdenum combinations commercially feasible. Selecting the combinations of chromium and molybdenum for commercial development is an interesting proposition of balancing the synergistic enhancement of corrosion resistance with cost. The contribution of molybdenum to corrosion resistance increases very strongly with increasing chromium contents above 16-18%. Chromium is less expensive than molybdenum, but molybdenum additions achieve higher levels of corrosion resistance with less sensitivity to degradation of mechanical properties by interstitial elements than if the same level of corrosion resistance is achieved with only chromium additions. It is possible to tailor chromium and molybdenum levels precisely to each application, but the economics of maintaining inventories of product forms for each grade encourages commercial development of a few multipurpose grades, each serving a large segment of the market. A much simplified approach is to suggest the need for four levels of corrosion resistance according to the environment: air; fresh water; chemical process streams; and seawater.

Role of Carbon in Ferritic Stainless Steels

Before discussing particular grades of ferritic stainless steel, it is useful to examine the effects of carbon and alternative methods for its control. Carbon is detrimental in two ways, reducing toughness with increasing severity at increasing chromium levels (Binder and Spendlow, 1951), and sensitizing the steel to localized attack after exposure to a thermal cycle as in welding. There are two ways to diminish the deleterious effects of carbon and other interstitial elements in these steels: to remove them from the steel by refining during steelmaking, or to precipitate them from solution by addition of stabilizing elements such as niobium and titanium (Lula, Lena and Kiefer, 1954). Lowering the interstitial content is beneficial to toughness, whether or not a stabilizing addition is made (Semchysheh, Bond and Dundas, 1971). The presence of stabilizing elements in excess of that required to react with the interstitial elements is also detrimental to toughness, especially in weld metal (Sawhill and Bond, 1976). As was the case for austenitic grades, the sensitization of the ferritic grades results from precipitation of chromium carbide, usually at a grain boundary, when the cooling rate from high temperature is too rapid to permit diffusion of chromium to smooth the adjacent concentration gradient. For the austenitic grades, the solubility of carbon is such that sensitization after welding can be avoided by having a carbon content of less than 0.03%. Although it is possible to avoid sensitization of the ferritic grades by lowering the carbon content, the maximum tolerable level of carbon is impractically low except for the 29% Cr grades and possibly the 26% Cr grades (Steigerwald and co-workers, 1977). Contrarily, the tolerance for the use of stabilizing elements in terms of their effects on mechanical properties diminishes with increasing alloy content (Streicher, 1974). Nevertheless, it is practical by either interstitial removal or by stabilizer addition to achieve good toughness and protection against sensitization for all chromium-molybdenum combinations. Field experience has on occasion reminded the user quite forcefully that the quality of the ferritic grades is based on low interstitial content, and that the use of these grades including welding must preserve the low interstitial content if the desired properties are to be maintained. While carbon is the primary cause of the detrimental effect, nitrogen is also detrimental and almost equally reactive with the stabilizing elements, particularly titanium (Semchysheh, Bond and Dundas, 1971; Steigerwald and co-workers, 1977). Consequently, the composition specifications for stabilizing elements are expressed as a function of carbon plus nitrogen (ASTM, 1982a). One of the difficulties encountered in developing the specifications for stabilizing elements was that the test methods applicable to austenitic stainless steels were not directly applicable to ferritic grades. For example, titanium carbide is directly attacked by nitric acid which is used in ASTM A262 Practice C. Furthermore, the range of corrosion resistance of the ferritic grades is wide enough that it is necessary to utilize test media of different corrosivities. This problem was addressed in great detail by a task group of the ASTM, resulting in a symposium (Steigerwald, 1977) and a new test procedure (ASTM, 1982b) for evaluation of sensitization of the ferritic stainless steels.

Applications of Ferritic Stainless Steels

Beginning at the lowest alloy level for stainless steels, a tough, weldable stainless steel can offer lower total lifetime costs than carbon steel in many engineering applications. In the United States, AISI Type 409 has grown to be one of the largest single grades because of its use in the automotive catalytic converter. It now appears that Type 409, and its modifications with improved strength, toughness, weldability, and oxidation resistance (achieved by use of niobium, molybdenum, nickel, and aluminum), may further expand its use for higher temperature, lighter weight, and more durable

exhaust systems from manifold to tailpipe. Produced with lower carbon levels and with titanium addition closely matched to carbon and nitrogen, grades such as 3CR12 offer improved toughness, weldability, and product uniformity. With these advantages 3CR12 represents a cost effective substitute for mild or low alloy steels in many constructional applications where protective coatings are impractical or inadequate. This grade is especially useful in corrosion-abrasion applications such as mine cars and conveyors in which abrasive removal of the surface oxides greatly accelerates corrosion and shortens the useful life of steel. The reduced cost of maintenance can give this stainless steel a lower "lifetime cost" than mild steel in hoppers, chutes, flooring, walkways, tanks, ducts, screens, shields, roofing, and other constructional applications.

For the handling of fresh water, ranging from potable water to mildly contaminated river water, the important new ferritic grade is AISI Type 444 containing 18% Cr and 2% Mo. As shown in Table 6, the crevice corrosion resistance of Type 444 approaches that of AISI Type 316. The largest single application to date, solar collector panels, makes full use of the technical capabilities of the grade. Type 444 does not experience SCC on the heat transfer surface despite the presence of high residual stresses associated with the forming of the panel. Types 304 and 316 failed by SCC under similar conditions (Weed, Redmond and Dundas, 1981). Type 444 is highly resistant to corrosion in the tight metal-to-metal crevices that typically result from low cost fabrication methods (Redmond, Lizlovs and Davison, 1977). Type 444 readily accepts a low cost chemical blackening treatment resulting in a selective solar coating of proven durability (Redmond, Baker and Davison, 1978; Redmond, 1981). Such panels are now manufactured in Japan, the United States, Europe, Australia and South Africa. The combination of crevice corrosion resistance and SCC resistance makes Type 444 an ideal material for heat exchangers such as those of refineries, chemical plants, and food and beverage processing equipment.

TABLE 6 Crevice Corrosion of Stainless Steels in Fresh Water Environments

	Weight Loss (mg/dm ² /day)	
	Solutions, Oxygen-Saturated, 90 °C	
	200 ppm Cl ⁻ , 1 ppm Cu ⁺⁺	600 ppm Cl ⁻ , 1 ppm Cu ⁺⁺
AISI Type 434	41.0	241.0
Type 439	9.6	400
AISI Type 304	15.0	11.8
AISI Type 316	2.6	3.5
AISI Type 444	0.2	0.8

For applications in which operating conditions are known and well controlled, it is possible to consider a slightly lower alloy content, such as type 439 stainless steel with 18% Cr. Compared to Type 444, type 439 has equal SCC resistance but somewhat lower crevice corrosion resistance. Type 439 has enjoyed considerable success in feedwater heaters and moisture separator reheaters. However, use of type 439 for flat plate solar collectors resulted in an unacceptable level of failures due to crevice corrosion, a problem resolved through the use of Type 444. For this reason, Type 444 is regarded as the multipurpose grade while type 439 is useful in carefully controlled situations.

The 26% Cr-1% Mo steels present an interesting case study for the technical and commercial development of new metallurgical products. Marketed by Airco Vacuum Metals, E-BRITE 26-1 was the first of the low interstitial ferritic grades to be produced on a commercial scale. The original ASTM specification

and ASME Boiler Code qualification of this steel, produced by electron beam refining under high vacuum, indicated no stabilizing addition, but the great majority of its production had a small niobium addition (proportional to its extremely low carbon and nitrogen contents). Early efforts to produce titanium-stabilized 26% Cr-1% Mo steel by AOD were not entirely satisfactory in terms of product yield and mechanical properties. The 26% Cr-1% Mo steels did not achieve the level of anticipated commercial success. Production costs restrained penetration of markets where 18% Cr grades were satisfactory. Later work demonstrated that the alloy content is insufficient for resistance to crevice corrosion in seawater at ambient temperatures. Nevertheless, the grade has given excellent performance in a range of chemical environments in which the common austenitic grades are constrained by their limitation to 18-20% Cr, or by their lack of SCC resistance. Allegheny Ludlum Steel requalified E-BRITE 26-1 specifying a niobium addition and reflecting the quality achieved by VIM production instead of electron beam refining. E-BRITE 26-1 has been used extensively in caustic evaporators, replacing nickel, and in heat exchangers in the chemical and petrochemical industries (Moller, Franson and Nichol, 1980; Nichol, Franson and Moller, 1981). The strength of the chromium-molybdenum synergism at higher chromium levels was clearly revealed (Streicher, 1974). The resulting stainless steels, AL 29-4 and AL 29-4-2, exhibit crevice corrosion resistance superior to other stainless steels, as shown in Table 2. These 29% Cr stainless steels are comparable to nickel-base alloys and titanium in resistance to many severely corrosive chemical environments. The addition of 2% Ni to the AL 29-4-2 provides excellent resistance to attack in boiling 10% sulphuric acid. These grades, produced by vacuum induction melting, have very low carbon and nitrogen contents and require no stabilizing additions to prevent sensitization to intergranular attack. Welding requires superior inert gas shielding to maintain the low interstitial level.

The success of ferritic stainless steels in providing high levels of corrosion resistance with an economical use of alloying elements is demonstrated by the seawater condenser tubing applications. While the austenitic AL-6X established stainless steels in seawater condenser tubing in the 1970's, it is the highly alloyed ferritic stainless steels that have now begun to dominate this market in North America. Table 3 summarizes the results of a seawater test programme involving a wide range of commercial and developmental steels. While generalizations about seawater corrosion resistance are made at great peril because of the variability of this environment, the completeness of this programme in terms of number of grades, full-season exposures, severe crevice specimens, welded specimens, and correlation with field experience at many locations, suggests some characterization of the new ferritic stainless steels. With correct production practice, low interstitial ferritic stainless steels with at least 26% Cr combined with at least 3% Mo are resistant to crevice corrosion in natural seawater. Ambient seawater is frequently a more aggressive corrosion medium than seawater heated to 50 °C. Filtered seawater is more aggressive than unfiltered seawater because the filtration eliminates macrofouling that would otherwise reduce the ratio of cathodic to anodic areas. Similar results have been observed in another major survey (Hack, 1982). Consistent with the test results, AL 29-4C and SEA-CURE tubing have achieved notable commercial success in the last three years (Kovach and Thackray, 1980), already accounting for some 2.4 million metres of condenser tubing in service. Most frequently, these installations have been the replacement of copper-nickel alloys that failed prematurely by sulphide corrosion, a form of attack of no consequence to these stainless steels. The low alloy cost and the ability to be produced as thin wall welded tubing give the ferritic stainless steels a cost advantage relative to the austenitic stainless steels and titanium. An additional advantage of the ferritic grades over titanium is that the higher modulus of the steel

permits a wider spacing of support sheets without problems of tube vibration (Maurer, 1980), enabling the stainless steels to replace copper-nickel tubing without respacing of the tube support sheets. Relative to copper-nickel, the stainless steels provide longer service lives, higher water flow rates, and superior heat transfer in long term service because of the absence of surface oxidation acting as a thermal barrier (AISI, 1976). It is expected that the success of these grades in North America will expand to other geographic markets, and that the higher alloyed ferritic stainless will find applications in desalination and chemical processing equipment.

Resistance to Stress Corrosion Cracking

The resistance of ferritic stainless steels to chloride stress corrosion cracking, already touched upon several times, is a complex issue. At very low nickel and copper levels, the ferritic stainless steels do not suffer SCC even in the highly aggressive boiling 42% MgCl_2 test (Steigerwald, Bond, Dundas and Lizlovs, 1977). The tolerance for nickel and copper in this regard decreases with increasing chromium and molybdenum content, but the required levels are still readily achieved in commercial production as indicated by the SCC resistance of AL 29-4. However, ferritic stainless steels may have significant nickel contents, either unintentionally through the scrap charge or the AOD lining when austenitic grades are processed ahead of the ferritic grade, or by intentional addition for its benefits to steel processing or to acid resistance. As shown in Table 5, none of the low interstitial ferritic stainless steels, whatever the nickel or copper content, had failed by SCC in the boiling 25% NaCl test or the wick test. More importantly, there has been no incident of SCC reported for these grades in field experience. Therefore, while it is incorrect to claim total immunity to SCC, the ferritic grades have demonstrated a practical immunity to SCC in engineering applications not involving high MgCl_2 concentrations, and several of the new ferritics would be satisfactory in concentrated MgCl_2 .

Toughness of Ferritic Stainless Steels

Even with the low levels of interstitial elements now achievable, the problems of toughness and weldability of the ferritic stainless steels are ameliorated but not eliminated. Sheet and tubing are now produced and fabricated with relative ease, but the development of plate products is far from complete. While some producers now offer some of the new ferritic grades in plate up to 12 mm thickness, and there are clad plates with up to 12 mm of ferritic stainless steel explosively bonded to steel plate, the development of ferritic stainless steels of adequate toughness and weldability in plate gauges remains a problem for the 1980's.

DUPLEX STAINLESS STEELS

By addition of austenitizing elements at a level insufficient for a fully austenitic structure, it is possible to achieve a mixed structure of ferrite and austenite. Ideally, such a structure would combine the toughness and weldability of austenite with the strength, corrosion resistance, and SCC resistance of the ferrite. With proper practice in control of composition and thermal history, these advantages can be substantially realized. One disadvantage is that the partitioning of chromium and molybdenum to the ferrite may result in an unequal corrosion resistance for the two phases. Furthermore, because the volume fraction balance of the two phases changes with temperature, a rapid change of temperature may produce short range depletion effects, somewhat analogous to carbide sensitization, as diffusion does not keep pace with the phase change and segregation. Therefore, the chloride crevice corrosion resistance of a duplex stainless steel is likely to be slightly less than that of the ferritic grade with the same total chromium and molybdenum contents. But stated in a more positive way, the

duplex stainless steels can match the corrosion resistance of ferritic grades for a relatively small increase of chromium and molybdenum and are readily produced in heavy sections with excellent toughness well beyond that of the ferritic grades.

Improvements in Duplex Grades

The superior control of nitrogen as an alloying element achieved by the AOD has made possible improved duplex stainless steels. As was the case for the austenitic grades, nitrogen, a powerful austenitizer, appears to reduce the degree of chromium partitioning. Furthermore, as was the case for the austenitic grades, nitrogen enhances the pitting resistance of the austenite bringing it into better balance with that of the ferrite phase which is rich in chromium and molybdenum. The corrosion resistance of duplex stainless steels is reduced by welding as a result of phase transformation and carbide sensitization of the ferrite. Nitrogen significantly reduces the deleterious effects of welding, apparently by quickly reintroducing austenite, to which the carbon diffuses, in the heat affected zone (Bernhardsson, Mellstrom and Oredsson, 1981). The optimal use of duplex stainless steels is in applications of plate, bar, and seamless pipe requiring high strength and toughness. One such application that is rapidly growing is the use of SAF 2205 or AF 22 for production tubing in corrosive oil and gas wells, with large installations already in place in the North Sea and North America. Duplex stainless steel might also be considered for use as heavy section tube sheets that would be compatible in strength and corrosion resistance with the highly alloyed austenitic and ferritic stainless steels.

Resistance to Stress Corrosion Cracking

The stress corrosion cracking resistance of duplex stainless steels is substantially higher than that of the common austenitic stainless steels such as Type 316. The critical stress for SCC failure in boiling $MgCl_2$ is high for duplex stainless steels, as shown in Fig. 1. Nitrogen may further increase this stress, but the effects of higher alloy content and nitrogen are not clearly separable in the work reported. Not all grades of duplex stainless steel consistently pass the previously discussed SCC test of U-bend specimen in boiling 25% NaCl. So some caution should be exercised in the selection and application of these grades in aggressive chloride environments above ambient temperatures, particularly when the steel is highly stressed or when hydrogen sulphide is present in the environment. However, the conditions of temperature, stress, chloride concentration, and hydrogen sulphide partial pressure have been thoroughly evaluated as to their effects on SAF 2205 and conservative guidelines for use have been recommended (Oredsson and Bernhardsson, 1982). Although not immune to SCC in chloride-containing solutions, duplex stainless steels have solved many SCC problems in practice. These grades also have shown good resistance to corrosion fatigue, a property that is especially useful in rotating equipment and equipment subject to frequent thermal cycling.

SUMMARY

Stainless steel refining techniques, originally introduced to permit use of more economical charge materials, have greatly expanded the commercially feasible composition ranges for austenitic, ferritic, and duplex stainless steels. Austenitic stainless steels can now be produced with molybdenum content as high as 6%. Nitrogen has become an important, controllable alloy addition in austenitic and duplex stainless steels, providing significant improvements in corrosion resistance. The ability to control carbon and nitrogen to very low levels has permitted commercial development of a very

wide range of ferritic stainless steels, from 12% Cr to 29% Cr-4% Mo, having improved toughness and weldability and achieving corrosion resistance with a highly efficient use of alloying elements.

These new grades of stainless steel offer levels of corrosion resistance not previously achieved by stainless steels, including resistance to corrosion by seawater. Practical engineering solutions to the problem of stress corrosion cracking are readily achieved. Modern stainless steels are now available to provide superior, reliable, and cost-effective service in an ever widening range of consumer and industrial products.

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Recent Developments on the Role of Molybdenum in Irons and Steels

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ABSTRACT

Recent technological developments in the physical metallurgy of molybdenum-containing wrought constructional steels, HSLA steels, and cast irons are described. Extensive reference is made to the original papers for these developments.

KEYWORDS

Molybdenum; carburizing steels; rail steels; HSLA steels; OCTG steels; elevated temperature steels; cast irons; ERW-pipe steels.

INTRODUCTION

The iron and steel industry represents about 85% of the annual demand for molybdenum. In recent years both producers and consumers of irons and steels have carried out aggressive research and development programmes leading to materials of improved strength, toughness, and corrosion resistance. These developed products are able to cope with a greatly extended range of temperatures and corrosive environments, and they are produced more economically with greater commercial performance reliability. The incentives for these developments are new technical challenges, the increased cost of energy, and inflationary cost pressures. Facilitating the development of new steels has been a better understanding of the physical metallurgy of steels and alloys, and the concomitant introduction of new steelmaking and processing technology. Examples of these technologies include ladle metallurgy leading to more accurate control of alloying and lower levels of impurities, continuous casting, controlled precise thermomechanical processing schedules, and accelerated cooling often with computer control. With these advances, alloying elements have taken on new and sometimes unforeseen roles in steels and irons. This discussion will summarize the latest trends for molybdenum-containing carburizing steels, elevated temperature steels, oil industry products, gas transmission line pipe, and rail steels. Significant advances in the use of molybdenum in cast irons will also be discussed. Numerous references have been provided for pursuit of details of the new developments.

CARBURIZING STEELS

For many years the alloy steel industry has pursued carburizing steels of improved toughness and fatigue resistance while at the same time seeking to utilize alloying and processing in an economically optimal way. The very large tonnage of these steels used each year in automobiles, commercial

vehicles, off-road equipment, and mining and manufacturing equipment implies a need for low cost steels. But the critical nature of these parts in equipment of substantially larger total cost establishes the need for superior performance and reliability. In applications ranging from the smaller but more highly stressed drive train components of "downsized" cars to the high performance rock bits for deep drilling, molybdenum usage in improved carburizing steels is growing.

The design and production of better carburized steels has been greatly facilitated by laboratory studies that have explained the role of metallurgical factors in the fracture properties of carburized steels. Experimental data have confirmed the predictions of a linear elastic fracture mechanics model for the different fracture modes of different regions of the carburized case. For example, microstructure and residual stress near the surface of the case influence fatigue properties but have little effect on impact properties, while the microstructure and residual stress deep in the case determine the ability of the case to tolerate stress peaks associated with overloading encountered in practical applications.

The fracture mechanics model for bending fatigue predicts that cracks at the surface of the case must exceed a critical length before propagating by fatigue (Kim, Diesburg and Eldis, 1982). One important factor in producing cracks of this length is oxidation during carburizing. This oxidation reduces fatigue properties in two ways: (1) the oxidized grain boundaries serve as crack initiation sites, and (2) the depletion of alloy in the matrix produces tensile or less compressive residual stresses at the surface (Hildenwall and Ericsson, 1980). Silicon and manganese are especially detrimental in increasing the depth of surface oxidation; chromium oxidation occurs at the surface with only limited grain boundary penetration (Mitchell, Cooksey and Dawes, 1968; Chatterjee-Fischer, 1978; Arkhipov, Batyrev and Polotskii, 1972). Molybdenum and nickel do not oxidize during carburizing so the fatigue limit of molybdenum steels, represented by Point A in Fig. 1, is expected to be higher than that of manganese-chromium steels which have more oxidation and hence less compressive stress than the molybdenum steels, represented as Point B. Figure 2 supports this analysis showing the superior fatigue properties of molybdenum-alloyed steels relative to those of manganese-chromium steels.

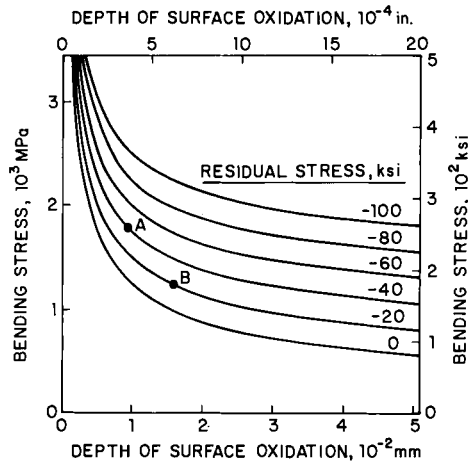


Fig. 1 Relationship between depth of surface oxidation and maximum stress required to propagate a crack by fatigue ($R=0.1$) for various surface residual compressive stress values (Diesburg, Kim and Bulla, 1981).

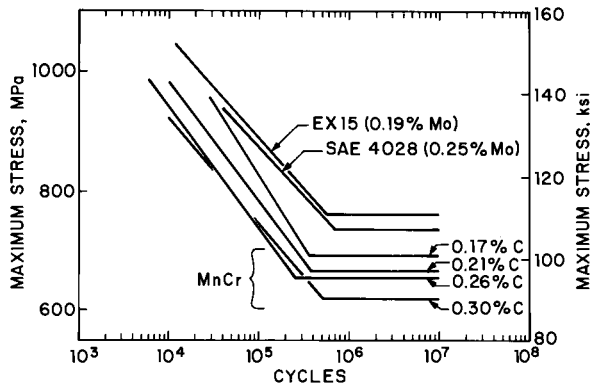


Fig. 2 Fatigue properties of six carburized steels (Diesburg, Kim and Bulla, 1981)

Impact bending fracture, as might characterize a gear tooth failure, has been predicted and shown to be controlled by the microstructure and residual stress deep in the case (Kim and Diesburg, 1982). Table 1 shows two examples of changing surface microstructure and residual stress without changing impact fracture strength. Shot peening, resulting in high compressive stresses, improved fatigue strength but did not change impact strength. Refrigeration treatment, resulting in a tensile stress in the remaining retained austenite, lowered the fatigue strength but did not change impact strength. These results suggest that surface conditions have little effect on impact strength or resistance to overload fracture.

TABLE 1 Effect of Residual Stress on Fracture Properties of Case-Hardened Steels (Kim, Diesburg and Buck, 1981)

<u>Steel</u>	<u>Condition</u>	<u>Residual Stress^a</u> MPa (ksi)	<u>Fatigue Limit</u> MPa (ksi)	<u>Fracture Strength</u> MPa (ksi)
I	Carburized, Quenched, and Tempered	-140 (-20)	730 (105)	2240 (325)
	Carburized, Quenched, Tempered and Shot Peened	-620 (-90)	1035 (105)	2265 (329)
II	Carbonitrided, Quenched, and Tempered	-140 (-20)	965 (140)	3220 (468)
	Carbonitrided, Quenched, Refrigerated and Tempered	69 (10)	420 (60)	3220 (468)

^aResidual stress 0.1 mm (0.002 inch) from surface; residual stress deep in the case is unchanged by the shot-peening or refrigeration treatment.

Steels with high case hardenability exhibit high impact fracture strength for two reasons: (1) a larger amount of martensite transformation produces a higher compressive residual stress deep in the case, and (2) higher fracture toughness results from a microstructure of tempered martensite rather than high carbon bainite. Figure 3 illustrates the role of molybdenum in suppressing bainite in favour of martensite in three carburizing steels. The impact fracture toughness of these steels increases with molybdenum content, with SAE EX-55 being used in the most demanding of applications such as rock bits.

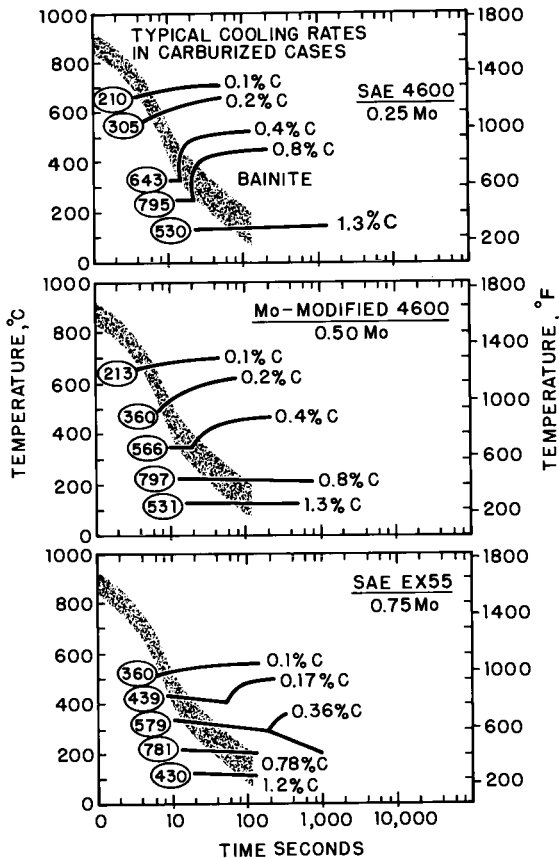


Fig. 3 Partial CCT diagram for three carburizing steels each with five levels of carbon. (Circled numbers are HV10 hardness after cooling to room temperature) (Diesburg, Kim and Fairhurst, 1981)

Even among steels having similar case and core hardenabilities, there can be differences in impact fracture strength. Figure 4 summarizes a comparison of Mn-Cr and Cr-Mo steels for many carburized conditions. These conditions include core carbon from 0.15 to 0.30%, surface carbon from 0.7 to 1.0%, and effective case depths from 1.14 to 1.40 mm (0.045 to 0.055 in). Such variations in surface carbon and case depths are to be expected in normal production. It is concluded that the Cr-Mo steels will, on the average, provide a better impact resistance than the Mn-Cr steels.

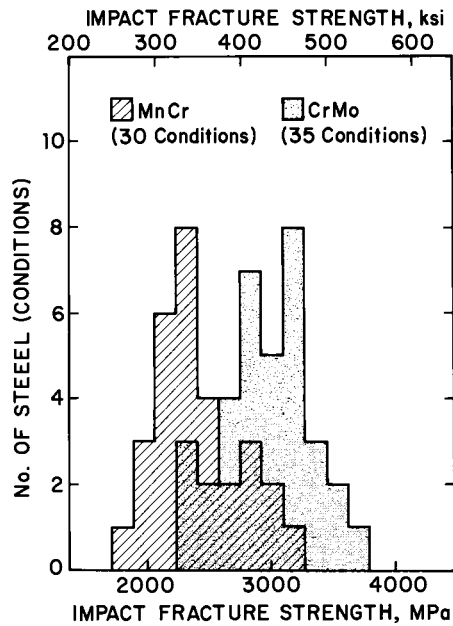


Fig. 4 Histogram of impact fracture strengths of several MnCr and CrMo steels tested at Climax Molybdenum Company Research Laboratory.

Besides the extensive research conducted on automotive carburizing steels, the Climax Molybdenum Research Laboratory is also evaluating carburizing steels capable of performing for extended periods of time at temperatures as high as 315°C (600°F). The foremost design requirement to be met by these carburizing steels is that the carburized case hardness remain above HRC 58 with prolonged exposure at elevated temperatures. Three steels capable of maintaining this hardness at 315°C (600°F) are CBS 1000 (Jatczek, 1978), VASCO X-2(M) (Fopiano and Kula, 1977), and CarTech X00053 (Krieble, and Philip, 1977). Another requirement of these steels is to maintain high fracture toughness in the carburized case, even after 1000 hours of service at temperature. Table 2 shows the nominal compositions of these three steels and the measured toughness values at two carbon levels representative of two case locations. Fracture toughness values are given with and without a 1000 hour heat treatment at 315°C (600°F). The steel with the highest fracture toughness after the 315°C-1000 hour treatment was CBS 1000, whereas the fracture toughness of steels X-2M and X-00053 decreased by about 50%. Research conducted at the Climax Molybdenum Laboratory, sponsored by U.S. Army Materials and Mechanics Research Center (Contract No. DAAG 46-80-C-0018) has suggested that a 0.14% C-1% Si-0.5% Mn-2% Ni-1% Cr-2.3% Mo-0.6% V steel when carburized will exhibit improved fracture properties after prolonged elevated temperature exposure compared to CBS 1000.

**TABLE 2 Composition and Fracture Toughness in Case of
Carburized Elevated Temperature Steels**

Steel	Core Composition, Wt %								
	C	Mn	Si	Ni	Cr	Mo	V	W	Cu
CBS 1000	0.14	0.58	0.52	3.00	1.00	4.17	0.37	--	--
VASCO X-2(M)	0.16	0.36	0.94	--	4.72	1.28	0.42	1.34	--
CarTech X-53	0.11	0.38	1.00	1.98	1.00	3.55	--	--	1.99

Steel	Carbon ^a Content, %	Fracture Toughness, K_{Ic} , MPa $\sqrt{m}$ (ksi $\sqrt{in.}$)		
		Before Exposure	After Exposure ^b	% Change
CBS 1000	0.50	44 (40)	33 (30)	-10
	0.75	21 (19)	26 (24)	+25
X-2(M)	0.50	45 (41)	21 (19)	-53
	0.75	25 (23)	13 (12)	-48
X-53	0.50	48 (44)	22 (20)	-54
	0.75	36 (33)	23 (21)	-36

^a Carbon content within the carburized case.

^b Exposure to 315°C (600°F) for 1000 hours.

ELEVATED TEMPERATURE STEELS

The role of molybdenum in providing high temperature strength, creep resistance, temper resistance, temper embrittlement resistance, and resistance to hydrogen attack for elevated temperature steels has been known for many years. Standard grades such as C-0.5% Mo, 1½% Cr-0.5% Mo, and 2½% Cr-1% Mo steels have been applied in power plants and process industries with a confidence based on long experience of satisfactory and reliable performance. New developments are focused on extending this family of ferritic steels to applications of higher temperatures, higher stresses, higher hydrogen pressures, and heavier plate thicknesses.

The use of only ferritic grade steels for the construction of power generating steam boilers offers the advantages of good resistance to chloride stress corrosion, higher thermal conductivity, lower cost and avoiding the troublesome problem of welds between the ferritic and austenitic metals. A cooperative development programme in the USA has resulted in a 9% Cr-1% Mo steel, modified with vanadium and niobium as a candidate for this application (Cunningham, Patriarca and Hoffman, 1981). The modified 9% Cr-1% Mo steel matches the elevated temperature strength and rupture strength of Type 304 stainless steel up to about 635°C (Sikka, 1981) and it is now under evaluation for inclusion in the ASME Boiler and Pressure Vessel Code for tubing and plate for fossil-fired power plants.

European manufacturers often use a ferritic 12% Cr-1% Mo steel for boiler tubing although welding of this steel requires a precise programme of pre- and post-weld heat treatment. This welding problem may be alleviated by reducing the carbon content of the steel while adding molybdenum and other elements to maintain properties. Two candidate steels have been identified. A 0.10% C-12% Cr-2% Mo-1% Ni-0.25% V steel (Wada, Grobner and Vineberg, 1981) has a duplex martensitic/ferritic structure and stress rupture properties equivalent to Type 304 and the new 9% Cr-1% Mo grade. A 0.08% C-12% Cr-2% Mo-6.5-8% Ni-0.25% V (Vineberg, Grobner and Biss, 1981) steel has a structure comprised of a fine dispersion of austenite in a martensite matrix and exhibits stress rupture properties superior to those of Type 304. Rupture properties of these grades are shown in Fig. 5.

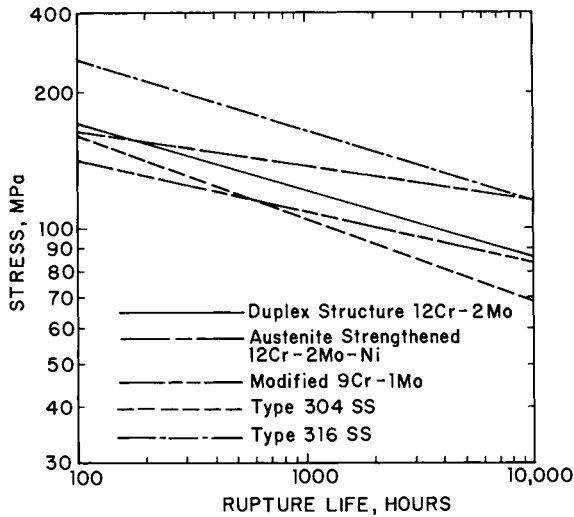


Fig. 5 Stress rupture strength of tubing steels at 649°C.

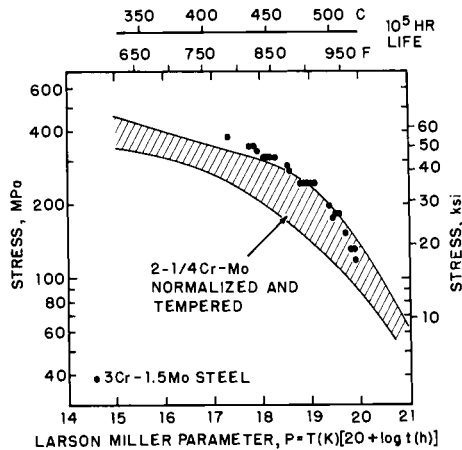


Fig. 6 Stress rupture strength of 3% Cr-1.5% Mo steel.

Many processes in refining of oil, production of petrochemicals, and conversion of coal to liquid and gaseous fuels require the use of hydrogen at high temperatures and pressures. While 2½% Cr-1% Mo steel has been commonly used for pressure vessels in these applications, recent designs call for wall thicknesses of greater than 400 mm. It is believed that 2½% Cr-1% Mo steel will not have sufficient hardenability and strength, and that hydrogen pressures as high as 21-28 MPa may be too severe for this standard grade. Extensive research has identified a new steel containing 1.4% Mn-3% Cr-1.5% Mo-0.08% V with elevated temperature strength superior to that of 2½% Cr-1% Mo steel, as shown in Fig. 6. The new steel has a critical cooling rate for ferrite formation of 0.7°C/min., compared with the 30°C/min.

of 2¼% Cr-1% Mo steel; the 3% Cr-1.5% Mo steel is expected to exhibit a fully bainitic structure in air cooled sections up to 500 mm thick. The resistance of the 3% Cr-1.5% Mo steel to temper embrittlement is equivalent to that of 2¼% Cr-1% Mo steel and may be further improved by reducing manganese to the minimum level required for hardenability. The new steel can be welded by the established practices for 2¼% Cr-1% Mo steel while the higher chromium and molybdenum contents provide superior resistance to hydrogen attack and to decarburization (Wada and co-workers, 1979). After appropriate field evaluation, it is expected that this new 3% Cr-1.5% Mo steel will become the accepted material for construction of very heavy section pressure vessels for hydrogen service.

H₂S - RESISTANT STEELS FOR THE OIL AND GAS INDUSTRY

The increased price of oil and gas has made development of deeper reservoirs of these products more attractive commercially. Many wells at depths in excess of 4500 m encounter high pressures, high temperatures, significant concentrations of H₂S, high concentrations of CO₂ and brine. The steels used in these wells for casing, tubing, couplings, and tool joints must combine high strength and resistance to sulphide stress cracking (SSC). Research has shown that SSC resistance is improved by fine, uniform microstructure, either of tempered martensite or fine bainite (Fraser and Eldredge, 1958; Hudgins and co-workers, 1966; Snape, 1967; Dvoracek, 1970; Hill, Kawasaki and Kronbach, 1972; Cain and Troiano, 1965; and Fletcher and Smith, 1978a). In recent years, highly SSC-resistant steels have been developed for the C-90 and C-100 (620 MPa and 690 MPa minimum yield strength, respectively) grades of casing and tubing, and for tool joints with 830 MPa minimum yield strength. The AISI/SAE 4100 series steels with 1% chromium and 0.4 to 0.8% molybdenum have been found to be the most SSC-resistant low alloy steels for tubular products. In the quenched and tempered condition, these steels provide the fine tempered martensite structure best for SSC resistance.

Molybdenum contributes to SSC resistance in several ways. It improves hardenability so that fine martensite or bainite is achieved in the as-quenched condition. Resistance to SSC is improved as tempering temperature is increased (Hudgins and co-workers, 1966; Snape, 1967; Grobner, Sponseller and Diesburg, 1975; Sponseller, Garber and Straatmann, 1982) and since molybdenum increases the temper resistance of the 4100 steels higher tempering temperatures are possible while still meeting the C-90 and C-100 specifications. Numerous studies have demonstrated that SSC resistance is improved if the steel is rapidly cooled from the tempering temperature (Troiano and Hetemann, 1981; Viswanathan and Hudak, 1977). These observations suggest that the same processes which cause temper embrittlement occur during normal air cooling of tubular products from the tempering temperature and reduce the resistance to SSC. Molybdenum is widely known to be beneficial in minimizing the effects of temper embrittlement, hence, its presence in commercially produced tubular products, which are usually air cooled after tempering, provides added resistance to SSC.

There is an optimal molybdenum content for SSC-resistant chromium-molybdenum steels, believed to be related to the amount of molybdenum in solid solution in ferrite, as shown in Fig. 7. On this basis, modifications of quenched and tempered AISI/SAE 4130 and 4135 steels with up to 0.75% molybdenum are the steels chosen for high strength tubulars for sour wells. Because the chromium-molybdenum steels are so resistant to tempering, some producers have difficulty tempering to the C-90 strength range. To facilitate tempering while maintaining SSC resistance, a Mn-Mo steel with 0.20% C-1.5% Mn-0.8% Mo has been developed (Fletcher and Smith, 1978a). This steel contains an optimal molybdenum content, as shown in Fig. 8. Commercially produced Mn-Mo casing with 178 mm diameter and 11.5 mm wall thickness, and drill pipe with 95 mm diameter and 10 mm wall thickness, both exhibit good SSC resistance.

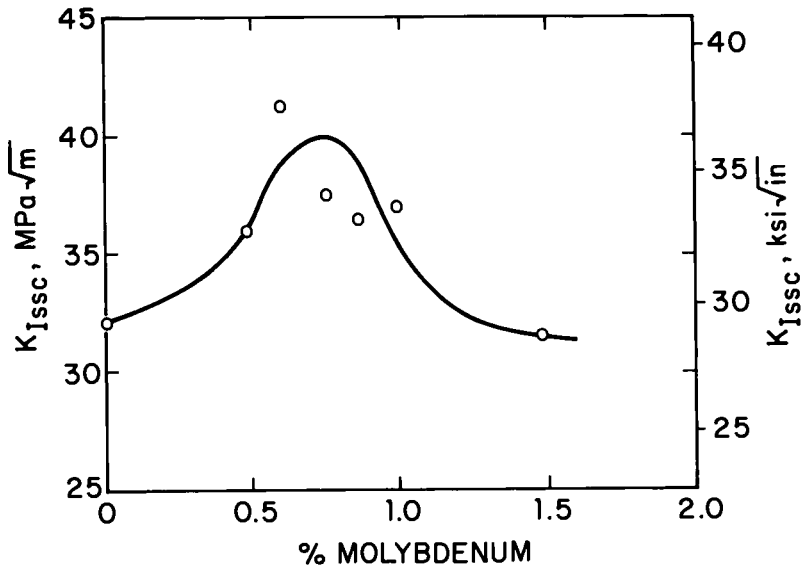


Fig. 7 Effect of molybdenum content on sulphide fracture toughness $K_{I_{SSC}}$ at a yield strength level of 760 MPa.

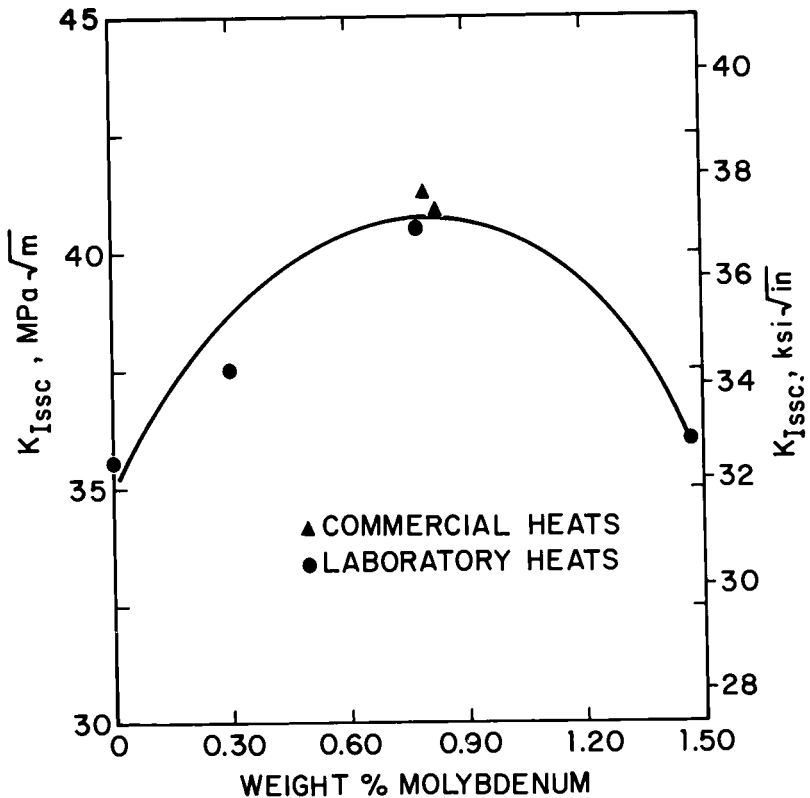


Fig. 8 Effect of molybdenum content on SSC resistance of a 0.20%C-1.5%Mn-Mo steel at a yield strength of 725 MPa.

Although not equal to quenched and tempered martensitic structures, fine bainitic structures also have good SSC resistance (Fletcher and Smith, 1978b). Therefore, SSC-resistance pipe can be produced without the necessity of water quenching. Bainitic steels for air-cooled pipe up to 19 mm wall thickness have been developed (Garber, 1982). To ensure a bainitic structure the hardenability of 0.75% Mo-0.035% Nb modified 4135 steel was increased by raising carbon to 0.40% and manganese to 1.0%. The beneficial effect of carbon on SSC resistance (Garber, Grobner and Sponseller, 1981) cancels the detrimental effect of the shift from martensitic to bainitic microstructure so that in the C-90 strength range the normalized and tempered bainitic steel has SSC resistance equivalent to the martensitic Mo-Nb modified 4135.

In order to insure the integrity of the joint, the couplings for casing have heavier wall thickness than the casing itself. Therefore, increased hardenability is required to obtain the SSC-resistance quenched and tempered martensitic structure in the couplings. SSC-resistant, water quenched C-90 couplings, with wall thickness up to 63 mm can be produced by adding 0.5% nickel to the Mn-Mo steel or 1.0% nickel to the Cr-Mo steel (Sponseller, Garber and Cox, 1982).

Extensive research indicates that by proper alloy design a materials solution to SSC in deep sour oil and gas wells is possible. Molybdenum is beneficial not just for hardenability but in its other more subtle effects as well. The observation of an optimal molybdenum content suggests an intrinsic beneficial chemical effect of molybdenum on SSC resistance.

STEELS FOR ELECTRIC RESISTANCE WELDED PIPE

Surges in oil and gas drilling activity such as that witnessed in 1978-81 have taxed the seamless pipe production capacity. As a result there is increased demand for electric resistance welded (ERW) pipe, particularly in the L-80 and N-80 casing and tubing grades (550 MPa minimum yield stress). These ERW tubulars are produced from hot band which is slit, formed, welded, and heat treated, either by normalizing or by quenching and tempering.

While 0.35% C-1.25% Mn steel is adequate for quenched and tempered N-80 ERW pipe up to 9 mm wall thickness, a new low alloy steel has been developed to provide for heavier walled quenched and tempered N-80 casing (Sponseller, Straatmann and Mincher, 1981). The approach taken was to lower carbon content to facilitate forming of the pipe and to make small additions of molybdenum to offset the decrease in hardenability. The resultant steel, 0.15/0.20% C-1.25% Mn-0.10/0.20% Mo, has less pearlite in the hot band and so has lower strength and higher ductility for the forming of the pipe. The strength of the quenched and tempered pipe is less sensitive to tempering temperature than that of conventional steel, a decided advantage in production. A trial heat with 0.21% C-1.17% Mn-0.15% Mo was successfully fabricated into 6 and 8 mm wall tubing and casing. The high strength of the finished pipe indicates that development of ERW S-95 and P-110 (665 and 760 MPa minimum yield strength, respectively) is possible.

Thinner walled ERW casing and tubing is often used in the as-normalized condition. However, the vanadium steel often used for normalized N-80 pipe is highly variable in its processing behavior, with poor yields on the slabbing mill, shattering of slit edges, cracking during pipe forming, and cracking after welding. It is common to anneal and pickle the hot band, diminishing some of these problems but adding to the steel cost. Research has identified a new Mn-Mo composition avoiding these processing problems (Sponseller, Straatmann and Mincher, 1981). The new Mn-Mo steel contains nominally 0.30% C-1.40% Mn-0.20% Mo and has a ferritic/bainitic microstructure meeting N-80 properties in the as-normalized condition. The strength of this steel is relatively insensitive to the variations in wall thickness between the tube body and

upset ends. Results of one particular commercial trial, shown in Fig. 9 demonstrate little variation in yield and tensile strengths over a wide range of normalizing temperatures. The new steel has gained rapid commercial acceptance because of its trouble-free fabrication. Numerous pipe makers report fabricating the new steel from as-rolled hot band without the necessity of prior annealing and pickling.

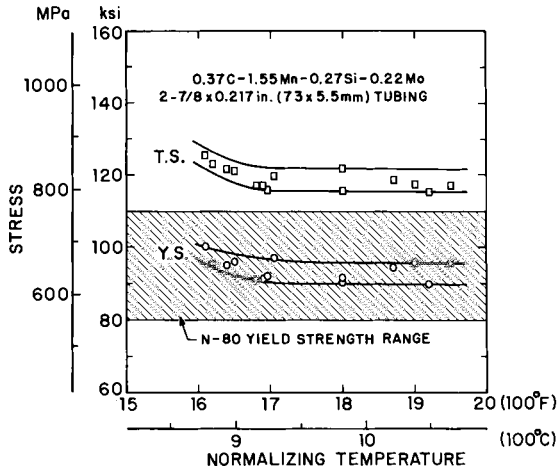


Fig. 9 Effect of normalizing temperature on yield and tensile strengths of commercially produced Mn-Mo ERW tubing.

RAIL STEELS

Rail used in heavy haul service, such as ore or coal hauling, is subject to high loads and abrasive wear. Many studies, confirmed by years of practical experience, have demonstrated that a finer pearlite microstructure in rails provides higher strength and greater wear resistance. Fine pearlite in rail steels may be achieved by heat treating, alloying, or both.

Research has shown that by properly balancing manganese, chromium, and molybdenum in high carbon rail steel, it is possible to produce a rail with both high strength and good weldability (Fletcher and Smith, 1978c). Molybdenum lowers the temperature of pearlite formation, resulting in finer pearlite. Manganese and chromium have a similar effect but at higher additions these elements degrade weldability.

As-rolled Cr-Mo rails, containing nominally 0.75% C-0.6% Mn-0.6% Cr-0.2% Mo, exhibit hardnesses in the range 321-388 HBN. These rails can be welded without pre- or post-weld heating without significant martensite formation. Such rails have been used in the Pilbara iron ore region of Western Australia and tested extensively in test tracks in the United States, and are now finding increasing use in revenue service throughout North America. Rail life in curves is increased by 60 to 100% through the use of Cr-Mo steel rails as is seen from the data in Fig. 10 comparing percent head loss of standard carbon rail with that of Cr-Mo rail as a function of tons of gross traffic. The rails also have a 30% higher fatigue strength without a sacrifice in fracture toughness relative to the standard rail steel chemistry (Park and Fletcher, 1982).

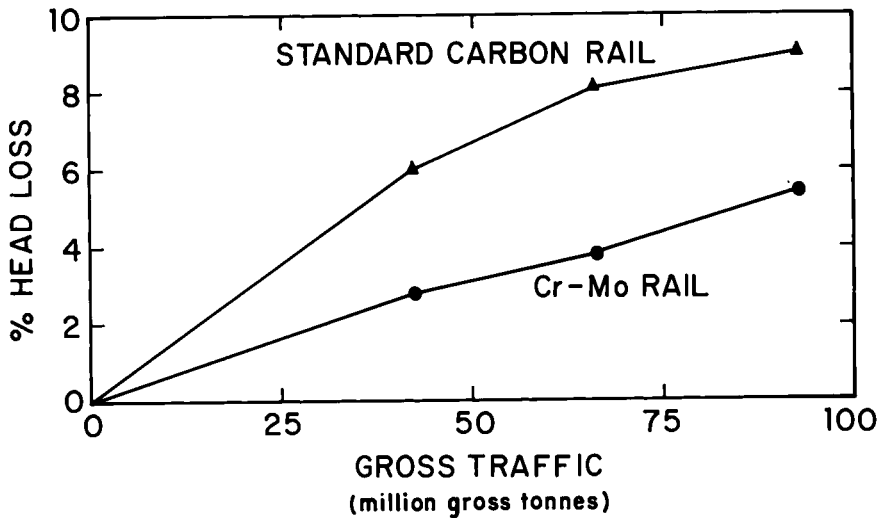


Fig. 10 Comparative performance of rails in test curves at Mt. Newman Mining Company, Australia (Curcio, 1978).

MICROALLOYED HSLA STEELS

Molybdenum has played a significant role in the development of microalloyed HSLA steels for many years. The Mn-Mo-Nb line pipe steels are typical of such developments (Cryderman and co-workers, 1972). Molybdenum contributes to strength through a) alteration of microstructures produced from the decomposition of austenite, and b) enhancement of the precipitation hardening obtained from microalloying elements. This second contribution is supported by a number of recent observations. As shown in Fig. 11, additions of molybdenum to a niobium-containing steel result in a substantial strength increase even though the microstructure consists primarily of ferrite and pearlite. Figure 12 shows the results of an analysis of the contributions to tensile strength from various mechanisms where intercritical hot rolling is employed. As can be seen, the precipitation hardening contribution obtained from Mo-Nb-V steels is higher than that achieved for combined niobium and vanadium additions alone.

The enhancement of precipitation hardening by molybdenum is the result of its effect on the kinetics of carbonitride precipitation in austenite. Figures 13 and 14 demonstrate that molybdenum retards precipitation in both vanadium and niobium microalloyed steels (Bacroix, Akben and Jones, 1981). An addition of 0.3% molybdenum reduces the precipitation of niobium by a factor of about two (Fig. 13) and vanadium by about a factor of five (Fig. 14). Retarding precipitation in austenite increases the potential for precipitation hardening in ferrite. Recent STEM analysis has shown that the precipitates formed in HSLA steels often contain more than one of the microalloying elements. As shown in Fig. 15, niobium, vanadium, and molybdenum have been identified in a single particle. Additional research is needed to correlate this phenomenon with the kinetics of precipitation and to determine whether it affects coherency strains when precipitation occurs in ferrite.

Taking advantage of the aforementioned mechanisms, an economical molybdenum-containing X70 line pipe steel has been developed. As reported in Table 3, an excellent strength/toughness balance can be obtained for this molybdenum-containing control rolled ferritic/pearlitic steel.

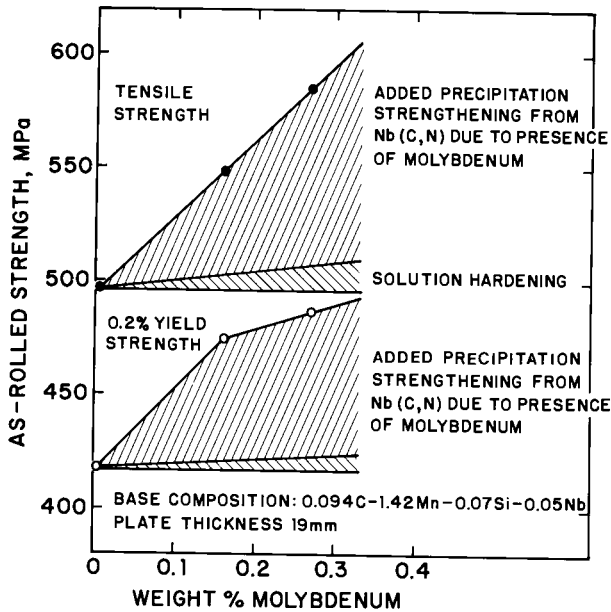


Fig. 11 Effect of molybdenum on yield strength and tensile strength resulting from both solid solution strengthening and precipitation strengthening. (All data corrected to an ASTM grain size No. 12) (Lander, Morrow and Coldren, 1981).

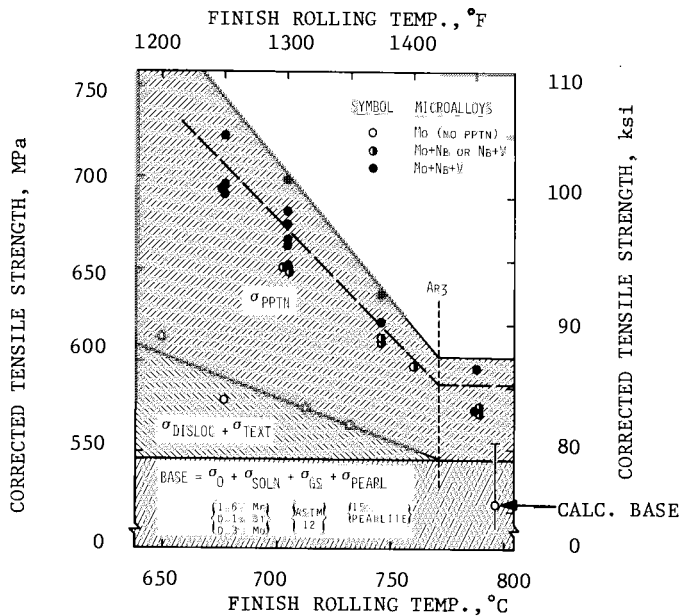


Fig. 12 Corrected tensile strength vs. finish rolling temperature for 19 mm (0.75 in) plates controlled rolled with 1040°C/900°C (1900°F/1650°F) hold. Contributions from precipitation strengthening (σ_{pptn}) and from dislocation substructure and texture strengthening ($\sigma_{disloc} + \sigma_{text}$) are indicated by shaded areas (Coldren, 1981).

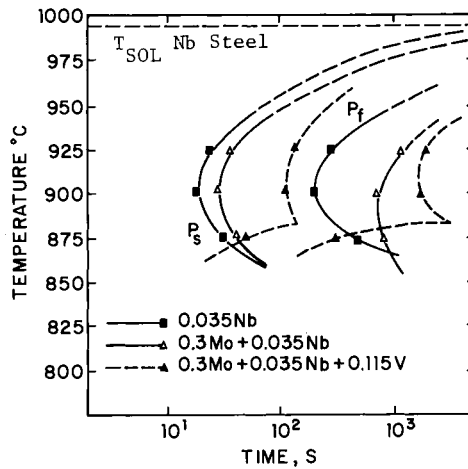


Fig. 13 Dynamic CTT curves for niobium containing steels.

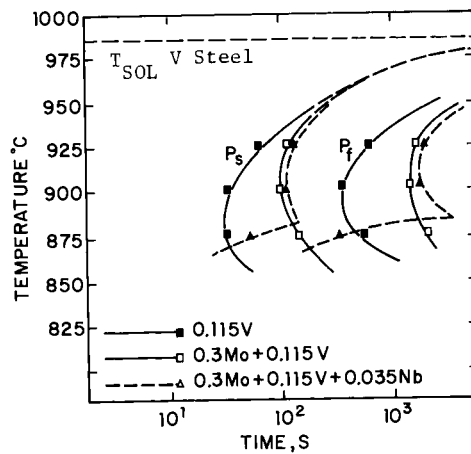


Fig. 14 Dynamic CTT curves for vanadium containing steels.

It is also reasonable to expect the trend of many years toward higher strength steels to continue, thereby permitting larger, higher pressure gas lines to transmit gas more efficiently. Within the next five to ten years, construction of major pipelines requiring X75 or even X80 strength levels is likely. Anticipating this need, research has identified compositions extending the present HSLA steel technology to these higher strengths. The participation of molybdenum in commercial production of these steels is assured as can be seen from the data shown in Fig. 16.

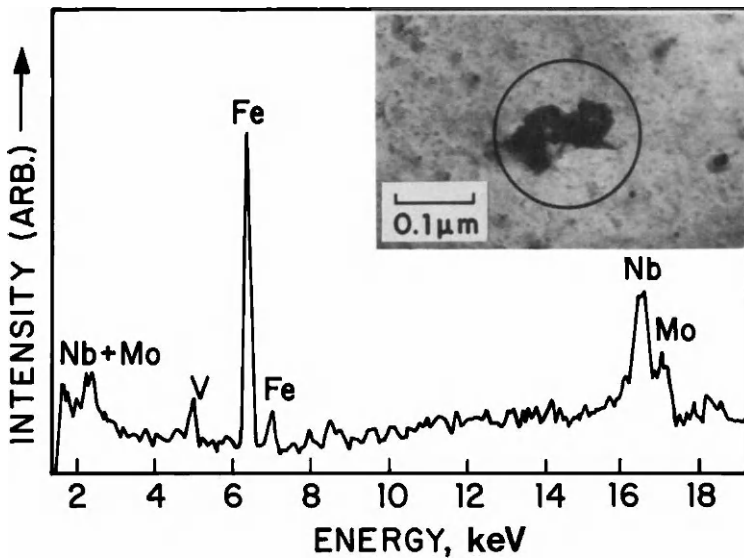


Fig. 15 X-Ray energy spectra from precipitates in a Mo-Nb-V steel (Coldren, Biss and Oakwood, 1981).

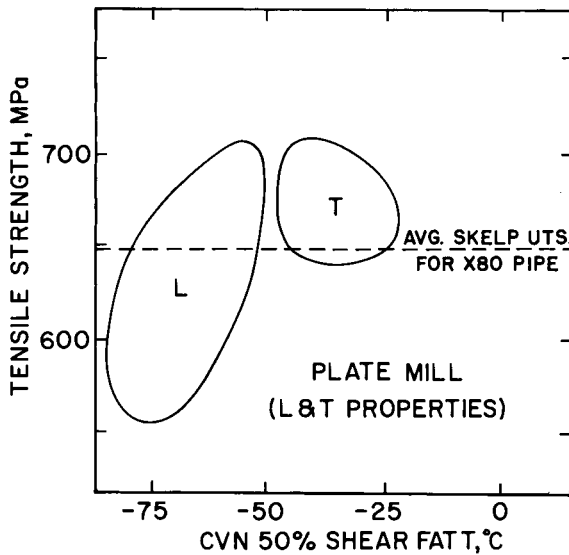


Fig. 16 Strength/toughness properties of controlled-rolled 19 mm plate of candidate steel for X80 line pipe application. Nominal composition: 0.10% Si-0.30% Mo-0.055% Nb-0.075% V-0.02% Si-0.005% N-0.02% Al-0.003% S-0.010% P. Rolled at 1375°C. L-longitudinal specimens; T-transverse specimens (Lander, Morrow and Coldren, 1981).

TABLE 3 X-70 LINE PIPE STEELS

Composition, Wt %						
C	Mn	Si	Mo	Nb	Ti	Al
0.07/0.09	1.4/1.6	0.20/0.35	0.13/0.17	0.03/0.05	0.015/0.025	0.02/0.05

Typical Transverse Properties				Charpy V-Notch Impact	
Strength, MPa (ksi)			Energy Absorbed, J (ft-lb)		50% Shear
0.2% Y.S.	1.5% Y.S.	U.T.S.	CV 100	at -20°C (-4°F)	FATT, °C (°F)
525 (76.2)	552 (80.1)	619 (89.9)	99 (73)	107 (79)	-85 (-125)

CAST IRONS

Molybdenum increases the strength of gray iron by refining the pearlite structure. So powerful is molybdenum in depressing the pearlite transformation temperature and thereby decreasing the interlamellar spacing that only a small addition is required. A small addition of molybdenum has little effect on castability and chilling tendency of the base iron and so creates no special problems for direct ladle addition. As shown in Table 4, molybdenum by itself or in combination with other elements is particularly effective in raising the elevated temperature strength of the pearlitic irons. As shown in Fig. 17, the improvements of creep and stress-rupture properties resulting from molybdenum additions are even greater than one might expect on the basis of the observed tensile strength improvements.

TABLE 4 540°C (1000°F) AND ROOM-TEMPERATURE STRENGTH OF GRAY CAST IRONS

Irons	Room-Temp.	540°C	Tensile
	Tensile Strength	(1000°F) Tensile Strength	Strength Ratio
	MPa (ksi)	MPa (ksi)	(540°C/20°C)

Gundlach (1978) Study

Base Iron (3.4% C-1.7% Si-0.6% Mn)	267 (38.7)	148 (21.5)	56
" " + 0.5% Cr-0.6% Ni-0.6% Cu	302 (43.8)	184 (26.7)	61
" " + 0.3% Cr-1.0% Ni-0.9% Cu-0.3% Mo	324 (47.0)	207 (30.0)	64
" " + 0.4% Mo-0.08% Sn	306 (44.4)	204 (29.6)	67
" " + 0.5% Cr-0.4% Mo	331 (48.0)	223 (32.3)	67

Kattus and McPherson (1959) Study

Base Iron (3.3% C-1.7% Si-0.7% Mn)	294 (42.7)	170 (24.7)	58
" " + 0.7% Mo	329 (47.7)	228 (33.1)	69
" " + 0.6% Cr-0.8% Mo	434 (63.0)	309 (44.8)	71

The benefits of improved creep resistance by molybdenum have been clearly shown through constrained thermal fatigue tests (Gundlach, 1979). The specimens were heated and cooled under constrained conditions such that their own thermal expansion generated high compressive stresses. In addition, the specimens were held at temperature for a period of time during each cycle to allow stress relaxation and creep to occur under sustained thermal stress. The selected test conditions simulate many severe thermal stress applications such as cylinder heads where constant temperature gradients exist, and exhaust manifolds where the manifold

is heated while under constraint by the engine block. The test results showed that only molybdenum and vanadium make a significant contribution to thermal fatigue resistance. As shown in Fig. 18, the molybdenum effect was found to increase exponentially with molybdenum additions up to 0.75%. Although not as well documented, the vanadium effect is believed to be similar in strength to the molybdenum effect. However, the total vanadium addition is limited to less than 0.15-0.30% in practice because of the strong tendency of vanadium to promote "chill" and intercellular carbides.

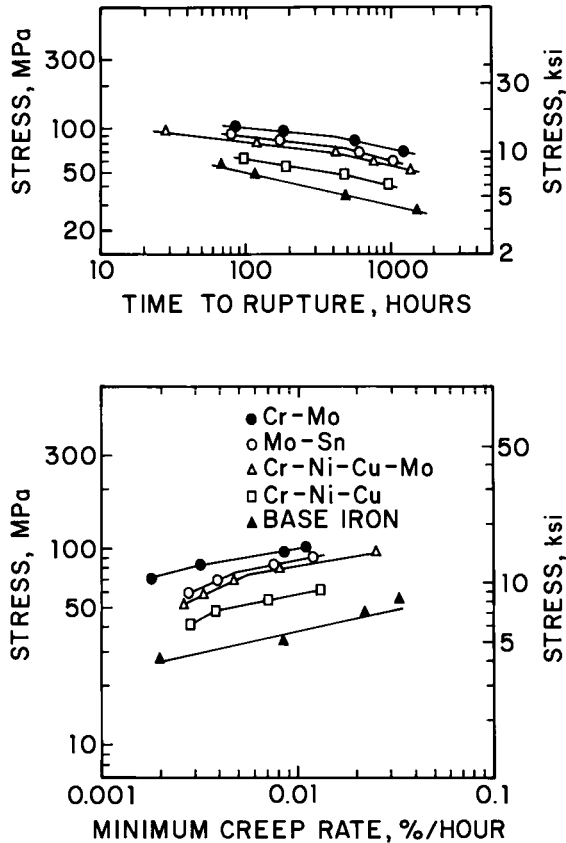


Fig. 17 Stress-rupture and creep properties of gray cast irons tested at 540°C (1000°F) (Gundlach, 1978).

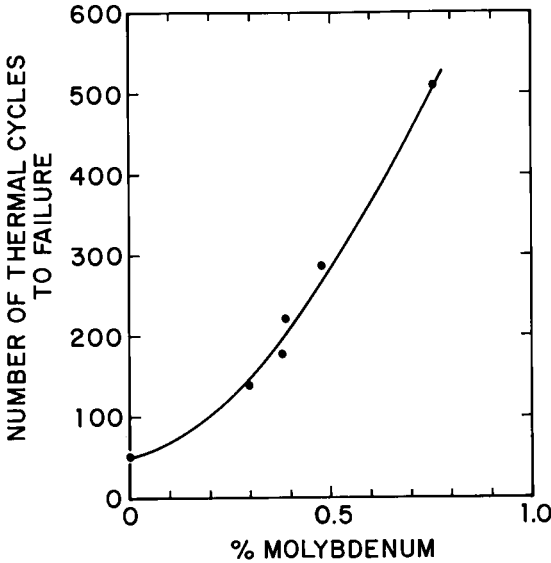


Fig. 18 Correlation of thermal fatigue life with molybdenum content in gray irons cycled between 100°C and 540°C.

NODULAR IRONS

Molybdenum also enhances the elevated temperature tensile, creep, and stress-rupture strengths of nodular irons. In recent years attention has been focused on development of high silicon (4-5%) irons for elevated temperature applications. Silicon and molybdenum are complementary alloys with silicon providing oxidation resistance and raising the ferrite-to-austenite transformation temperature (A_1) while molybdenum increases the elevated temperature strength and creep resistance, as shown in Fig. 19. Constrained thermal cycling tests of ferritic Si-Mo nodular iron demonstrate a strong beneficial effect of molybdenum, as shown in Table 5. It is interesting to note that molybdenum additions to Type D5S Ni Resist, an austenitic iron, have similar effects.

TABLE 5 RESULTS OF CONSTRAINED THERMAL FATIGUE TEST (Janowak and co-workers 1981)

Cycled Between 200 and 650°C	Number of Cycles To Failure
<u>Ferritic Irons</u>	
Unalloyed (2.1% Si)	80
3.6% Si	173
3.6% Si-0.4% Mo	375
4.4% Si-0.2% Mo	209
4.4% Si-0.5% Mo	493
<u>Austenitic Irons</u>	
Type D5S	364
Type D5S + 0.9% Mo	566

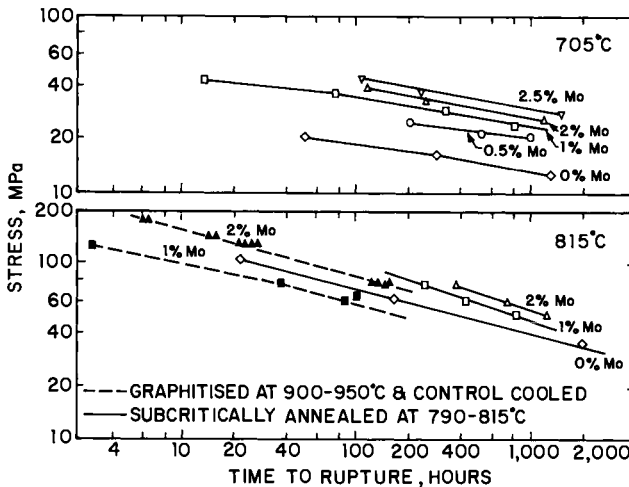
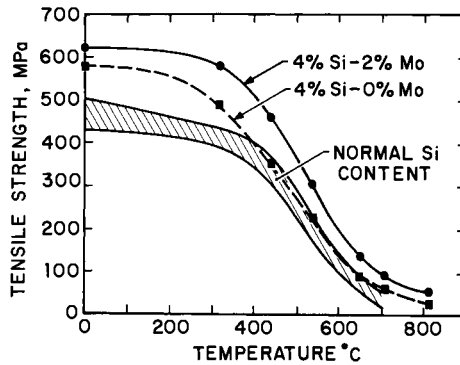


Fig. 19 Stress Rupture strength of 4% Si ferritic nodular-graphite irons (Fairhurst and Rohrig, 1979).

An exciting new class of nodular iron is being developed world wide, austempered nodular iron. Austempering is not new, but recent studies have provided new insight for the application of this process to nodular iron. As shown in Fig. 20, austempering can produce a unique microstructure consisting of acicular (bainitic) ferrite in austenite. The austenite is stabilized by high carbon content (2%) as the ferrite being formed rejects carbon into the austenite during isothermal transformation. The resulting structure can contain up to 40% austenite stable to -80°C or lower (Johansson, 1977). This structure provides a combination of tensile strength, elongation, and toughness far superior to that of quenched and tempered nodular irons, Fig. 21. These properties will permit nodular iron to be considered for more critical applications such as gears and crankshafts. Molybdenum is used to avoid pearlitic transformation during cooling to the austempering temperature without the necessity for major capital investment in quenching facilities. Manganese, while an effective hardenability agent, must be kept low (less than 0.3%) to

develop maximum elongation and toughness. Large additions of nickel or copper could supply the required hardenability, but nickel-molybdenum or copper-molybdenum combinations are more cost effective because of the synergistic effects of these elements on hardenability.

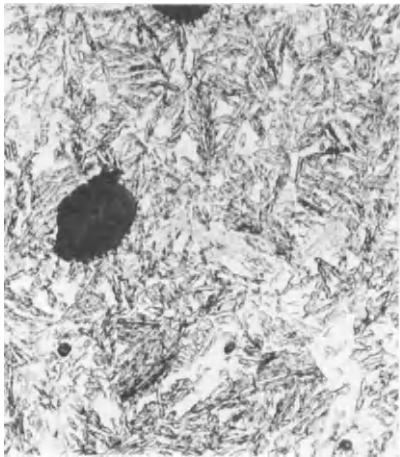


Fig. 20 Microstructure of nodular iron alloy austempered at 370°C for 128 minutes (magnification X500).

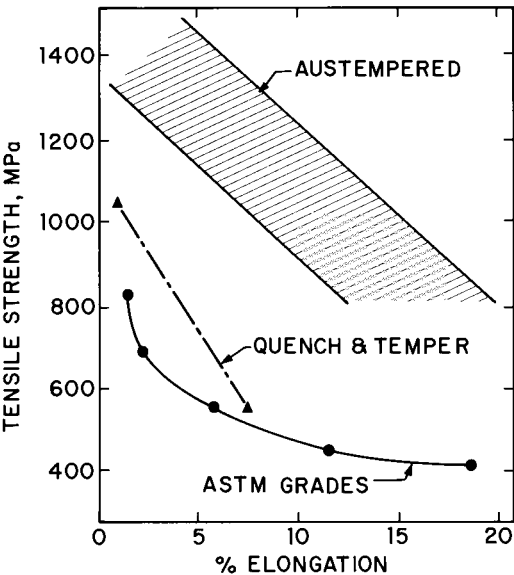


Fig. 21 Comparison of properties for austempered nodular irons with standard ASTM grades and Q&T nodular irons.

WHITE CAST IRONS

Molybdenum provides hardenability for high chromium irons and indefinite chill NiHard irons. In recent years there has been a trend toward replacement of NiHard with the high chromium irons where high wear resistance and toughness are required. Applications include crushers and mills for the mining industry and coal pulverizers for the electric power industry. These irons have also been used in rolls for both hot and cold rolling of steel with substantial improvements in roll life.

Research has focused on efforts to quantify the effects of various elements on the hardenability of the white irons. Molybdenum has a strong effect on delaying pearlitic transformation (Dodd, Gundlach and Morton, 1981). There is also a strong synergistic relation between molybdenum and nickel, manganese, or copper in their combined effect on hardenability; 0.5% molybdenum is usually necessary to realize substantial benefits from these other elements. In addition to delaying the pearlite transformation, these elements can also depress the martensitic transformation range. Alloy elements must be selected so as to avoid a very low M_s temperature with consequent large amounts of retained austenite that resist transformation even in protracted tempering. Molybdenum lowers the M_s temperature less strongly than the other elements and so permits higher hardnesses and greater abrasion resistance. This effect is especially important in heavy section castings that must be fully hardened and free of retained austenite. Retained austenite appears to be the cause of premature and catastrophic failures in heavy section castings subject to repeated impact loading, such as roller pulverizers. The most successful approach to this problem has been to limit the austenite formers, nickel and manganese, to 1% in combination with 1-1.5% molybdenum to achieve sufficient hardenability to avoid pearlite on air cooling from the austenitizing temperature.

SUMMARY

Molybdenum alloy technology is responsive to the emerging needs of industry and the world society. Through integration of the newest concepts of metallurgy and a long established understanding of the versatility of molybdenum, and by utilization of the most modern of production methods, materials of superior properties, reliability, and economy have been developed. This brief discussion has focused on a few of the many newer developments in the use of molybdenum in wrought constructional alloy steels and cast irons. Yet these applications account for only slightly over half of the total molybdenum consumption. Discussed elsewhere in this symposium are the contributions of molybdenum to corrosion resistance in stainless steels and to abrasion resistance in tool steels, hardfacing alloys, and carbides. After more than a half century of intensive research and development, molybdenum alloy technology is still growing rapidly, making molybdenum one of the most effective and versatile alloying elements of ferrous metallurgy.

ACKNOWLEDGEMENT

Although this paper is under a single authorship, in reality it could not be created without the excellent input and cooperation of the Climax Molybdenum Company Research and Metallurgical Development personnel; my appreciation for their contribution is acknowledged. My gratitude is extended to members of our R&D staff including A.P. Coldren, T.B. Cox, R.M. Davison, D.E. Diesburg, G.T. Eldis, F.B. Fletcher, R.B. Gundlach, T.G. Oakwood and my special thanks are expressed to Dr. H.N. Lander.

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The Use of Vanadium in Low Alloy Structural Steels

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ABSTRACT

The various mechanisms by which vanadium and other microalloying elements affect the microstructure and hence strength, toughness and weld properties of HSLA steels are reviewed. The use of vanadium in steels currently produced is summarised and an indication is given of how vanadium could be used in HSLA steels if other microalloying elements were in short supply.

KEYWORDS

Vanadium; HSLA steels; microstructural effects; mechanical properties; welding characteristics.

GENERAL EFFECTS OF MICROALLOYING ELEMENTS ON MICROSTRUCTURE AND PROPERTIES

For many years certain alloys which form fine precipitates of carbides and nitrides have been used to increase the strength of carbon structural steels. These precipitates can be present in austenite or ferrite and the role of any precipitate will depend on the temperature at which it forms in relation to the A_{r3} temperature. When they are present in austenite they contribute to grain refinement and hence strength, and low temperature toughness. This is because they either prevent grain growth of austenite, as in normalised steels, or they prevent recrystallisation of austenite grains which on deformation form pancake grains, as in control rolled steels. (The effect of these alloys on recrystallisation has also been attributed to their presence in solid solution causing solute drag). In both normalised and control rolled steels the fine austenite grains transform to fine ferrite grains which in the case of control rolled steels have a grain diameter about half that of the minor axes of the pancaked grains. Fine precipitates formed in ferrite contribute to strength directly although they tend to reduce low temperature toughness.

Most HSLA steels are produced as aluminium treated silicon killed steels and the effect of aluminium on the alloy nitrogen balance has to be taken into account. In the U.S.A. some semi-killed steels are still produced where the

effect of nitrogen on ageing has to be considered. With increasing use of continuous casting however the importance of semi-killed steels is decreasing.

In the last ten years it has also been found that the presence of the micro-alloys in solid solution in austenite can influence the transformation to ferrite and pearlite. Low carbon bainite structures (sometimes called acicular ferrite) or polygonal ferrite with islands of martensite can be produced. Both these microstructures enable the steels to extensively work harden with relatively small deformations and this can be used to produce high strength line-pipe and cold pressings, such as automobile wheels, where the steels are subjected to cold work during fabrication.

Microalloy elements in solid solution in austenite can also lead to the presence of bainite in weld metal and the heat affected zones of welded structures and these can have detrimental effects on the toughness of welded joints.

THE SPECIFIC ROLE OF VANADIUM ON MICROSTRUCTURE AND PROPERTIES

Plates, Strip and Sections

Vanadium can influence the microstructure and properties of steels by most of the mechanisms mentioned above. Its precise role in any given steel however will depend on:

- a) The level of vanadium
- b) The levels of carbon and nitrogen
- c) The amounts of other microalloys present which form carbides and nitrides
- d) The amount of other alloy elements present such as Mn which lower the A_{r3} temperature
- e) The rate at which the steel is cooled after rolling or heat treatment.

The various mechanisms by which vanadium affects steel microstructures are illustrated in Fig. 1. The role of the precipitate depends on the temperature of precipitation in relation to the transformation temperature. In the absence of other microalloy elements the effect of vanadium will be determined by the carbon and nitrogen levels and the rate at which the steel cools after rolling. If the solubility product $[V][N]$ is sufficiently high VN (vanadium nitride) will precipitate in austenite while the steel is being rolled. Under equilibrium conditions this will occur at a very high temperature as can be seen from the data given in Fig. 2 for a V-N steel of commercial composition. VN if present when the steel is austenitic, will prevent grain growth and if the steel is deformed after precipitation it will prevent recrystallisation.

The most important use of VN to control grain size is found in normalised aluminium treated silicon killed steels where high strengths are required, especially in thick plates. In these steels the nitrogen content is increased above the normal levels of BOF or BOH steels to about 0.015% and the vanadium level is about 0.15%. During normalising of such steels the VN and AlN formed in austenite do not redissolve at the normalising temperature and therefore prevent austenite grain growth, and on cooling a fine ferrite grain size results. In semi-killed steels vanadium will cause some grain refinement of austenite during rolling.

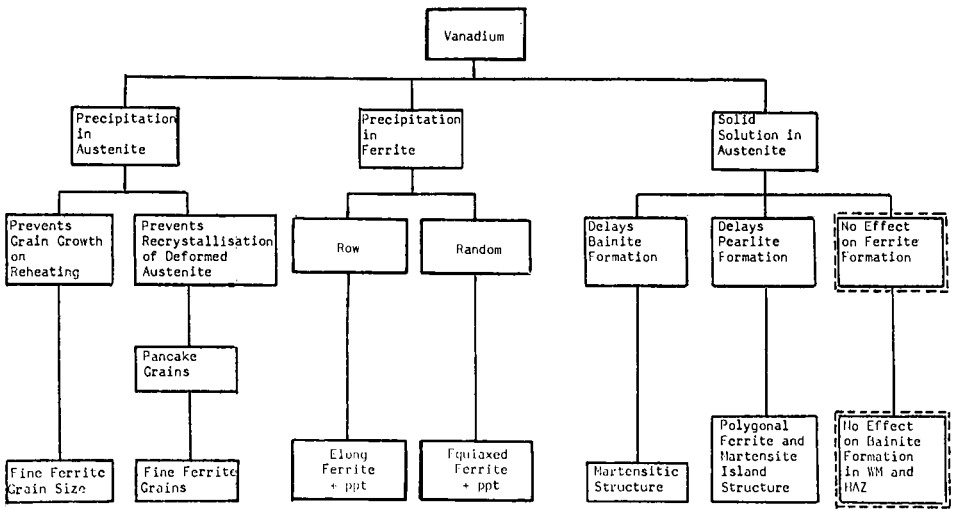


Fig.1. The role of vanadium as a microalloying element

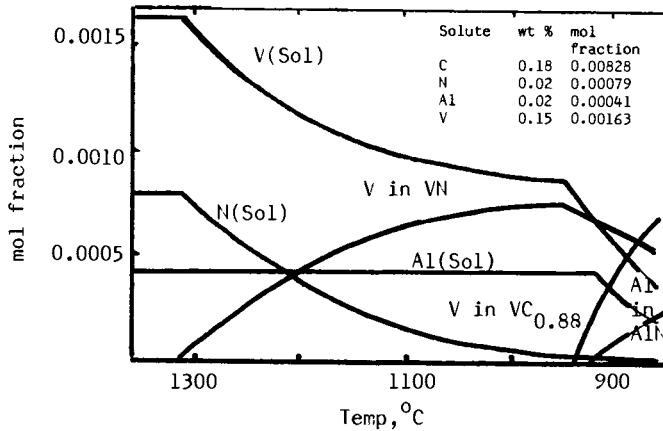


Fig. 2. Temperature dependence of solute concentration in solution and in compounds for a V-N normalised steel

VN has a potential use in control rolled steels and White and Owen (1980) have shown that in steels containing 0.2% V and 0.02% N, VN precipitates in austenite and prevents recrystallisation when deformed under compression. (Further it has been shown (Sage 1981) that in a ferrite - martensite island steel containing 0.45%V and 0.007%N, discussed later, VN precipitates in austenite and prevents recrystallisation during control rolling.)

In ferrite-pearlite steels however, VN precipitates are unlikely to be used if

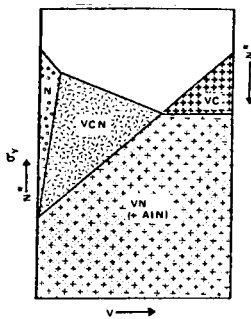
niobium is available because a) VN precipitates at a lower temperature than NbC and it would be expected that control rolling would have to be carried out within a narrower temperature range with heavier drafts involving higher mill loads, b) at the V and N levels required it would (under normal circumstances) be economically unattractive. (On the other hand VC and VN go into solution at a lower temperature than NbC and lower reheating temperatures can therefore be used for vanadium steels).

Vanadium plays a major role in HSLA steels as a ferrite precipitation strengthener. VC under equilibrium conditions usually forms below the Ar_3 temperature and in practice invariably forms as VCN because if the solubility product $[V][N]$ is too low for the formation of VN in austenite, or if the cooling rate is too high, VN does not precipitate in austenite but only on transformation, and as VN and VC are isomorphous the precipitate occurs as VCN which may contain 0 to 100% C or N, depending on the C and N contents and cooling rate.

In practice the kinetics of precipitation are such that in BOF or BOH steels having nitrogen levels of the order of 0.007%, not all the vanadium will precipitate even though there is sufficient carbon in the steel. The amount of vanadium precipitating can however be increased by raising the nitrogen content as has been shown for example by Sage (1976) for reinforcing bar steels and Korchynsky and Stuart (1970) for hot rolled strip steel. If however, the added nitrogen is too high VN will precipitate in austenite and a reduction in ferrite precipitation and strength will result from the increased nitrogen content as has also been shown by Sage (1977). The use of nitrogen to increase the strength of a structural steel is more important for thin plates and strip where the cooling rate is higher and the suppression of precipitation in austenite is greater.

The precipitates of VCN occur in normalised steels where the vanadium not precipitated as VN during rolling, precipitates as VCN, goes into solution at the normalising temperature and reprecipitates on cooling. VCN precipitates in ferrite are also important in hot rolled and control rolled steels. In control rolled Nb steels where greater strength is required than can be achieved with grain refinement, V is added to give precipitation strengthening - V being more effective for precipitation strengthening than Nb because Nb mostly precipitates at higher temperatures where the steel is austenitic and such precipitates grow to be too coarse to affect strength. In steels where low temperature toughness is not so important and where a fine grain size is not required hot rolled vanadium steels without niobium which rely mostly on precipitation for their increased strength are found to be more economic (because the restriction in output by low temperature rolling is not involved). In some mills when thin plates are rolled the finish rolling temperature is naturally low and control rolling is virtually achieved and vanadium steels without niobium can be used to produce a fine grain size.

At lower carbon contents, and in thinner sections which cool faster after rolling the precipitation of vanadium may not go to completion and some vanadium will remain in solution. In such cases the proportion of vanadium precipitated in ferrite and hence its efficiency as a precipitation strengthener can be increased by raising the nitrogen content above that normally found in BOF or BOH steel. On the other hand, raising the nitrogen above a certain maximum will cause vanadium nitride to precipitate in austenite and so reduce the volume fraction in ferrite and hence lower the strength of the steel. The effect of vanadium and nitrogen on the strength of steel is illustrated in Fig. 3.



* Increases in nitrogen at low vanadium levels increase yield strength but at high vanadium levels decrease yield strength.

Fig. 3. Yield strength vs vanadium content for a 0.12%C, 1.4%Mn, V-N steel

The precipitation of VN in austenite can be suppressed by accelerated cooling and this can result in increased precipitation of nitrogen bearing VCN precipitate in ferrite if the accelerated cooling is applied through the temperature range 800 to 500/600°C. This delay in precipitation is achieved in rolling of strip in which the accelerated cooling applied to the steel to cool it for coiling has the effect of suppressing precipitates of VN in austenite and increasing the precipitation of VCN in ferrite during coiling. The effect of nitrogen on the strength of strip steel is illustrated in Fig. 4. The OLAC process recently developed in Japan for plates up to 38 mm thickness involves the same principle.

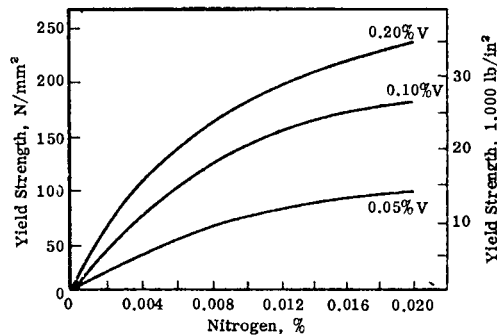


Fig. 4. Yield strength increment as a function of vanadium and nitrogen contents (Korchynsky and Stuart, 1970)

Nitrogen, in addition to its effect on the amount of vanadium precipitating in ferrite, can also indirectly affect the form of the precipitate. This may in turn, affect the condition of the ferrite, which can affect the toughness of the steel. Sage (1979) has shown that in steels with relatively high V and N contents, but not sufficiently high to cause precipitation of VN in austenite, coarse rows of interphase precipitates can form on transformation, whereas in steels with low nitrogen contents the precipitates occur as light rows or as random precipitates. This work has further shown that there is evidence to suggest that the heavy row precipitates prevent recrystallisation of ferrite during subsequent rolling whereas in steel with random precipitates

further rolling produces recrystallised ferrite which has greater low temperature toughness. In these circumstances therefore, a high nitrogen content may be beneficial to toughness. The advantages in the use of nitrogen to increase strength or toughness of a vanadium steel which is welded has to be weighed against the adverse effect which a high nitrogen content can have on other weld properties discussed below.

The ferrite precipitation strengthening of vanadium is also influenced by the presence of other microalloying elements particularly Al, Ti and Nb. These elements form nitrides at generally higher temperatures than vanadium. In the case of Ti as little as 0.03% can combine with all the nitrogen normally present in a B0F steel and the presence of Ti can effectively force all the vanadium to precipitate as VC in ferrite and reduce the potential for precipitation in austenite.

Precipitates of Nb C(N) formed at high temperatures in austenite have been shown to contain V and the presence of Nb in V steel can therefore tend to reduce the precipitation strengthening effect of V in ferrite.

The role of vanadium in HSLA steels is also influenced by other alloys present particularly manganese. Manganese is reported to increase the solubility of VN in austenite (Irvine, Pickering and Gladman, 1967) thus increasing the volume of precipitate which can form on transformation to ferrite. It also lowers the A_{r3} temperature thereby refining the particle size of precipitates. A high manganese content therefore tends to increase the effectiveness of vanadium precipitation strengthening.

Precipitates of vanadium carbonitride are also employed in the higher strength structural steels which are supplied in the quenched and tempered condition. These steels often contain additions of chromium with molybdenum or boron which increase hardenability (ensuring a martensitic structure on quenching) and additions of vanadium, which also contribute to the hardenability, on quenching remain in solution to precipitate during tempering giving secondary hardening and thus contributing to the high strength of these steels.

It was mentioned in the introduction that some HSLA steels are still made as semi-killed steels and do not contain aluminium. In such steels more nitrogen will be available to form nitrides with other microalloying elements, particularly vanadium and providing that the VN solubility product is not too high, precipitation strengthening can result from vanadium additions. A semi-killed vanadium steel will have less tendency to strain ageing than a semi-killed steel not containing vanadium.

The effect of vanadium in solid solution in austenite in delaying bainite and pearlite formation has only been realised in recent years. It has been shown by Sage (1981) and Cochrane and Morrison (1981) that the delay in pearlite formation in low carbon high manganese steels produced by molybdenum plus niobium in rolled plate can also be produced by 0.45% vanadium and this can be used to produce structures consisting of islands of martensite in precipitation strengthened polygonal ferrite. The CCT curves for this type of steel are shown in Fig. 5 and typical microstructures are shown in Fig. 6. Such structures can also be produced by higher manganese contents so that it would probably be more correct to say that vanadium like molybdenum can be used to partly replace manganese in such steels. The vanadium steels are however easier to produce than the high manganese steels. Rashid (1978) has shown that similar structures can be produced by intercritically annealing (0.1%V) strip steel followed by accelerated cooling. Steels with these structures have a high co-efficient of work hardening and the plate can be

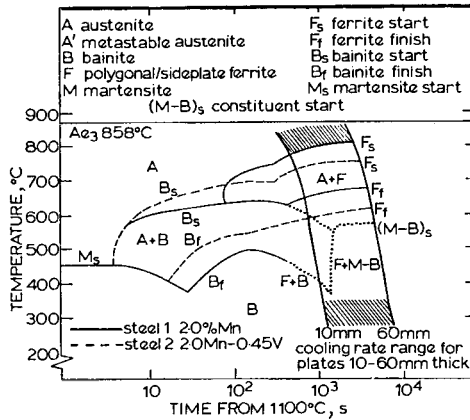


Fig. 5. CCT diagram showing effect of 0.45% V on transformation behaviour of 2.0% Mn steel

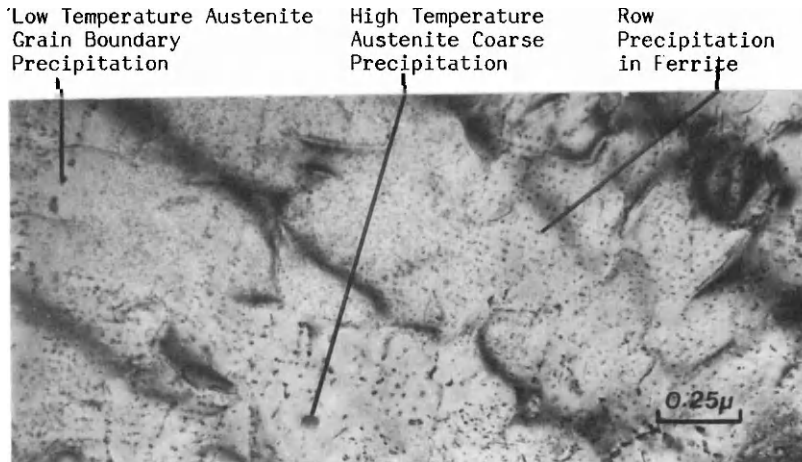


Fig. 6 Electron micrograph showing three forms of precipitate in 20 mm plate used for production of pipe by the UOE and spiral processes, and the strip for the production of cold pressings such as automobile wheels and bumpers.

Vanadium however unlike molybdenum and niobium appears not to delay ferrite formation and vanadium steels are therefore less likely to contain bainite or acicular ferrite and are therefore less prone to embrittlement in higher carbon steel. This is particularly so for rolled sections where vanadium steels are for this reason preferred. It also means that vanadium steels are less prone to weld metal HAZ embrittlement; this is discussed in more detail below.

Welded Microstructures

Thousands of tons of HSLA steel plates and sections are used in the as-rolled or heat treated conditions. An increasing tonnage, however, is also welded. The composition of the as-cast structure of the weld metal diluted by the parent metal controls the properties of the weld, and the heating of the metal during welding can change the microstructure and properties of the heat affected zone (HAZ).

In many engineering structures, especially those operating at low temperatures, the toughness of the weld metal and/or the HAZ is a critical factor in the selection of a steel and not all HSLA steels can be used economically in welded structures. The importance of the weld and HAZ properties depends on the application and whether the steels are only shop welded or welded on site. In shop welding conditions can be more carefully controlled and sophisticated techniques involving controlled cooling can be applied more easily than on site welding, where such control is more difficult and expensive. Indeed for many structures such as bridges and penstocks site joints today are invariably bolted. In other structures such as pipelines and pressure vessels, however, site welding is essential.

Microalloying elements are important in connection with three properties of welds, i.e. resistance to cold cracking in the HAZ, toughness of the weld metal and toughness of the HAZ.

Cold Cracking of HAZ

Cold cracking usually occurs in the HAZ and is due to the rejection of hydrogen on the formation of martensite which has lower solubility for hydrogen than austenite from which it is formed. The use of vacuum melted steel, preheating, or the use of low hydrogen electrodes invariably lowers the hydrogen to a level which eliminates this problem, but where these procedures are not economically feasible the composition of the steel has to be modified to avoid the presence of martensite in the HAZ. Various formulae such as the International Welding Institute Equation have been adopted to give a maximum carbon equivalent considered allowable to avoid this phenomenon.

These formulae however are inapplicable for steels with carbon contents below 0.15% and new methods of assessing the susceptibility of a steel to cold cracking in HAZ are being established. Vanadium, because of the hardenability effect (suppression of bainite formation) is usually included in these formulae. Nitrogen is also a strong martensite former and thereby can contribute to cold cracking at all levels of carbon. There are cases where some restrictions are made on the use of vanadium-nitrogen steels for welding but providing sufficient preheat and/or post heat is applied, cold cracking in any steel can always be avoided at a cost.

Weld Metal Toughness

The cast structure of the weld metal in arc welds of most carbon structural steels consists of a form of bainite (sometimes referred to as acicular ferrite) which may be surrounded by ferrite in the grain boundaries, and ferrite aligned with martensite/austenite constituent. Vanadium, which is a ferrite stabiliser and suppresses pearlite formation, has little effect on the grain boundary ferrite or toughness of the weld metal, (unlike niobium which suppresses ferrite formation and increases the volume of the bainite or acicular ferrite structure). Further the acicular ferrite structure found in welds of vanadium steel tend to be finer and the cementite laths are

irregular whereas in niobium steel, possibly through precipitation of carbide in the austenite grain boundaries, coarse carbide plates tend to be formed in the acicular structure which traverse the whole grains, producing what is sometimes called side plate structure which tends to embrittle the weld metal. These embrittling microstructures, in niobium steels can often be avoided by using appropriate fluxes and filler metal, but such precautions are less important with vanadium steels.

HAZ Toughness

The toughness of HAZ's is affected by a coarse grain size, interstitial nitrogen or precipitates of carbonitride. Coarsened grains occur in all steels except those containing titanium (because TiN does not dissolve even at high temperatures whereas precipitates of vanadium and niobium do) and vanadium steels are no more susceptible to embrittlement from this coarse grain size than other microalloyed steels not containing titanium. Interstitial nitrogen arises from dissolution of nitrides in the steel which under the rapid cooling conditions existing in the HAZ of many welds do not have time to recombine. Obviously steels with added nitrogen are more susceptible than lower nitrogen steels, vanadium steels of normal nitrogen content are however no more susceptible than other microalloyed steels except those containing titanium and the problem can be avoided in high nitrogen steel if the HAZ's are slowly cooled. Precipitation of coarse vanadium carbonitrides may occur during welding and cause some embrittlement, but this effect of vanadium is probably confined to higher carbon steels (greater than 0.15%). It is probably for this reason that a limit of 0.08/0.10% is sometimes specified for vanadium in structural steels. The effect of carbon content on this phenomenon is at present under investigation, but it has already been shown (Boothby and Hart, 1981) that adequate HAZ toughness for at least some grades of Arctic line pipe can be achieved in 0.06%C steels with 0.45%V.

CURRENT USE OF VANADIUM IN STRUCTURAL STEELS

Vanadium is used in many different types of HSLA steels and typical examples of each are given below.

Hot Rolled Steels

Hot rolled vanadium steels have been produced for reinforcing bars, plates and sections for over 20 years from BOH and BOF steels with normal nitrogen contents (0.005-0.007%).

Vanadium is widely used in hot rolled weldable rebar sometimes with added nitrogen where strength is provided from precipitation of VCN in ferrite. Vanadium finds wider applications than niobium for this product because the properties can be achieved regardless of finishing temperatures, and are unaffected by interruptions in production. Where continuous casting is employed its use is unaffected by casting machine design.

Where plates of high strength without special low temperature toughness are required these steels can be produced by rolling with normal finishing temperatures (over 900°C) as the strength can be produced almost entirely by precipitation of VCN in ferrite. A higher nitrogen content is sometimes used in such steels to ensure maximum precipitation and to provide some grain refinement (by inhibiting grain growth of austenite). Compositions and properties available for plates to the ASTM specification 572 grades 42 to 65 are given in Table 1.

TABLE 1. Chemical Composition and Properties for
ASTM A572 Specification

ASTM A572 Grade	Thickness	Composition-weight %							Y.S.	U.T.S.
	mm	C max	Mn max	P max	S max	Si max	V min	N max	N/mm ²	N/mm ²
42	≤ 38	0.21	1.35	0.04	0.05	0.30	0.01/0.10	-	289	414
	≤ 100	0.21	1.35	0.04	0.05	0.15 0.3	0.01/0.10	-	289	414
45	≤ 38	0.22	1.35	0.04	0.05	0.30	0.01/0.10	-	310	414
50	≤ 38	0.23	1.35	0.04	0.05	0.30	0.01/0.10	0.015	345	448
55	≤ 38	0.25	1.35	0.04	0.05	0.30	0.01/0.10	0.015	379	483
60	≤ 25	0.26	1.35	0.04	0.05	0.30	0.01/0.10	0.015	414	517
65	≤ 13	0.26	1.35	0.04	0.05	0.30	0.01/0.10	0.015	448	552

These steels if rolled with appropriate reductions and if finish rolled at reasonably low temperatures will have sufficiently fine grain size to be supplied at least in plates up to 12 mm in thickness to specifications, such as B.S 4360 Grade 50D, where a guaranteed minimum toughness of 27 J @ - 30°C is required. For thicker plates it is more usual to normalise the steels, especially when low temperature toughness is required.

Vanadium steels, because vanadium does not suppress ferrite formation, do not usually have microstructures containing bainite even in thin sections which cool relatively quickly after rolling. They are therefore often preferred to niobium steels for rolled sections where the relatively rapid cooling of the flange can introduce bainite into the microstructure which lowers the toughness of the steel.

Normalised Steels

Apart from the use of aluminium to produce fine grained steel, normalised vanadium nitrogen steels originally developed in Germany were probably the first microalloy steels to be produced. A wide range of normalised vanadium steels are produced in plates up to 100 mm in thickness with strengths in the range 345-448 N/mm² (50-65 k.s.i) together with various minimum low temperature impact values depending on the application. For the lower strengths additions of up to 0.1% V are made to steel of normal BOF nitrogen content (0.007%), when high strength 448N/mm² (65 k.s.i) are required, vanadium contents up to 0.15% are used together with increased nitrogen contents (up to 0.015%).

In these steels vanadium (and aluminium) nitrides ensure fine ferrite grain size which contributes to strength and toughness and VCN precipitates in ferrite give further strength as described above. The grain size and precipitate size tend to increase with plate thickness resulting in consequent loss in strength and toughness. This can however be compensated to some extent by higher carbon levels which increase the volume fractions of precipitates and of pearlite. The higher carbon content, however, reduces weldability.

V-Nb steels (with lower nitrogen) in which niobium carbide replaces vanadium nitride for grain size control have been used and are less susceptible to cold cracking. They are however more prone to weld metal and HAZ embrittlement. The vanadium-nitrogen steels especially when preheating or post heating procedures are available to avoid cold cracking, are more usually employed.

Recently more weldable vanadium normalised steels have been reported by Wada and co-workers (1981), Smith and co-workers (1981), and Blondeau, Cadiou and Pont (1981). These steels have a lower carbon content (0.06%) (to increase resistance to cold cracking) but this without compensation would lead to a lower strength steel, particularly in thicker sections. Additions of molybdenum and copper are therefore made which refine the vanadium precipitates hence increasing their effectiveness in increasing the strength of the steel. At the lower carbon content niobium has a less detrimental effect on the weld metal and HAZ toughness and NbC can be tolerated for grain refinement in place of VN which means that high nitrogen contents are not necessary and further improvement in resistance to cold cracking and improvement in HAZ toughness is possible. Typical compositions and properties of V-N and V-Mo-Cu steels are given in Table 2 and the effect of thickness on strength (and toughness) are shown in Fig. 7.

TABLE 2. Typical Composition and Properties
of V-N and V-Mo-Cu Steel Plates

Steel Type	Chemical Composition-weight %										
	C	Si	Mn	S	P	Ni	Cr	Mo	Cu	V	C.E.
V-N	0.22*	0.20	1.60	0.05*	0.05	-	-	-	-	0.02	0.45
V-Mo-Cu	0.073	0.28	1.07	0.005	0.005	0.60	0.12	0.24	0.15	0.077	0.39
Mechanical Properties											
	Thickness	Y.S.	U.T.S.	Elongation	Charpy at 0°C						
	mm	N/mm ²	N/mm ²	%	Joules						
V-N	12	494	633	20	54min						
	25	463	618	22	54min						
	38	432	602	25	54min						
	63.5	448	602	25	54min						
V-Mo-Cu	20	608	678	26.7	> 132						
	45	569	646	23.6	> 132						
	70	534	617	26.4	> 156						

* maximum values

Control Rolled Steels

Control rolling was introduced for microalloyed steels on a production basis in the early 1970's as a means of producing fine grained steels with low temperature toughness without normalising. The degree of grain refinement and the thickness of plate which can be produced is limited by the separating force of the rolling mills. The production of plates up to 15 mm thickness with strength up to 414 N/mm² (60 k.s.i) was quickly established for a large proportion of the world's plate mills. This strength can be achieved in plates up to 40 mm in thickness in certain mills. It was found that 0.03% niobium was the most economic addition to prevent recrystallisation of austenite in these steels.

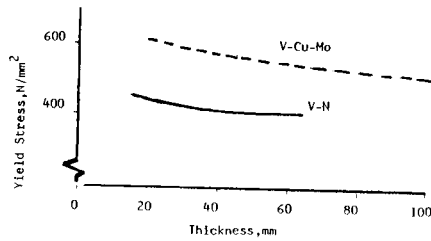


Fig. 7. Yield stress vs thickness for commercial V-N and V-Cu-Mo steels

Although niobium in large amounts can also give some strength from precipitation, vanadium is a more effective precipitation strengthening alloy. Up to 0.1% vanadium is frequently added to steels with 0.03% niobium (added for grain refinement) and such steels are well established for plates with a higher yield strength than 414 N/mm² or for thicker plates of lower strength steels.

The comparative effect of niobium up to 0.2%, and vanadium up to 0.2% in a 0.03% niobium steel can be seen from Fig. 8.

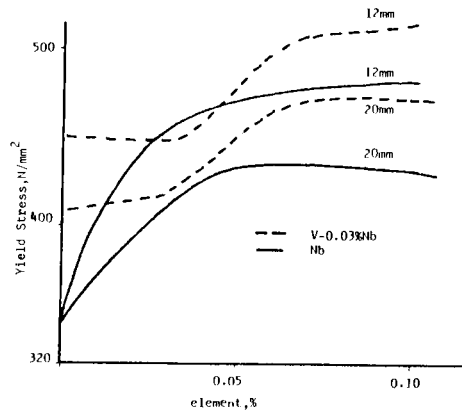


Fig. 8. Yield stress vs % element for V-0.03Nb and Nb steels

Accelerated Cooling and Strip Steels

For many years high strength steels have been produced in strip form, these steels are finished rolled at 800°C, quenched to about 650°C and cooled slowly in coils. Niobium is usually added to such steel to produce strengths up to 517 N/mm² (75 k.s.i). This is achieved mainly through the effect of Nb on grain size as it prevents recrystallisation of austenite in the last stand of the continuous mills and also gives some precipitation strengthening of NbC

in the coil. When higher strengths ($550-586 \text{ N/mm}^2$) (80-85 k.s.i) are required vanadium is added to the steel to increase the precipitation strengthening. (In the past vanadium nitrogen steels were used but these have been replaced by a lower carbon (0.09%) vanadium niobium steel which has a finer grain size, lower pearlite content, and better low temperature toughness.

The accelerated cooling (OLAC) process has recently been applied to plate rolling in Japan (Ouchi and co-workers, 1979) with the result that V-Nb steel plates having yield strength up to 550 N/mm^2 (80k.s.i) are now produced.

Heat Treated and Direct Quenched Steels

Quenched and tempered structural steels containing chromium, molybdenum and/or boron to provide increased hardenability (i.e. to ensure a fully martensitic structure on quenching) have been produced for many years. Vanadium is frequently added to such steels to give secondary hardening (i.e. precipitation of carbides during tempering to enhance the strength of the tempered martensite) for high strength steels made in thick sections.

Recently the direct quenching process has been developed in Japan to quench the steels directly after rolling thus avoiding reheating. This process, because of the distortion which is produced by quenching is restricted to plates of 38 mm and over. The aluminium and nitrogen contents are limited to 20 and 35 ppm respectively in order to ensure a relatively coarse grained austenite which increases hardenability and 0.1% vanadium is added for the same purpose. Such steels auto temper and the vanadium probably contributes to the final strength of the steel by precipitation of carbide in the tempered structure.

POTENTIAL USE OF VANADIUM IN THE PLACE OF STRATEGICALLY IMPORTANT ALLOYS

There is considerable interest in strategic materials and the possible substitution of one metal for another. Rarely can one alloy be substituted for another in that the substitute steel has the same microstructure and properties as the original and is produced by the same processing. Normally the substitution is achieved by different microstructures and different processing (rolling and heat treatment) from the original.

The role of vanadium in structural steels discussed in the previous section of this paper is based on the assumption that other alloys, particularly niobium and molybdenum are available at prices which make their use economic. In this section the possible role of vanadium in structural steel is discussed assuming that other microalloying elements are not available or only in limited supply.

Hot Rolled Steels

Vanadium can be used to replace niobium in all hot rolled reinforcing bar regardless of the mill involved. The vanadium steel would however rely on VCN precipitates more than grain refinement especially in thicker bars. Similarly V could be used to replace niobium in all hot rolled plates and sections except where special low temperature toughness was required, again the vanadium steel would rely more on precipitates than on grain size control. Where exceptional toughness is required it may be necessary to substitute a V-N normalised steel.

Control Rolled Steels

Many plate steels are control rolled in order to achieve combinations of strength and toughness. Plates and bars of the thinner gauges, especially when rolled in older, slower, mills, are, deformed under conditions which enable a fine grain size to be produced if recrystallisation of austenite can be prevented. Niobium is added to most of these steels but as indicated at the beginning of this paper VN precipitates in austenite at a lower temperature than NbC. It is therefore possible that the V-N steels could be control rolled to replace Nb steel but 0.15%V and 0.015%N would probably be required and rolling would have to be carried out with a narrower temperature range and with fewer drafts and heavier reductions.

It may be possible to use lower levels of vanadium and nitrogen for steels supplied to specifications where toughness requirements are not severe for example for BS4360 Grade 50D. In this case the vanadium would have less effect on recrystallisation of austenite, but prevent grain growth.

If steel involving higher nitrogen contents are used the steel will have an increased susceptibility to cold cracking and HAZ embrittlement and additional preheat during welding and/or applying post heat to the weld may be necessary. Normalised vanadium (nitrogen) steel can also be employed as an alternative to control rolled niobium steels. In this case a higher carbon content will be required and appropriate modification will have to be made to the welding conditions if the steels are welded.

In steels where medium strength is required but where high toughness at low temperatures is not specified, but where control rolled fine grained niobium steels are used at present (being the cheapest steel for such purposes), hot rolled vanadium (nitrogen) steel can be used, the strength in this case coming more from precipitation and less from grain refinement.

Pipe Steels

It has been shown by Sage (1981) that 0.45% V (and perhaps less) can be used to replace both niobium and molybdenum in Mo-Nb pipe steels having a polygonal ferrite structure with martensite islands. In this case VN (at low N levels (0.006%)) can replace NbC to control grain size and V replaces Mo + Nb in giving the M/A structure.

Strip Steels

Niobium or niobium plus vanadium steels are used for HSLA strip steel today because this gives the lowest cost steel. Vanadium and V-N steels can be substituted for these if niobium is not available. In the case of the vanadium steel more strength would probably come from precipitates but a fine grain size would however be produced by the quenching of the strip for coiling.

Quenched and Tempered Steels

In as much as molybdenum is used to give hardenability (delay in bainite formation) in quenched and tempered steels, it may be possible to replace the molybdenum with an increased amount of vanadium. It has been mentioned above that vanadium can be used with low nitrogen and aluminium contents to delay bainite formation and give a fully martensitic structure to direct quenched steels. It has also been claimed (Mangonon, 1980) that vanadium can replace

or partially replace molybdenum in medium carbon chromium-molybdenum forging steels. It would seem reasonable to suppose therefore that similar replacements could be made in 0.15/0.20% carbon structural steels but a small amount of molybdenum should be retained.

ACKNOWLEDGEMENT

The author would like to thank his colleagues Dr. J.C. Greenbank and Mr. D.J.H. Griffin for their assistance in preparing this paper.

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Toughness in High Speed Steels and Hard Metals

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ABSTRACT

Toughness being usually assessed by transverse rupture testing, a fracture mechanical discussion is given of flaw-induced rupture in semi-brittle materials. Fracture toughness data for high speed steels and hard metals are reviewed. Typical flaws acting as fracture sources in hard metals are pores, inclusions, and eta phase regions. In high speed steels, critical flaws form by subcritical growth of cracks in the stringers. This explains the strong directionality of rupture strength, its dependence on hot reduction, and its absence in powder metallurgy materials. The complex of properties which determines the 'toughness' of a cutting edge is distinguished as 'microtoughness' from the 'macro-toughness' reflected in the transverse rupture test. Its most important aspect is the nature of the nucleation sites for fracture in extremely small stressed volumes. These are certainly not the coarse defects revealed by the transverse rupture test, but rupture experiments do indicate that microfracture may be caused by debonding at carbide-carbide or carbide-matrix interfaces. The stepping stones for an understanding of microtoughness are discussed.

KEY WORDS

High speed steels; cemented carbides; transverse rupture strength; fracture toughness; structural flaws; micro- and macro-toughness; cutting performance.

INTRODUCTION: THE 'TOUGHNESS' OF TOOL MATERIALS

Toughness is a poorly defined concept for tool materials. While it is true that all its implications are basically concerned with 'resistance to failure by fracture', the fracture processes involved vary widely. At the one extreme, we have the transverse or torsional rupture of a tool bit or drill shaft. At the other, there is the removal of tiny fragments from a cutting edge termed 'attrition wear', 'edge crumbling', or 'microchipping' by tool engineers. Underlying the association with toughness of all these is the idea that the fragments are severed from the bulk by a fracture process. These two aspects of toughness are worlds apart, and it would be desirable always to distinguish between *macro*-toughness for the first and *micro*-toughness for the second

(Fischmeister and Olsson, 1981). This paper is mostly concerned with *macro*-toughness because this can be constructively discussed at the present state of the art, and it provides stepping stones also for the understanding of microtoughness. Having made the distinction, we will omit the prefix in what follows, as long as we are referring only to macro toughness.

Usually, (macro-) toughness is assessed by measuring the transverse rupture strength (σ_F) of a test bar in bending. In addition, the deflection at yield (ϵ_y) and at fracture (ϵ_F) may be measured, and the total work of fracture

$$W_{\text{tot}} = \int_0^{\epsilon_F} \sigma d\epsilon \quad (1)$$

or the plastic work of fracture

$$W_{\text{pl}} = \int_{\epsilon_y}^{\epsilon_F} \sigma d\epsilon \quad (2)$$

are sometimes used as toughness indicators. For materials which rupture without much plastic deformation, W_{pl} is very difficult to measure, and W_{tot} is not much different from $\sigma_F^2 \cdot E/2$, with twice the scatter of σ_F (Almond 1982).

Impact tests like Izod or Charpy, which measure the energy consumed in fracturing a bar under dynamic loading conditions, were popular up to the fifties, but have virtually fallen out of use because of their large inherent scatter.

The seventies brought a wave of interest in fracture toughness, with the hope that this new parameter should prove more relevant to the operating performance of tool materials. Disillusionment followed when it was realized that within each of the families of hard metals and high speed steels, respectively, the variations of fracture toughness were too small to be related to the materials' widely different performance. Its culmination was marked by the statement (Lardner, 1979) that 'fracture toughness is just an expensive way of measuring elastic modulus'.

For hard metals, a test originally devised by Palmqvist (1957, 1962), in which the cracks formed around a hardness indentation are measured, has gained considerable popularity. Much work has been devoted to its experimental refinement (Exner, 1979; Peters, 1979) and theoretical understanding (Lawn and Wilshaw, 1975; Lawn and Fuller, 1976; Exner, Pickens, and Gurland, 1976; Perrott, 1978; Peters, 1979). The property determined has been shown to be related, with good approximation, to the material's resistance to crack propagation in a region close to the surface ('surface fracture toughness'). The Palmqvist test has become especially popular for rock cutting grades of hard metals.

However, none of the parameters discussed above has fully satisfied the users and developers of tool materials as a true reflection of practical toughness behaviour. Rupture strength remains the most universally accepted toughness parameter, but more by dint of simplicity than by true merit.

FRACTURE MECHANICS AND THE RUPTURE TEST

For the fracture of a test bar, two things are necessary:

- presence of a crack nucleus,
- extension of the crack to the surfaces of the bar.

These two components of the fracture process have entirely different causes and mechanisms.

Both hard metals and tool steels contain internal flaws in a statistical distribution throughout their volume. If the surface of the test bar has been machined to sufficient smoothness, they assume the role of crack nuclei. In a bend test, the local stress at the site of a flaw varies with depth below the tensile surface; in three point bending, it varies also with distance from the support point. Fracture will originate from one particular flaw which happens to have the most unfavourable combination of local stress, flaw size and notch geometry. The fatal flaws may often be detected by inspection of fracture surfaces under a low power microscope and analysed further by scanning electron microscopy. Examples will be shown later.

Because of the stochastic distribution of flaws throughout the volume, a crack may start anywhere in the stressed part of the test bar. This explains the volume dependence of average fracture stress in brittle materials as well as the observation that in three point bending, the fracture often starts at some distance from the point of loading (= maximum stress). A defect of specially large size and/or especially severe notch effect can start a crack off-center. Once the crack has formed, it will usually deviate towards the region of maximum stress, giving rise to the characteristic fracture path shown in Fig. 1.

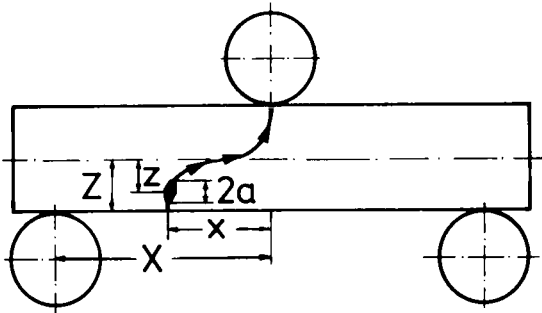


Fig. 1
Flaw-induced transverse
rupture

Using a basic expression of linear elastic fracture mechanics (a good enough approximation in the case of hard metals and fully hardened high speed steels), the *nominal* stress at which fracture occurs in a three point bend test can be written

$$\sigma_F = \frac{Z}{z} \cdot \frac{x}{(X-x)} \cdot \frac{K_{IC}}{\sqrt{a \cdot Q}} \quad (3)$$

K_{IC} is the fracture toughness of the sound material (regardless of flaws); the quantities x, X, z, Z define the site of the crack nucleating flaw as shown in Fig. 1; a is the flaw size, and Q is a factor related to the geometry (= notch severity) of the flaw. Rounded flaws have smaller Q than sharp ones; for an ideally sharp, penny shaped internal microcrack of radius a , $Q_{th} \approx 1.26$; for a semicircular surface crack of radius a , $1.34 \lesssim Q_{th} \lesssim 1.52$ (Rooke and Cartwright, 1976; Tiffany and Masters, 1965).

Equation (3) also explains the *role of fracture toughness* in the transverse rupture test. Fracture toughness reflects the material's ability to impede crack propagation by dissipation of energy at the crack tip, which in turn is related to the plastic deformation properties of the material through which

the crack propagates. Normal flaw densities in tool materials are far too low to affect this. As will be shown in the next section, K_{IC} in hard metals is a function of the microstructure (the distribution of Co and WC), while in high speed steels, K_{IC} is essentially determined by the secondary hardening state of the matrix and hardly affected by the distribution of the coarse carbides.

Consequently, *the bend test may be said to reveal selectively the severest flaws present in the stressed volume*. In that capacity, it is much more powerful than metallography because the probability of intersecting the one fatal flaw with the plane of polish is so small (Amberg and Doxner, 1977). It is quite normal to find flaws of 10-100 μm size on fracture surfaces of hard metals with pore ratings better than A, which means 'no pores greater than 10 μm on a standard polished section'. From a practical point of view, the transverse rupture strength is primarily a test for the soundness of the material.

Exner, Walter and Pabst (1974) were the first to show that equation (3) could be applied to interpret the distribution of rupture strength in terms of a size distribution of flaws in brittle materials. For hard metals, Anderson (1967) showed that fracture in transverse rupture test bars could normally be traced to discrete structural defects, and from an analysis of these defects he derived a method of substantially improving the toughness of hard metals (Anderson, 1976). His observations were extended by Suzuki and Hayashi (1975) and refined by Bartolucci-Luyckx (1975) and others (Amberg and Doxner, 1977; Almond and Roebuck, 1977). Similar studies on high speed steels were first published by Johnson (1977) and Johansson (1978).

FRACTURE TOUGHNESS OF HARD METALS AND HIGH SPEED STEELS

Precracking

Fracture toughness measurements require a very sharp precrack in the specimen to study the resistance to crack propagation under valid conditions. The normal method of precracking by fatigue cannot be applied to hard metals and tool steels. Early measurements used diamond saw cuts or spark eroded slits for precracks; these were not sharp enough and the results must be regarded with caution (Almond and Roebuck, 1978; Bretfeld and co-workers, 1981). At the present state of the art, valid measurements appear possible by precracking with wedge indenters (Harris and Dunegan, 1968; Lueth, 1974; Almond and Roebuck, 1978) or by controlled crack propagation in a chevron-notched specimen (either of the short round rod geometry, Barker, 1977; Bretfeld and co-workers 1981, or of bend type, Hübner and Engel, 1978).

Hard Metals

A critical evaluation of published measurements (excluding data obtained with imperfect precracking methods) by Almond (1982) shows that for WC-Co hard metals, K_{IC} generally falls with increasing hardness (Fig. 2). The influence of structural variables has been studied mostly with spark-eroded specimens, but the trends observed have been verified at least partially with other precracking methods. Chermant and Osterstock (1976) showed that the fracture toughness of WC-Co alloys increases with increasing binder content, carbide grain size, and mean free path in the binder, and that it falls with increasing contiguity. The influence of binder content and carbide size was verified by Almond and Roebuck (1978), that of the mean free path in the binder by Lueth (1974), Pickens and Gurland (1978), Nidikom (1980) and Nakamura and

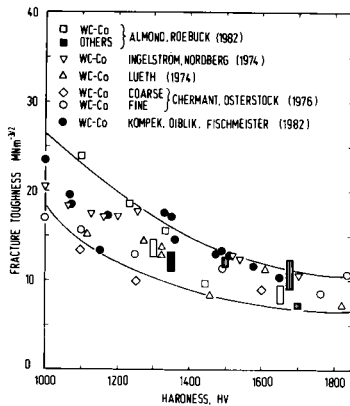


Fig. 2
Fracture toughness of
hard metals

Gurland (1980). These microstructural effects can be understood if one assumes (plausibly) that what impedes the propagation of the crack is mostly the deformation of the binder in the vicinity of the crack path. Theoretical treatments based on this assumption have been developed by Lindau (1977) and by Nakamura and Gurland (1980). It is assumed that the crack propagates predominantly in the binder or along binder/carbide boundaries. This latter assumption has, however, been subjected to doubt by Lea and Roebuck (1981) on the basis of Auger electron spectroscopy. At any rate, increasing fracture along carbide/carbide boundaries or through carbide grains is expected as the binder content falls, and there is evidence for this from fractographic and Auger microprobe studies (Chermant and Osterstock, 1976; Viswanadham and co-workers, 1981; Lea and Roebuck, 1981). A complete model for the influence of microstructure on the fracture toughness of hard metals has yet to be developed, but the existing ones provide satisfactory qualitative understanding. Very little is known about the fracture toughness of hard metals with cubic (TiC- and/or TaC-containing) carbides. In a paper by Stjernberg (1980), data are given for two alloys of roughly comparable binder content and carbide size, which show decidedly lower toughness for the TiC-containing grade. It is not clear to what extent the difference is due to the greater carbide contiguity characteristic of all TiC-containing alloys, or whether one has to assume greater inherent fragility of the cubic carbide. Accepting the assumed relation of surface to bulk fracture toughness, the work of Viswanadham (1979) verifies (and explains in terms of a simple model) the inverse relation of hardness to fracture toughness, and shows that the family of WC-Co alloys is principally superior in fracture toughness to grades based on (Ti,V)C with (Ni,Mo) binders.

There is one set of measurements which seems to contradict the universally accepted dependence of K_{IC} on binder content in WC-Co alloys (Bretfeld and co-workers, 1980). Since great care was taken about precracking, the discrepancy is serious. A tentative explanation is that the expected effect of binder content might have been fortuitously offset by a difference in the state of solute strengthening in the binder. Renewed studies of the influence of compositional and microstructural variables on the fracture toughness of hard metals, using valid precracking methods, appear highly desirable.

High Speed Steels

Conventionally produced high speed steels have strongly anisotropic properties because of the arrangement of the carbides in stringers. Olsson and Fischmei-

ster (1978) found that in steels tempered to low hardness levels (50-60 HRC), fracture propagates most easily along the stringers, resulting in low values of K_{Ic} . The highest values are obtained when the crack has to cut perpendicularly across the stringers (Fig. 3). Microscopic study verifies that cracks propagate preferentially within the carbide stringers.

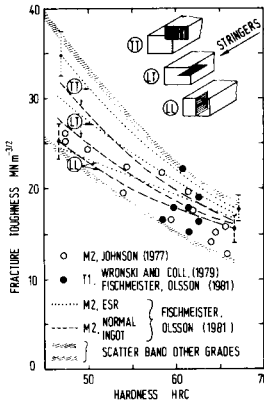


Fig. 3
Fracture toughness of
high speed steels

At higher hardness levels, including the customary range for cutting tools (around 65 HRC), the influence of stringer direction virtually vanishes. Also the carbide particle size and the chemical composition of the steel exert little influence on fracture toughness in this hardness range. The scatter band in Fig. 3 comprises data for steels of type M1, M2, M2/3, M7, T1 and T6, partly at various degrees of hot reduction, and made via different processing routes such as ESR, conventional ingot processing, and powder metallurgy. Details are given in Fischmeister and Olsson (1981) and Olsson and Fischmeister (1978). Very careful measurements by Pacyna and Mazur (1982) indicated no difference in K_{Ic} at equal hardness beyond the experimental uncertainty (4 %) between steels M2 (6-5-2) and T1 (18-0-1) over a wide range of tempering conditions. Neither was there a significant difference between over- and under-tempered specimens.

The fact that microstructure, composition and process variables seem to lose most of their influence on the fracture toughness of high speed steels at the secondary hardening peak implies that crack propagation is essentially determined by the state of the matrix with respect to secondary hardening precipitates. This conclusion was drawn already by Johnson (1977) and verified by several later authors (Fischmeister and Olsson, 1981; Wronski, Hussein-al-Yassari and Jagger, 1979). Olsson and Fischmeister (1978) demonstrated that above 60 HRC, the size of the plastic zone becomes too small to be affected by the primary carbide distribution. At lower hardness, the plastic zone is large enough to be influenced by the carbide stringers.

FLAW-INDUCED FRACTURE

If a flaw of size a_c is responsible for rupture, the effective local stress at rupture is

$$\sigma_{\text{eff}} = \frac{(X-x)}{X} \cdot \frac{z}{Z} \cdot \sigma_F = \frac{K_{Ic}}{\sqrt{Q}} \cdot \frac{1}{\sqrt{a_c}} \quad (4)$$

One can usually identify the fatal flaw in the scanning microscope, taking guidance from the radial pattern on the fracture surface. It is useful to

compare both sides of the fracture, as demonstrated in a different context by Bartolucci-Luyckx (1977), and to use stereo images for flaws whose appearance does not clearly differentiate them from the surrounding region of unstable crack propagation. The procedure is time-consuming, but it allows the size of fracture-causing flaws to be assessed with reasonable certainty. The area of the flaw in the projection of the image plane (A) is determined by tracing its outline on a digitizing tablet. An effective flaw size can then be defined as the radius of a circle of matching area, for internal defects ($a_{\text{eff}} = \sqrt{A/\pi}$), or of a semicircle of matching area, for cracks originating from the surface ($a_{\text{eff}} = \sqrt{2A/\pi}$). If rupture is always caused by these flaws turning into unstable cracks at a critical stress σ_{eff} , then according to equation 4 the data points should arrange themselves along a straight line of slope $Q^{-1/2}$ in a plot of $\sigma_{\text{eff}}/K_{\text{IC}}$ vs. $a_{\text{eff}}^{-1/2}$. This method of testing the model of flaw-induced rupture in the transverse bend test has been used independently since 1977 by the author's group (Olsson 1977; Kompek, 1978; Karagöz, 1979; Fürst, 1982) and by several other authors (Almond and Roebuck, 1977; Johnson, 1977; Johansson, 1978; Johansson and Sandström, 1978) with good success.

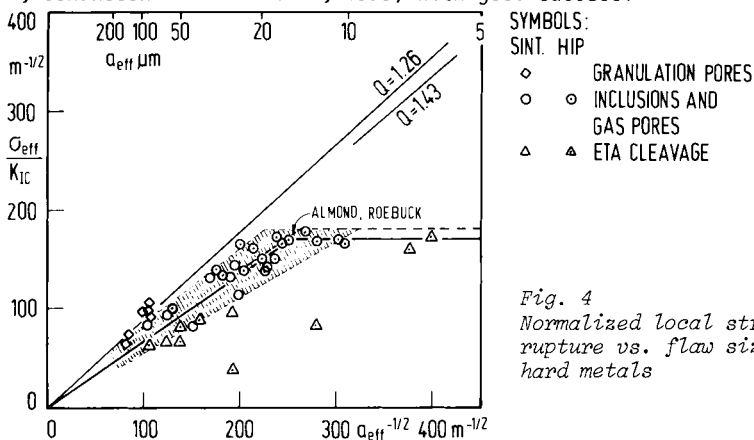


Fig. 4
Normalized local stress at
rupture vs. flaw size,
hard metals

Figure 4 shows data for hard metals (Kompek, Diblík and Fischmeister 1979) for an experimental WC-Co alloy with 5.82 wt% Co, mean linear intercepts $d_{\text{WC}} = 1.00 \mu\text{m}$, $\ell_{\text{Co}} = 0.45 \mu\text{m}$; hardness HV30 = 1550; $K_{\text{IC}} = 11.64 \text{ MNm}^{-3/2}$. It was tested in the as-sintered and in the HIP-treated condition. Also shown is the scatter band of the data reported by Almond and Roebuck (1977) for a commercial alloy with 11 wt% Co, carbide grain size $1.41 \mu\text{m}$ (method of measurement unspecified), hardness HV30 = 1320, $K_{\text{IC}} = 15.5 \text{ MNm}^{-3/2}$.

The two sets of measurements are in very good agreement. Both show a plateau of rupture stress at flaw sizes below ca. $20 \mu\text{m}$, which is interpreted by Almond and Roebuck (1977) as the limiting strength of the material, where fracture is initiated by large carbide grains at the coarse end of the grain size distribution. A carbide intercept distribution measured for the material of Kompek, Diblík and Fischmeister (1979) indicates a probability of one grain in 10^4 having a size of $20 \mu\text{m}$ or above. At the other extreme, the lowest rupture strength among all the alloys tested corresponds to a flaw size of the order of $150 \mu\text{m}$, in keeping with the practical range of pore sizes in hard metals.

The flaws at the origins of the fractures evaluated in Fig. 4 were of three types:

- (i) in sintered material, the dominant type were large pores containing granules of the original WC-Co powder mix which had not bonded complete-

ly to the surrounding material during sintering (Fig. 5a). These pores were completely eliminated as fracture sources by HIP treatment.

- (ii) Foreign inclusions (usually of silicate type) and free graphite acted as fracture nuclei in both sintered and HIP-treated materials (Fig. 5b).
- (iii) A third type of fracture-nucleating flaw manifested itself in the form of planar regions on the fracture surface (Fig. 5c). These are probably due to cleavage of regions where the binder has formed eta carbide $(\text{Co,W})_6\text{C}$.

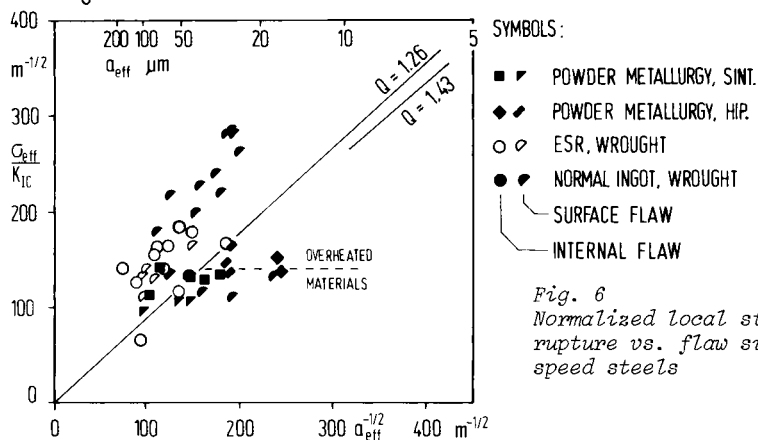
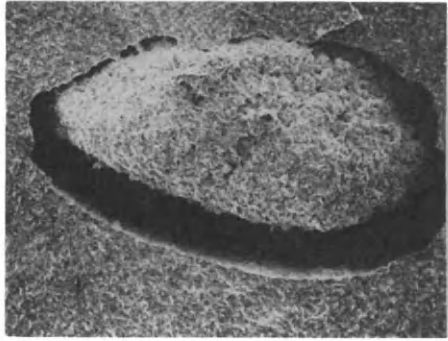


Fig. 6
Normalized local stress at rupture vs. flaw size, high speed steels

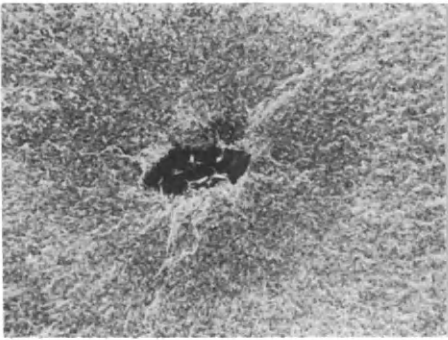
The plot for high speed steels in Fig. 6 contains data from four series of materials, produced partly from ingots and partly from water atomized powders by cold pressing and sintering in the region of incipient melting. Details are compiled in Table I in the Appendix. According to Fig. 3, a fracture toughness of $K_{IC} = 16.0$ may be assumed for all these grades. The scatter band of the high speed steel data is broader than that for hard metals, but the correlation is still good enough to support the view that the flaws whose sizes are entered in Fig. 6 were actually responsible for the fracture of the test bars. A plateau ($\sigma_{eff} = \text{const.}$) is indicated for materials austenitized above 1200°C . The powder metallurgy materials and the cast-and-wrought material which had been austenitized at 1230°C show carbide precipitation at grain boundaries; material quenched from 1250°C shows considerable amounts of eutectic melt. The fracture surfaces contain smooth regions where the material seems to have separated along such extensive carbide/matrix interfaces.

Two types of fracture-initiating flaws were found:

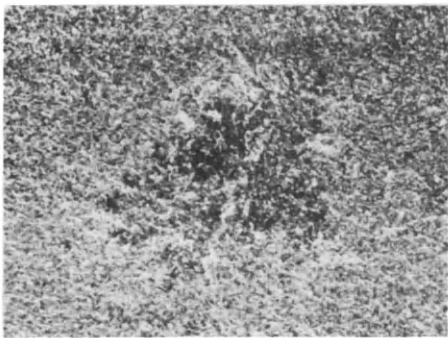
- (i) In sintered materials, the most common fracture sources are pores of the type shown in Fig. 7a. After HIP treatment pores no longer occur as fracture sources.
- (ii) In HIP-treated powder metallurgy material, fracture was usually nucleated at large individual carbides or clusters of carbides, see Fig. 7b. In the cast-and-wrought materials studied by Fischmeister and Olsson (1981) and Karagöz and Fischmeister (1982), fracture was often nucleated in carbide clusters, and especially in aggregates of M_6C with MC which had been formed during decomposition of eutectic M_2C during hot working. Apparently the $\text{M}_6\text{C}/\text{MC}$ interface is especially weak. In cast-and-wrought material, large primary MC particles are often found to have crystallized around platelets of Al_2O_3 (Fischmeister and coworkers 1992). Cracked particles of this kind are often observed at the fracture origin (Fig. 7c). One might speculate that thermal expansion mismatch may have created microfissures



a) 100 μm



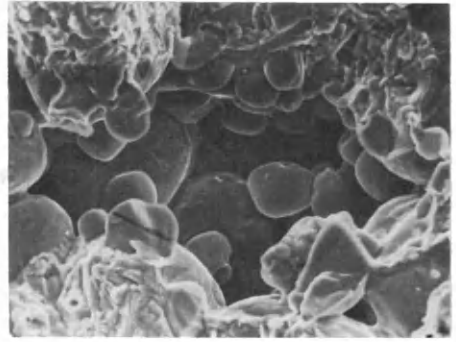
b) 100 μm



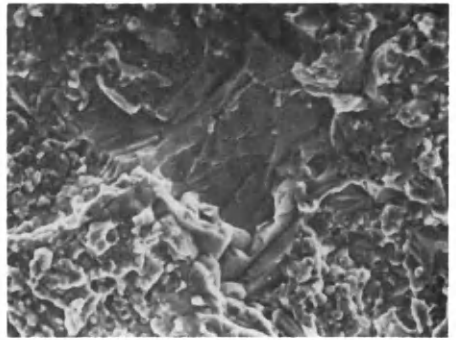
c) 100 μm

Fig. 5: Fracture initiating flaws in hard metals.

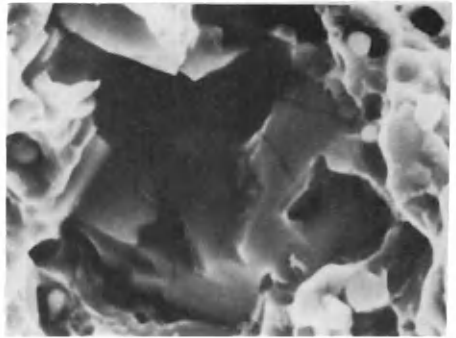
- a) granulation pore
- b) silicate inclusion
- c) eta phase cleavage



a) 50 μm



b) 20 μm



c) 5 μm

Fig. 7: Fracture initiating flaws in high speed steels.

- a) pore in sintered material
- b) carbide debonding in HIP material
- c) complex carbide in cast-and-wrought material

at boundaries of types M_6C/MC or MC/Al_2O_3 .

The slopes of the best lines in Figs. 4 and 6 reflect the notch severity of the flaws. Lines corresponding to the theoretical values for sharp circular and semicircular cracks ($Q = 1.26$ and $Q = 1.43$) have been drawn for reference.

Virtually all hard metal data fall below these lines. Only the granulation pores have $Q = 1.26$. The best line for inclusions and gas pores gives $Q = 2.2$. This high value might be explained by the ellipticity of these defects. The planar defects have $Q = 5.5$. Conceivably, these defects were surrounded by hairline cracks not visible on the fractographs. At any rate, their true area is very difficult to assess.

The high speed steel data (Fig. 6) - excepting the overheated specimens - present no such problem. They indicate either sharp cracks ($Q = Q_{\text{theor}}$) or somewhat blunt defects with $Q < Q_{\text{theor}}$. - Interpreting measured distributions of transverse rupture strengths with the Q values for sharp cracks, one obtains the ranges of defect sizes stated in Table II (appendix).

For the sintered materials, the largest defect sizes inferred from the TRS distribution agree well with the size of pores. In HIP material, these large defects have been removed, and the range inferred from TRS values is in good agreement with the size of large carbides as revealed by deep etching. (The high sintering temperature of these materials produces considerable coarsening of the carbides.) For the cast-and-wrought materials tested with crack direction perpendicular to the stringers, the size of the defects inferred from the TRS values decreases with hot work as expected, which agrees with the idea that large carbides or carbide aggregates act as fracture nuclei. In a series with varying degrees of hot reduction (Karagöz and Fischmeister, 1982) a clear correlation was observed between average carbide size (decreasing with hot work) and transverse rupture strength (increasing). Powder metallurgy materials produced by various routes take their places in this series in accordance with their carbide sizes.

Tests in which the cracks run parallel to the stringers indicate much larger crack nuclei. Fracture toughness being virtually independent of direction, the directionality of rupture strength can only be explained by directionality of the crack-nucleating flaws. The large defects inferred from the low TRS values (60 and 200 μm) obviously cannot be single carbide crystals or intergrown aggregates. The materials were clean enough to exclude nonmetallic inclusions of that size as fracture sources, and this was borne out by SEM fractography. One is forced to conclude (Fischmeister and Olsson, 1981) that the *critical flaws form by subcritical growth within the stringers*. Microscopic study of cracks formed in controlled growth (Olsson and Fischmeister, 1978) show that stringers are strongly favoured crack paths, and it appears that carbide-matrix debonding and rupture of narrow metal sections between carbides are the dominant mechanisms of propagation. Growth along such

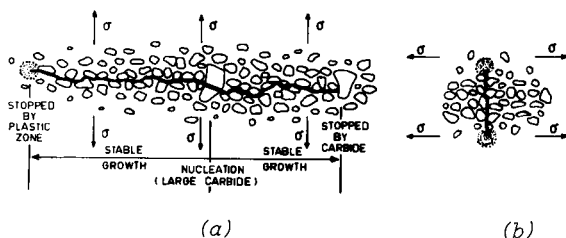


Fig. 8
Formation of critical defects by subcritical growth within stringers
a) transverse loading
b) longitudinal loading

paths will occur at low stress intensities because only a small volume of matrix material is deformed; it will stop when the crack runs against a large carbide particle or out of the stringer into the matrix where it must form a large plastic zone (Fig. 8). This model also explains the strong anisotropy of transverse rupture strength in cast-and-wrought materials, its decrease with area reduction in hot working (Karagöz and Fischmeister, 1982), and its absence in powder metallurgy materials. - In overtempered high speed steels, rupture strength increases approximately linearly with hardness, and reaches a plateau at the secondary hardness peak (Fischmeister and Olsson, 1981). Yield strength increases in the same fashion, merging with rupture strength at the peak (Olsson, Lampe, and Fischmeister, 1978). The increase of rupture strength with hardness is the more remarkable in the light of decreasing fracture toughness which makes the material more susceptible to flaws. This, too, can be understood in terms of crack nucleation by subcritical crack growth in stringer regions: as the yield strength increases, it becomes more and more difficult to achieve the matrix strain necessary to produce decohesion ahead of the crack tip as it passes from one carbide to the next through an interlayer of matrix metal. Also the well-known effect of austenitizing temperature on rupture strength can be understood via its effect on the solute content and the hardening properties of the matrix.

CONCLUDING REMARKS

The elementary fracture mechanical view of transverse rupture strength presented here has its main merit in revealing the rupture test as an indicator of structural defects. In addition, it may be a stepping stone towards an understanding of microtoughness which, as mentioned in the introduction, is the aspect of toughness most germane to cutting performance.

For a rational understanding of microtoughness, the following problems will have to be solved:

- 1) The volume dependence of fracture nucleation sites.
The stressed volume of a cutting edge is two or three orders of magnitude smaller than that of a rupture test bar. The coarse defects which cause fracture in test bars are too far apart to be involved in the crumbling of a cutting edge. In fact, the size of the attrition fragments is similar to that of the crack nuclei in the best materials discussed here, of the order of a few micrometres. At the present state of knowledge, however, the rupture tests at least show up weak links in the structures of tool materials as likely nucleators of microfracture: carbide/carbide boundaries in hard metals and composite carbides in steels. Metallurgical measures could be directed at reducing the area of carbide/carbide interfaces, eliminating complex carbides, and at improving carbide-carbide bonding.
- 2) The volume dependence of fracture stress is given by the density of potential crack nucleation sites. Almond (1982) has pointed out that simple Weibull statistics cannot be applied when different types of fracture mechanisms occur in different ranges of stressed volume. However, there are extensions of the Weibull treatment which are able to deal with distributions of defect type and size in combination with inhomogeneous stress fields and even with locally varying material properties, e.g. in thermal gradients (Jayatilaka and Trustrum, 1977; Hunt and McCartney, 1979; McCartney, 1979). A beautiful worked example is the treatment of the life time of drawing dies on the basis of FEM-calculated stress distributions and of information on the distribution and nature of fracture nuclei derived from TRS data by Almond, Gee and McCartney (1982).
- 3) To obtain complete information on the spatial and size distribution of

various defect types, measurements with systematically varied stressed volumes would be desirable. We still largely lack methods for small volumes. Almond's (1982) proposal of a bend specimen with a knife edge at the tensile side (to lower the probability of defect-induced failure), and of an edge flaking test in which ball indentations are placed closer and closer to the specimen edge until flaking occurs (Almond, 1982) are interesting, but their capabilities are not yet sufficiently explored. - The stress situation in cutting tools is normally multiaxial. A test for fracture at different ratios of $\sigma_x:\sigma_z$ has been developed by Almond, Irani and Roebuck (1980). All these tests^x have the advantage that they could be carried out at realistic tool operating temperatures.

- 4) At the high temperatures of cutting edges, the relative values of the energy of debonding at carbide/carbide and carbide/matrix interfaces will very likely be different from those at room temperature. Suzuki, Hayashi and Taniguchi (1977) have shown that above 700 °C, rupture of hard metal test bars is nucleated at binder grain boundaries. While these are again too far apart to be of interest for tool edges, it stands to reason that the binder phase may play a more important role in elevated temperature fracture than at room temperature. Little information is available on the high temperature fracture of tool materials. Ingelström (1975) and Johansson and Sandström (1978) have reported on fracture toughness and rupture strength of high speed steels, and Osterstock (1980) has studied the creep behaviour of WC-Co alloys. A large amount of data has yet to be assembled to develop an understanding of high temperature fracture along similar lines to those presented here for room temperature.
- 5) Intermittent and cyclic loading at high stress rates are characteristic for the operating conditions of most cutting tools. Data on fatigue crack propagation in hard metals and tool steels are scarce; references have been given by Fischmeister and Olsson (1981) and by Almond (1982). Actual measurements, extending to typical tool operating temperatures and related to structural parameters, are urgently required, as are data on thermal fatigue. The statistical methods for incorporating subcritical crack growth by fatigue into life time predictions of defect-infested brittle materials are available (McCartney, 1980; Almond, Gee and McCartney, 1982).

* * *

A pessimist's summary would be that an appalling amount of work remains to be done before speculation can be replaced by assured knowledge. The author prefers the optimistic view that we have most of the experimental methods and the conceptual elements for an understanding of the toughness of cutting tools at hand, and that the selective generation of required data - guided by available physical models - will be a manageable task.

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APPENDIX

Table I. HIGH SPEED STEEL GRADES AND HEAT TREATMENTS

No	wt%	W	Mo	V	Co	PROCESS	QUENCHED °C	TEMPERED °C	HARDNESS HRC	REFERENCE
1	6	5	2	-		ESR, wrought	1200	2x560	65.5	Fischmeister, Olsson 1981
2	6	5	2	-		normal ingot, wrought	1170 1190 1210 1230 1250	3x550	64	Karagöz, Fischmeister 1982
3	6	5	2	5		sintered	1250	2x530, 1x540	65	
4						sint. + HIP	1210	3x530	65	Fischmeister, Karagöz, Fürst 1982
5	12	1	5	5		sintered	1220	2x530	65	
6						sint. + HIP	1220	2x530, 2x540	65	

TABLE II. SIZE OF FRACTURE-NUCLEATING FLAWS

MATERIAL	ORIENTATION OF CRACK PLANE WITH RESPECT TO STRINGERS		FRONT	PCT. HOT REDUCTION	FLAW SIZES, μm INFERRED FROM T.R.S. MIN. MAX
6-5-2-5 sintered	—	—		as sintered	27 - 83
6-5-2-5 sint. + HIP	—	—		as sintered	25 - 27
6-5-2 normal ingot	perpend.	perpend.		99.7	8 - 10
6-5-2 normal ingot	perpend.	perpend.		98.5	13 - 20
6-5-2 ESR ingot	perpend.	perpend.		91.0	13 - 20
6-5-2 normal ingot	parallel	parallel		98.5	26 - 63
6-5-2 ESR ingot	parallel	parallel		91.0	39 - 200

Microstructure and Deformation Aspects of Some Specialty Steels and Hard Metals

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ABSTRACT

Some aspects of the basic microstructure and deformation mechanisms of metals have been considered in relation to specialty steels and hard metals. In particular, the strength-ductility properties of dual-phase steels, the work hardening behaviour of austenitic stainless steels and the influence of the martensite transformation, and the grain size control and plasticity of tungsten carbide.

KEYWORDS

Deformation mechanisms; dual phase steels; dispersion strengthening; austenitic stainless steel; stacking fault energy; work hardening; martensite transformation; tungsten carbide; grain growth inhibitor.

INTRODUCTION

A review of some deformation aspects of metals and alloys (in this case some specialty steels and hard metals) necessitates a consideration of the interaction of dislocations with the microstructural features of the materials, i.e. grain boundaries, solutes, particles, etc. This interaction controls the strength, work hardening, ductility and failure and is the reason for microstructural control. Plastic deformation generally starts at a stress level where dislocation sources create slip bands usually given by $\sigma_y = \sigma_s + \sigma_i$. Here σ_s is the dislocation source stress and σ_i the friction stress opposing the motion of the dislocations from the source, arising from the lattice itself (Peierls-Nabarro (P-N) stress), precipitates, other dislocations, etc. Yielding sometimes starts discontinuously, usually because the density of mobile dislocations ρ_m is very low and the plastic strain rate $\dot{\epsilon} = \rho_m b v$ can then match the applied rate only if the dislocation velocity is high. In a material with a significant P-N stress, e.g. steels and hard metals, high stresses are required to produce this velocity and under such conditions dislocations multiply so that ρ_m increases rapidly.

This increase in dislocation content causes some work hardening but the increase in stress level is outweighed by the drop in stress because the larger population of dislocations may now move much more slowly. In steels the density of mobile dislocations is virtually reduced to zero by the segregation of carbon and nitrogen, thereby producing strong pinning. Many metals exhibit a dependence of the yield strength, σ_y , on grain size ($2d$)

according to the Hall-Petch relationship $\sigma_y = \sigma_i + K_y d^{-\frac{1}{2}}$, where σ_i is the friction stress and K_y is related to resistance of the grain boundary to the propagation of slip from one grain to the next. The term K_y is given

by $m \sigma_d r^{\frac{1}{2}}$ where m is an orientation factor and σ_d the local stress at r ahead of the slip band needed to start yielding in the next grain. In steels the dislocations are usually too strongly locked to be unpinning and the Luders band is then propagated by creating new dislocations from the grain boundary region.

For general plasticity in a polycrystalline material it is necessary for the grains to deform on several differently oriented systems. If each grain is to remain in contact with its neighbours it must be able to change its shape arbitrarily and this requires at least five independent slip or shear modes. The metals with cubic structure easily satisfy this criterion but crystals with hexagonal and lower symmetry experience difficulty because the number of independent glide systems with comparable resolved shear stress is usually too small. This problem is relevant to deformation in some of the hard metals. Usually, grain boundary sliding and additional 'hard' slip systems can help at elevated temperatures but limited ductility remains a difficulty.

Alloying elements produce strengthening in many different ways which are often interdependent, e.g. by altering the grain size, stacking fault energy γ or transformation behaviour. However the direct effects are solid-solution strengthening and precipitate or particle strengthening. Solutes which as a result of their misfit, produce tetragonal or non-symmetrical lattice distortions solid-solution harden more strongly (e.g. for interstitial solutes $d\sigma/dc \sim \mu/3$) than those that produce symmetrical distortions (e.g. for substitutional solutes $d\sigma/dc \sim \mu/10$). When the solute atoms cluster together to form second phase particles the deformation behaviour depends on whether the particles are coherent and deformable (when the strength results from coherency strains and the process of cutting through the particle) or incoherent and non-deformable (when a low initial yield stress is followed by a high rate of work hardening).

In general, work hardening arises from the increase in dislocation density, ρ , with increasing strain and the flow stress to maintain deformation is given by $\sigma_f = \sigma_i + \alpha \mu b \rho^{\frac{1}{2}}$, where $\alpha \sim 0.5$. The flow stress arises from the various ways the dislocations interact. The dislocation density is particularly high in the tangles which form near obstacles and with increasing strain a ragged cell-like structure develops surrounding the active primary slip sources. Such sub-structure strengthening is often related to the cell size by a Hall-Petch relationship. The ability of the dislocations to cross-slip to avoid interaction will affect the work-hardening rate, and this is very dependent on temperature and γ ; low temperatures and low γ produce planar dislocation arrays and high work-hardening rates. The relationship between true stress σ_t and true strain, ϵ_t , during a tensile

test often obeys the Ludwig equation $\sigma_t = K \epsilon_t^n$ where the work-hardening exponent n is usually between 0.1 and 0.3. The index n is numerically equal to the true strain at the UTS, and therefore is a measure of the uniform extension and thinning which can occur in uniaxial tension before unstable plastic flow (necking) occurs.

For a matrix containing non-deformable particles the primary dislocations bypass the particles by leaving Orowan loops around them. These loops give rise to large stresses at the particle and are relaxed by cross-slip and secondary slip in the matrix surrounding the particle. The principal contribution to work hardening is then given by the interaction of primary dislocations with the high dislocation density. One treatment of this interaction, due to Ashby (1966) gives $d\sigma/d\epsilon = \alpha \mu (b/\epsilon)^{\frac{1}{2}} (f/d)^{\frac{1}{2}}$ where f is the volume fraction of particles of average diameter d . A limit to the strengthening that can be achieved by this mechanism is ductile failure which is initiated either by the fracture of the particles or by decohesion at the particle/matrix interface. This void nucleation is followed by void growth and finally void coalescence to give ultimate failure.

DUAL PHASE STEELS

Much research into the deformation behaviour of specialty steels has been aimed at producing improved strength while maintaining good ductility. The conventional means of strengthening, outlined in the introduction by grain refinement, solid solution additions (Si, P, Mn) and precipitation hardening by V, Nb or Ti carbides (or carbonitrides) have been extensively explored and a conventionally treated HSLA steel would have a lower yield stress of 550 MNm^{-2} (80 ksi), a UTS of 620 MNm^{-2} (90 ksi) and a total elongation of about 18%. In recent years an improved strength-ductility relationship has been found for low carbon low alloy steels rapidly cooled from an annealing temperature at which the steel consisted of a mixture of ferrite and austenite. Such steels have a microstructure principally containing low-carbon fine-grained ferrite intermixed with islands of fine martensite and are known as dual-phase steels. Typical properties of this group of steels would be a UTS of 620 MNm^{-2} , a 0.2% offset flow stress of 380 MNm^{-2} and a 3% offset flow stress of 480 MNm^{-2} with a total elongation $\sim 28\%$.

The implications of the improvement in mechanical properties are evident from an examination of the nominal stress-strain curves, shown in Fig. 1. The dual phase steel exhibits no yield discontinuity but work hardens rapidly so as to be just as strong as the conventional HSLA steel when both have been deformed by about 5%. In contrast to ferrite-pearlite steels the work-hardening rate of dual phase steel increases as the strength increases. The absence of discontinuous yielding in dual phase steels is an advantage during cold pressing operations and this feature combined with the way in which they sustain work hardening to high strains makes them very attractive materials for sheet forming operations. The flow stress and tensile strength of dual phase steels increase as the volume fraction of hard phase increases with a corresponding decrease in ductility; about 20% volume fraction of martensite produces the optimum properties.

Microstructure. The dual phase is produced by annealing in the $(\alpha + \gamma)$ region followed by cooling at a rate which ensures that the γ -phase transforms to martensite; some retained austenite is also usually present. To allow air-cooling after annealing, microalloying elements are added to low

carbon-manganese-silicon steel particularly vanadium or molybdenum and chromium. With vanadium, for example, it is thought that the vanadium carbonitride dissolves during intercritical annealing and the resulting vanadium in solid solution in the austenite increases the hardenability. However, Balliger and Gladman (1981) propose that the enhanced hardenability is due to the presence of fine carbonitride precipitates which are unlikely to dissolve in either the austenite or the ferrite at the temperatures employed and which inhibit the movement of the austenite/ferrite interface during the post-anneal cooling.

The martensite structure found in dual phase steels is basically similar and characteristic of plate martensite having internal microtwins. The retained austenite can transform to martensite during straining thereby contributing to the increased strength and work hardening. Interruption of the cooling, following intercritical annealing, can lead to stabilisation of the austenite with an increased strength on subsequent deformation. The ferrite grains ($\sim 5 \mu\text{m}$) adjacent to the martensite islands are generally observed to have a high dislocation density resulting from the volume and shape change associated with the austenite to martensite transformation. Dislocations are also usually evident around retained austenite islands due to differential contraction of the ferrite and austenite during cooling.

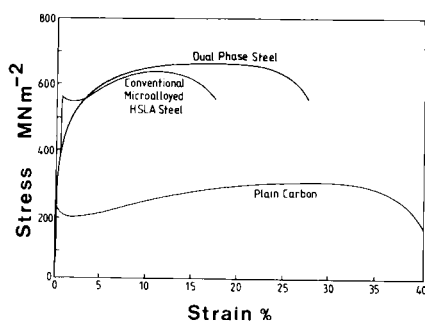


Fig. 1. Typical stress-strain curves for dual phase, HSLA and low-carbon steels.

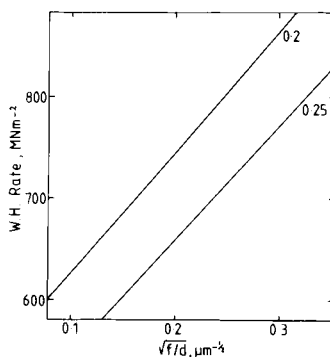


Fig. 2. Dependence of work hardening rate on $\sqrt{f}/d$ measured at strain values of 0.2 and 0.25. f is the volume fraction and d the diameter of second phase particles.

Deformation Models. The simplest model, due to Mileiko (1969), assumes both phases are ductile and obey the Ludwig relationship, with equal strain in both phases. Davies (1978 a, b) has reported some experimental results in good agreement with the linear relationship expected between the mechanical properties and volume fraction of martensite but the approach is not generally applicable since the assumption of equal strain in the two phases is certainly not verified. Measurements by Balliger and Gladman (1981) have clearly shown a partitioning of strain between the martensite and ferrite, with the mixed martensite-austenite (M-A) constituent exhibiting no strain until deformations well in excess of the maximum uniform strain. Models based on the partitioning of strain (e.g. Araki, Takada and Nakaoka

(1977) also predict a linear relationship between yield stress, UTS and volume fraction of martensite and hence it appears that a linear relationship is not sensitive to the model. An alternative approach to modelling the deformation of dual phase steels, suggested by Owen (1980), is to consider the microstructure as approximating that of a dispersion-strengthened alloy. This would be appropriate when the martensite does not deform and still be a good approximation when the strain difference between the two phases is large. Such a model affords an immediate explanation of the high work hardening rate, as outlined in the introduction, arising from the interaction of the primary dislocations with the dense 'tangle' of dislocations generated in the matrix around the hard phase islands.

Structure-Property Relationships. Balliger and Gladman (1981) have examined several dual phase steels to determine the effect of size and volume fraction of the hard phase. Figure 2 shows their results at two different strain values and confirms the linear relationship between work hardening rate ($d\sigma/d\epsilon$) and $(f/d)^{1/2}$ predicted by the dispersion hardening theory. Increasing the hard phase volume fraction while keeping the island diameter constant increases the work hardening rate, increases the UTS but decreases the elongation. At constant volume fraction of hard phase, decreasing the mean island diameter produces no effect on the tensile strength but increases the work hardening rate and the maximum uniform elongation (Fig. 3). Thus the strength is improved by increasing the volume fraction of hard phase while the work hardening and ductility are improved by reducing the hard phase island size. Although dual phase steels contain a complex microstructure it appears from their mechanical behaviour that they can be considered as agglomerates of non-deformable hard particles, made up of martensite and/or bainite and/or retained austenite, in a ductile matrix of ferrite. Consistent with the dispersion strengthened model, the Bauschinger effect is rather large in dual phase steels and increases with increase in martensite content up to about 25% (Ray, 1982).

Davies (1978c) considers the ferrite grain size to give significant strengthening. This is true at small strains but an increasing proportion of the strength arises from work hardening and this is independent of grain-size changing from about 3-30 μ m. Solid solution strengthening of the ferrite e.g. by silicon, enhances the work hardening rate; P, Mn and V are also beneficial. The absence of a sharp yield point must imply that the dual phase steel contains a high density of mobile dislocations. The microstructure exhibits such a dislocation density around the martensite islands but why these remain unpinned at ambient temperature is still in doubt, particularly as strain-ageing is significant on ageing between 423 and 573 K. Inter-critical annealing allows a partitioning of the carbon to produce very low carbon ferrite, while aluminium or silicon killed steels have limited nitrogen remaining in solution. Whether the concentration of interstitials is sufficiently low to prevent strain-ageing at low temperature is doubtful and hence it is considered more likely (Balliger and Gladman, 1981) that continuous yielding is due to the residual stress fields surrounding second phase islands. Discontinuous yielding on ageing at higher temperatures is then interpreted in terms of the relaxation of these residual stresses, followed by classical strain ageing.

Deformation Applications. In dual phase steels the n value ~ 0.2 gives the high and sustained work hardening rate required when stretch formability is the limiting factor in fabrication. However, when fracture per se is limiting, dual-phase steels probably perform no better than other steels with controlled inclusion content. Tensile failure of dual-phase steels

is initiated either by decohesion of the martensite-ferrite interface or by cracking of the martensite islands. Improved fracture behaviour is obtained when the martensite islands are unconnected, when the martensite-ferrite interface is free from precipitates to act as stress raisers and when the hard phase is relatively tough (Koo and Thomas, 1977). The optimum martensite content is considered to be 20% because above this level void formation at hard islands increases markedly.

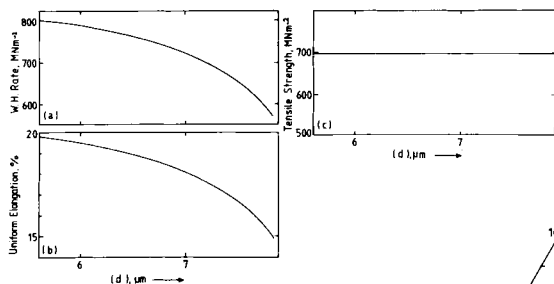


Fig. 3. Effect of second phase size d at constant volume fraction f , on (a) work hardening rate (b) elongation and (c) tensile strength.

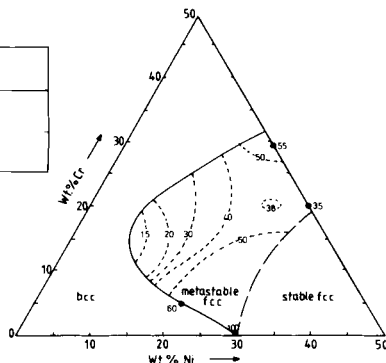


Fig. 4 Room temperature section of Fe-Cr-Ni phase diagram showing the metastable region and corresponding stacking fault energies.

AUSTENITIC STAINLESS STEELS

The austenitic structure can be retained at room temperature either in a metastable or stable condition for a wide range of Cr and Ni contents. Fig. 4 shows an approximate, non-equilibrium, room temperature isothermal section of the Fe-Cr-Ni ternary phase diagram. The large possible range of Cr and Ni leads to alloys which can have very different responses to stress, as manifested by work hardening behaviour, transformation to martensite and other properties such as creep and fracture as well as texture characteristics. In this section the properties of a range of high purity stainless steels are therefore discussed in terms of the Cr and Ni contents. Alloys of the following compositions were prepared from high purity iron, ferrochrome and ferronickel, namely 26Cr/22Ni, 21Cr/22Ni, 16Cr/22Ni, 21Cr/14Ni and 16Cr/14Ni with C and Si levels of 0.01 or less, 0.08 Mn and 0.02 Mo.

Stacking fault energy. γ has a significant influence on the properties of austenitic stainless steels. Many measurements of γ have been made but the results show a wide variation. γ appears to be a minimum around the composition 18Cr/8Ni and increases with increasing Ni content. Weak beam electron microscopy in our laboratory (Bampton, Jones and Loretto, 1978) on faulted defects in a wide range of austenitic alloys shows that the most reliable value of γ is obtained from measurements of the separation of partial dislocations in isolated dislocations. The value of γ increases with increase in temperature, which is consistent with the f.c.c. phase becoming more stable and a decreased tendency for a martensitic transformation induced by deformation as the temperature is raised. Table 1 gives the values of γ obtained at room temperature for the various Fe-Cr-Ni alloys. The effect of Cr on γ is not large and appears to depend on the Ni content.

By contrast Ni increases γ quite markedly, as expected, since Ni stabilises the f.c.c. structure. For a fixed Cr content an increase in the Ni reduces the tendency to transform martensitically.

Table 1 Values of γ for Fe/Cr/Ni Alloys

Alloy wt% Cr/wt% Ni	γ mJ m ⁻²
26/22	35
21/22	33
16/22	31
21/14	18
16/14	23

Deformation Behaviour. In general f.c.c. crystals such as austenite, exhibit a higher work hardening rate than b.c.c. However, within the austenite range the work hardening is determined by (i) the value of γ and (ii) the tendency for a strain-induced transformation to martensite. The transition from stage II work hardening to the lower rate stage III is delayed by lowering γ , thereby restricting cross-slip. When martensite forms during straining, the transformation strain produced contributes to and increases the total strain. Initially this reduces the work hardening but as the martensite participates in the deformation process the stress level and work hardening rate increases much above that for stable austenites at the same strain.

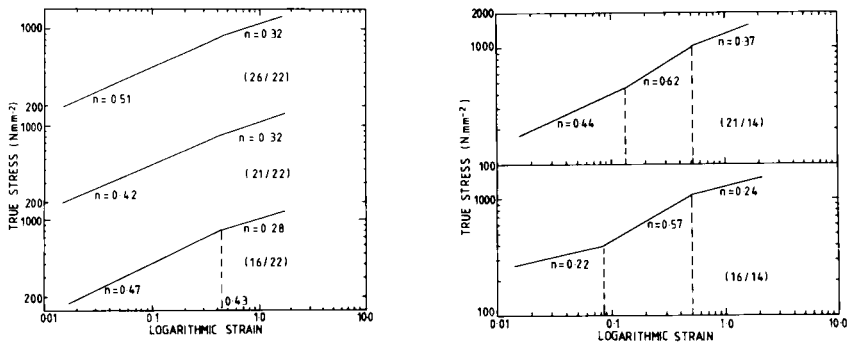


Fig.5. Logarithmic stress-strain relationships for 22% Ni - Chromium and 14% Ni - Chromium alloys.

To compare the deformation response of the above steels plane strain compression tests have been carried out to a plastic strain of 2, i.e. far greater strains than are available in tensile tests. Log σ /log ϵ plots are shown in Fig. 5. and the gradient of the graphs gives n , the work hardening exponent. It is clear from these plots that the alloys containing 22% Ni have only two regimes of work hardening, whereas the alloys containing 14% Ni show three. A further difference between the two groups of alloys is that the 14% Ni alloys become ferromagnetic after sufficient plastic deformation. Considering first the 22% Ni alloys, at strains > 0.4 it can be seen that the lowest work hardening exponent is obtained for the lowest Cr content, i.e. the 16/22 alloy. At the high stresses associated with these high strains the role of γ in determining the work hardening rate, by limiting cross slip, is expected to be minimal. The other important factor in controlling n is the Cr content which leads to increased lattice

friction and this accounts for the difference in n at the high strains, 16Cr having the smallest n despite having the smallest γ . At lower ϵ (i.e. <0.4 in the region where stage II hardening is appropriate) both cross slip and frictional stress are important and the role of Cr is more complex. The 26/22 alloy shows the highest value of n , implying that at this composition the friction stress dominates. Reducing the Cr content to 21% results in a very significant decrease in n , but a further reduction in Cr content apparently changes γ sufficiently so that n increases for the 16/22 alloy to a value between those of the 26 and 21 Cr alloys.

The results for the 14%Ni alloys show, as expected on the above arguments, that in the high strain (>0.5) region n is greater for the higher Cr content. In the low strain region (<0.08 corresponding again to Stage II hardening) the high Cr alloy again has the higher n value both because of the decrease in γ and the increase in frictional stress associated with the high Cr content. The intermediate range of strain (between ~ 0.08 and 0.5) does not appear in the 22% Ni alloys and it is likely that it is associated with the formation of strain-induced martensite; ferromagnetism is observed in the 14% Ni alloy after deformation. On this basis the alloy with the lower fault energy (the 21/14 alloy) would be expected to transform at lower strains, contrary to the observations. The role of Cr, in limiting movement of dislocations may, however, inhibit the formation of the necessary dislocation structure so postponing the transformation to higher strains.

Martensite transformation. Some insight into the basic dislocation mechanisms which gives rise to the formation of martensite, has been obtained in our laboratory by in-situ HVEM observations during either cooling or straining of the 16Cr/14Ni alloy as well as a 16Cr/12Ni alloy (Brookes, Loretto and Smallman, 1979). In all cases it has been found that stacking faults are formed either by emitting partial dislocations with $b = a/6 \langle 112 \rangle$ from grain boundaries or by the dissociation of unit dislocations with $b = a/2 \langle 110 \rangle$. In regions of the grain where on cooling or deformation a high density of stacking faults developed, the corresponding diffraction pattern revealed c.p.h. ϵ -martensite. On subsequent deformation or cooling, regions of ϵ -martensite transform rapidly into b.c.c. α -martensite, and indeed the only way in which α -martensite, was observed to form was from an ϵ nucleus.

Because straining or cooling could be interrupted it was possible to carry out a detailed analysis of the defect structure formed prior to a region becoming recognizably (from diffraction patterns) martensitic. In this way it could be shown that the interplanar spacing across the individual stacking faults in the austenite decreased to the (0001) spacing appropriate to ϵ -martensite. Figure 6. shows micrographs which reveal this change of spacing; no contrast being expected in Fig. 6(b) if the faulted $\{111\}$ planes remained at the f.c.c. spacing. The formation of regions of α from ϵ could also be followed although in this case the speed of the transformation precluded detailed analysis. Figure 7. shows a micrograph taken after the formation of α -martensite and this, together with continuous observations, show that the martensite/matrix interface changes from $\{111\}$ to the well known $\{225\}$ as it propagates. Clearly one of the important roles that the formation of ϵ -martensite plays in acting as a precursor for the formation of α -martensite is in the generation of close packed planes with ABAB, stacking so that atomic shuffles can subsequently transform these planes to $\{110\}$ b.c.c. which are of course stacked ABAB.

In view of the necessity that glide of $a/6 \langle 112 \rangle$ partials takes place before either ϵ or α martensite can form, it is not surprising that the role of

Cr in lowering γ but increasing the friction stress can give rise to the complex strain hardening behaviour noted above.

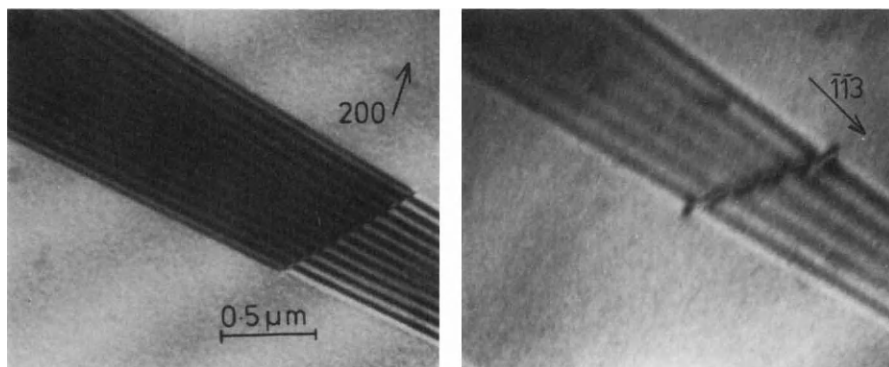


Fig. 6. Electron micrographs of stainless steel after in situ cooling showing (a) overlapping stacking faults and (b) residual contrast arising from a supplementary displacement across the faults; beam direction $[031]$.

HARD METALS

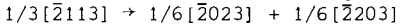
The transition metal carbides are a very important group of compounds, providing precipitates in low alloy steels which control grain size and flow strength and in tool steels providing major alloying additions. Perhaps the most significant role for the carbides is in cutting tools and dies. In all of the applications the high elastic limit and hardness of the carbides are particularly important but there is a necessity for some toughness. In the case of cemented carbide composites for cutting tools the toughness is improved by adding Co (which is also essential for successful sintering of WC powder composites) and it is clear that the Co relieves imposed stresses by plastically deforming during use of the cutting tool. It is equally clear, however, that there is a necessity for WC itself to deform plastically since only in a few regions between the WC grains is there adequate Co to accommodate the imposed shape change although, as will be discussed later, the evidence is that there is a Co layer around all WC grains.

In this brief review it will not be possible to discuss the deformation characteristics of all the transition metal carbides and attention will be concentrated on WC, perhaps the most important carbide with the possible exception of Fe_3C . In the following sections the deformation mechanisms in WC and grain size strengthening together with the related problem of abnormally large grains will be discussed.

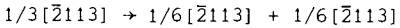
Slip Systems in WC

The structure of WC is hexagonal with $c/a = 0.976$ having tungsten atoms located at 0, 0, and 0 and carbon atoms at $2/3$, $1/3$ and $1/2$. There have been many investigations aimed at determining the slip systems in WC, but the degree of agreement between the investigators is limited. The earlier work led to the conclusion that the operative slip systems were $[0001]\{10\bar{1}0\}$ and $\langle 11\bar{2}0 \rangle \{11\bar{0}0\}$, but in the more recent studies the $\langle 11\bar{2}3 \rangle \{11\bar{0}0\}$ slip sys-

tem has been clearly identified. There is however significant disagreement as to the detailed slip mechanisms which operate. Thus Johannesson and Lehtinen (1971) and Bolton and Redington (1980) both suggest that the $1/3 \langle 11\bar{2}3 \rangle$ dislocations dissociate on the $\{2\bar{1}\bar{1}2\}$ according to



On the other hand, Hibbs and Sinclair (1981) from a study of WC single crystals and Greenwood, Loretto and Smallman (1982) examining WC-Co composites suggest that $1/3 \langle 11\bar{2}3 \rangle$ dislocations dissociate on the $\{01\bar{1}0\}$ into two identical partials as follows:



A critical assessment of the evidence for these two dissociations (Greenwood, Loretto and Smallman, 1982) shows clearly that the second reaction is the only one for which there is unambiguous evidence. An example is shown in Fig. 8. The fact that the $1/3 \langle 11\bar{2}3 \rangle$ -type dislocations exist as pairs of $1/6 \langle 11\bar{2}3 \rangle$ partials separating stacking fault indicates that the stacking fault energy of WC is not high, even though it is a covalent compound.

Measurements made on both polycrystalline WC-Co and single crystals of WC

indicate a value around 50 mJm^{-2} . Undissociated dislocations with $b = [0001]$, $1/3 \langle 11\bar{2}0 \rangle$ and $1/3 \langle 11\bar{2}3 \rangle$ have also been observed, with $1/3 \langle 11\bar{2}0 \rangle$ predominating in undeformed WC or WC-Co. During deformation these dislocations are glissile but from the magnitude of the increase in fault density it is clear that the $1/6 \langle 11\bar{2}3 \rangle \{10\bar{1}0\}$ deformation mode is very important to the plasticity of WC.

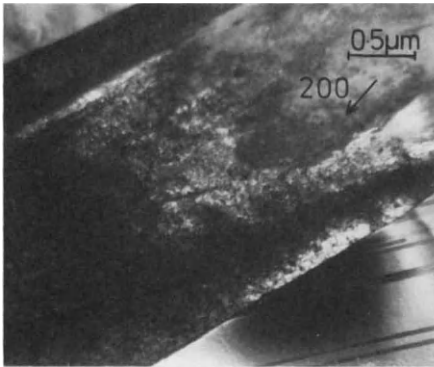


Fig. 7. Electron micrograph showing an α -martensite platelet and the austenite-martensite interface; beam direction $[011]$.

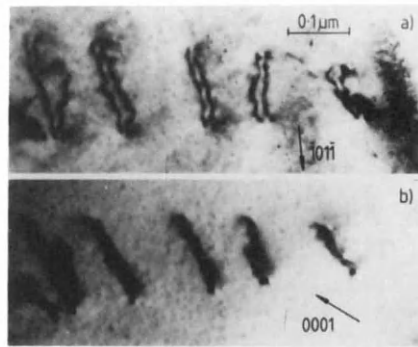


Fig. 8. Electron micrographs showing $1/6 \langle 11\bar{2}3 \rangle$ partial dislocations and associated stacking fault on $(0\bar{1}10)$ in WC-Co.

Fig. 9. shows schematically the perfect structure (a) of WC projected onto the slip plane ($1\bar{1}00$) and the faulted structure (b) by displacing the top layer of W over the layer of C atoms by $1/6[11\bar{2}3]$. The preference for slip on $\{1\bar{1}00\}$ rather than the basal planes may arise from the fact that fewer W-C bonds must be broken per carbon atom and also that $1/6 \langle 11\bar{2}3 \rangle$ fault vector preserves the trigonal prismatic coordination of the carbon atoms by tungsten atoms. Since WC is highly stoichiometric with directional bonding between C and W it is to be expected that faulting would have to

maintain the number and angular relationship of the W-C bonds. These factors would ensure that the P-N stress for the movement of dissociated dislocations on $\{1\bar{1}00\}$ is relatively low.

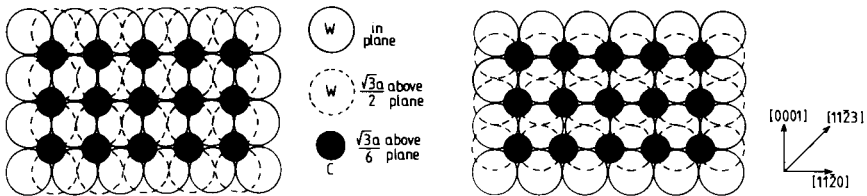


Fig.9. $(1\bar{1}00)$ projection of WC structure (a) perfect and (b) faulted by $R = 1/6[11\bar{2}3]$ (after Hibbs and Sinclair 1981).

The significant observation that deformation takes place by the movement of $1/3\langle 11\bar{2}3 \rangle$ dislocations as $1/6\langle 11\bar{2}3 \rangle$ partials shows that cobalt, although it does deform plastically, is not essential for polycrystalline ductility, since the combination of $1/3\langle 11\bar{2}0 \rangle$ and $1/3\langle 11\bar{2}3 \rangle$ dislocations provides the required number of independent slip systems for a general shape change and the Peierls stress is lower than it would be if dislocations of $b = [0001]$, $1/3\langle 11\bar{2}0 \rangle$ or undissociated $1/3\langle 11\bar{2}3 \rangle$ dislocations were to control deformation. WC is therefore correspondingly less prone to fracture at low strains. In fact one of the main sources of fracture in WC-Co composites is the presence of a significant number of abnormally large grains and in the following section this aspect will be considered further.

Grain size control of WC-Co composites. As with metals, the grain size of WC-Co composites has an important effect on the mechanical properties; the smaller the WC grain size the higher is the hardness but the lower the transverse rupture strength. Control of the amount of Co and the sintering conditions enables the grain size and hence the mechanical properties to be optimised for specific applications. The influence of Co content on hardness shows that at 25% Co the hardness is significantly reduced because of the increase in average grain size. An additional method of grain size control involves the use of grain growth inhibitors such as chromium carbide (Cr_3C_2), vanadium carbide (VC) and tantalum carbide (TaC). Typical optical micrographs illustrating the influence of Cr_3C_2 addition to a WC-10%Co composite are shown in Fig. 10. Observations on samples containing 25%Co show that there is no corresponding grain refinement effect when the same amount of Cr_3C_2 is added. Although the average grain size is decreased from $1\mu\text{m}$ to about $0.4\mu\text{m}$ by Cr_3C_2 additions to the 6% and 10% Co alloy there is still a significant number of abnormally large grains (defined as grains with diameters ≥ 5 times the mean grain diameter) present and these are grains which are likely to be associated with fracture. The properties of such a composite are therefore not as good as might be expected in a material of uniform mean grain size. The origin of the large grains therefore needs to be understood since if they could be eliminated the toughness of the composites would be correspondingly improved without a reduction in hardness.

STEM/EDX analysis has shown (Birmingham, 1981) that all WC grain boundaries appear to contain a significant amount of Co; even when there is no diffraction or micrograph evidence, EDX clearly shows a significant Co count over and above the background. In addition it has also been shown that detectable amounts of Cr are present both in the Co lakes and the Co in boundaries in composites to which Cr has been added. These observations, taken in conjunction with the fact that Cr acts as a grain refiner but that no refinement occurs in the WC-25%Co alloy, strongly suggest that a minimum Cr concentration in the Co is necessary for grain refinement. The presence of abnormally large grains in the WC-Co composites thus implies that the boundaries around such grains were at least initially very mobile during sintering and that this high mobility is associated with a low Cr concentration. On this basis a more intimate alloying of Co and Cr before sintering could be beneficial and lead to WC-Co composites with significantly improved grain size distribution and hence resistance to premature fracture.

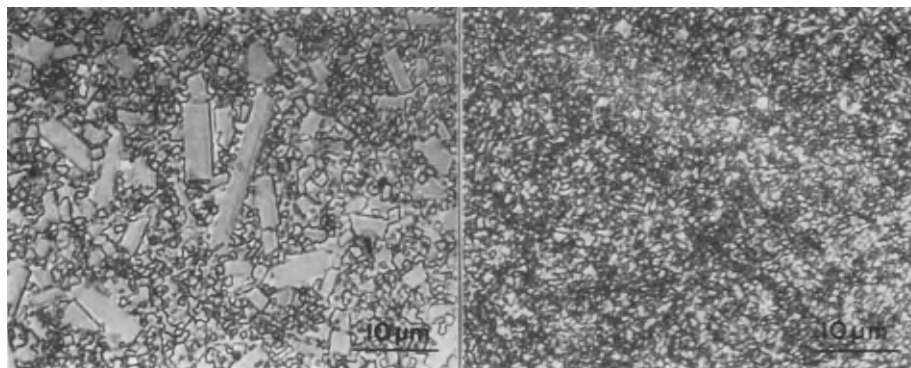


Fig.10. Micrographs of (a) WC-10%Co and (b) WC-10%Co + Cr_3C_2 .

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Microstructural Design and Control of Sintered Hard Materials

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ABSTRACT

The importance of microstructure in the four technologically important groups of hard materials, namely, tool steels, cemented carbides, ceramics and so-called super-hard materials is discussed. Powder technology opens new ways for tailoring the microstructure of such materials to their specific application conditions. Some basic principles for controlling the size of the individual crystals and the phase distribution in such materials are outlined.

KEY WORDS

Cutting materials: tool steels; cemented carbides, special ceramics, super-hard materials; microstructural geometry: size, arrangement, distribution, and contiguity of crystals; mechanical properties: hardness, toughness, wear resistance, and strength.

INTRODUCTION

High resistance to wear and failure (arising from both mechanical or thermal effects) are the most significant properties of the industrially important hard materials, which are used in applications such as metal cutting and forming, and rock fracture. In the laboratory, these two properties are most usually assessed by measurements of hardness (which is qualitatively related to wear resistance) and strength (or toughness). High wear resistance and toughness are mutually exclusive; a bilaterally favourable combination has not been found in any element or compound.

Successful ways to produce materials capable of withstanding the extremely hostile operating environment during metal cutting have been to toughen the hard phases by adding a component having higher fracture energy, or to harden the tough phases by adding a component of high hardness. The performance of such composites is determined by the properties of the individual components and by their microstructural features, i.e. by the size, the shape, the spatial distribution and the mutual arrangement of the hard and the tough phases.

Conventional fabrication techniques such as melting and casting often do not allow the microstructure to be designed in an optimum way; the powder metallurgy route including sintering or hot pressing is usually advantageous or even mandatory. Figure 1 shows the cutting tool materials used in industry in a graph adapted from Becker (1981), indicating the ranges of hardness, strength and temperature stabilities. The classical tool materials known as high speed steel (or tool steel) and cemented carbides (often referred to as hardmetals), both invented around the turn of this century, dominate the cutting tool industry, principally due to their high toughness, while ceramics and the specialty high hardness materials have at present a small yet secure niche in a number of special problem areas, where they provide the only acceptable solutions. In this paper, the importance of microstructural design in these four groups of materials will be discussed, with particular reference to their use in metal cutting applications.

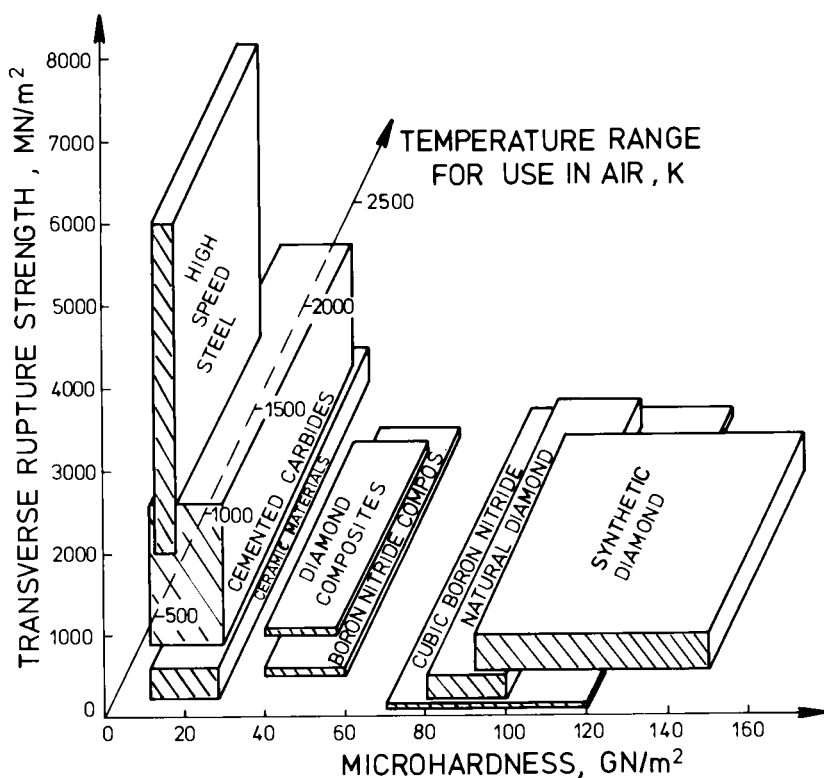


Fig. 1. Schematic diagram of the property ranges of hard materials used in metal cutting applications. The hatched areas show room temperature properties, the temperature axis gives the maximum range of application in air disregarding temperature dependence of properties (data adapted from Becker, 1981).

HIGH-SPEED STEELS

The most successful cutting materials are the large variety of tool steels. Their essential microstructural features are hard carbide particles with a size between 1 and 20 μm dispersed in a steel matrix (martensite hardened by submicron carbide precipitates). An inhomogeneous distribution of primary carbide particles is unavoidable in large-sized ingots due to segregation during solidification. The banded structure and the large variation in carbide particle sizes (Fig. 2) result in anisotropic mechanical properties, distortion during hardening (necessitating grinding to maintain tolerances), and reduced toughness and wear resistance.

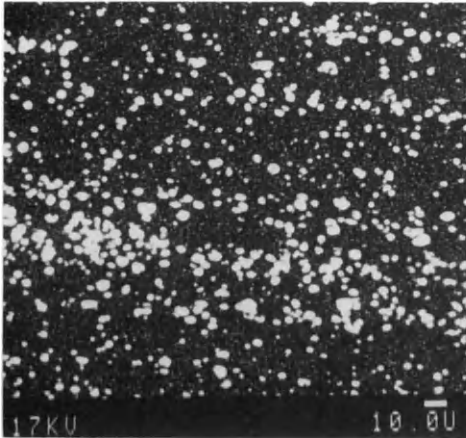


Fig. 2. Conventional high-speed steel. Note the heavy banding and wide size distribution of carbides. (Scanning electron micrograph).

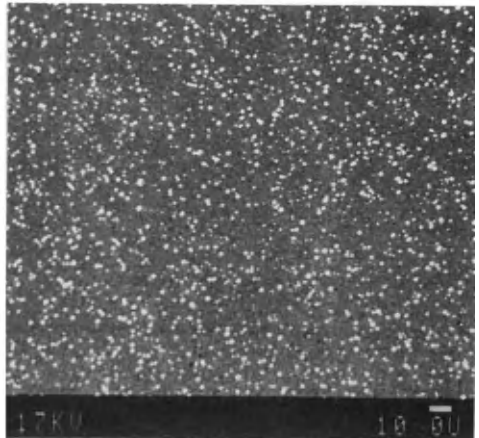


Fig. 3. High-speed steel prepared by powder metallurgy. Note the uniform carbide distribution. (Scanning electron micrograph).

Improving the microstructure has been a major concern of tool steel producers during the last 70 years and great progress has been made. A major breakthrough was the achievement of a more suitable microstructure by using extremely small ingot sizes, i.e. atomized powders to prepare material for rolling or, more recently, pressing and sintering of tool shapes. Several commercial processes using isostatic cold and hot pressing or isostatic cold pressing and sintering have been developed (Hellman, 1970; Dulis, 1972; Takigawa and co-workers 1981; Podob and co-workers, 1981). The products show a much more homogeneous distribution of fine carbides in a narrow size range (Fig. 3), and pronouncedly better performance.

Figure 4 shows a comparison of the out-of-roundness distortion during hardening, the grindability in continuous and interrupted plunge grinding and the drilling performance in soft and in hard steels. Though these significant improvements were not always reproducible and achievable, and though the advantages of sintered high-speed steels have been reduced by developments in casting technology, the trends are nevertheless significant. Efforts to improve the microstructural design of high-speed steels lead to improved performance in practical applications. Future development seems possible in two directions; one is to reduce the amount of expensive alloying elements by avoiding large clustered carbides, and the other one is to increase the

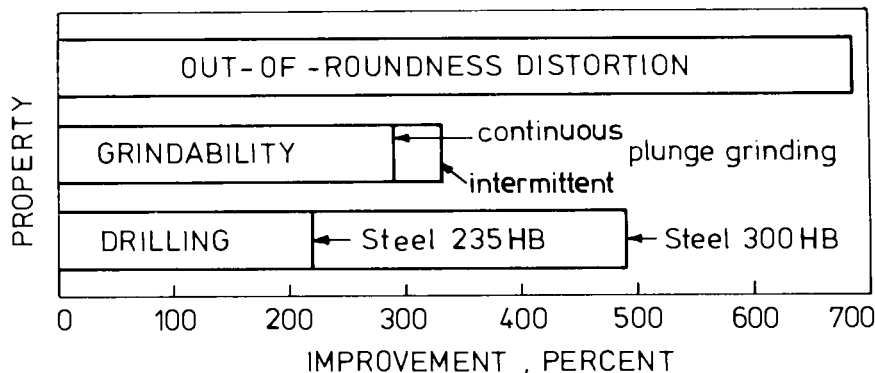


Fig. 4. Comparison of some properties of a conventional and a powder-metallurgy high-speed steel. Improvements are given in relation to the conventional material (data taken from Dulis, 1972).

carbide content of sintered tool steels by mechanical alloying in order to fill the gap between present high-speed steels and cemented carbides.

Close control and quantitative assessment of the microstructure must play a decisive part in these developments. Little work has been done to date in this direction with a few notable exceptions; Werlefors, Eskilsson and Ekelund, (1979) characterized the arrangement of the carbide particles by the distribution of the distances between nearest neighbours. Clustering and banding can be described quantitatively in this way. Together with the size distribution of the carbide particles (and, if relevant, their shape) these microstructural parameters can be determined completely automatically by modern image analysers connected to a light microscope in the case of coarse carbides, or in the case of fine carbides or those of variable composition by using detection means possible with scanning electron microscopy.

CEMENTED CARBIDES

For high stock removal rates, cemented carbide tools usually provide the best compromise between sufficient toughness and high wear resistance. This is due to the exceptionally successful combination of hard carbide particles and a more or less ductile binder phase. The reasons for this success are in part due to the special microscopical features of these composites (Fig. 5). The carbide particles form a rigid skeleton which can bear high loads even at elevated temperatures without significant plastic deformation. The binder fills the spaces in between forming a continuous network as well which precludes unimpeded crack propagation through the brittle carbide.

Since Gurland showed how microstructures may be quantitatively described, cemented carbides (particularly the straight tungsten carbide-cobalt grades) have become model alloys for such studies. A considerable amount of theoretical knowledge is available for interpreting the numerous empirical relationships between mechanical and physical properties (i.e. hardness, fracture toughness, transverse rupture strength, abrasive wear resistance, modulus of elasticity, coercivity, thermal conductivity) and microstructural parameters (i.e. volume fraction, domain size and mean linear free path of the binder,



Fig. 5. Typical microstructure of a coarse straight grade cemented carbide (grey: tungsten carbide, black: cobalt). Note that both phases form a continuous network in three dimensions. (Scanning electron micrograph)

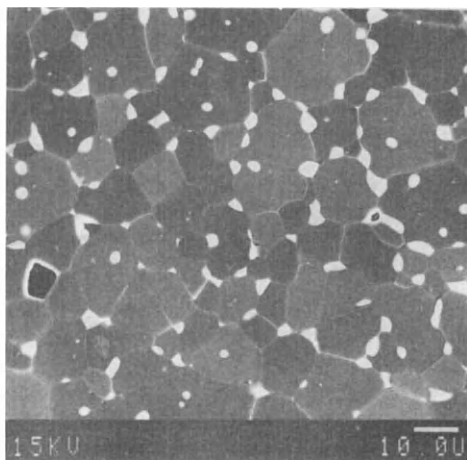


Fig. 6. Microstructure of a heat treated alumina-zirconia composite (grey: alumina, white particles: zirconia). Note: for strengthening, finer zirconia particles are used. (Scanning electron micrograph)

relative amounts of binder/carbide and carbide/carbide interfaces or contiguity, size and size distribution of the carbides, size and location of flaws etc). Recent work by Gurland and co-workers (Gurland, 1979; Nakamura and Gurland, 1980) and by Zum Gahr and Fischer (1981) give prominent examples. (For recent reviews of earlier work see Fischmeister, 1982; Gurland, 1979; Exner and Gurland, 1970; Exner, 1979, 1982).

In the complex application of cemented carbides in metal cutting, some empirical rules for optimum microstructural design have been established, some of which have been described in the patent literature. Due to the difficulties of assessment of the parameters relevant in cutting applications (see, for example, Almond, 1982; Sessions, 1982) a more scientific approach to microstructural design for optimum cutting performance has not yet been successful. With the invention of coatings to reduce wear, and with the increasing knowledge about high-temperature wear mechanisms, the requirements on the microstructure of cemented carbides used for cutting applications are becoming more precisely defined (Trent, 1977, 1982; see also Almond 1982; Lardner, 1982). According to Lardner (1982), high-temperature strength is the limiting property for increasing cutting speeds for coated tools. This property can be measured in the laboratory much more easily than wear resistance, and further improvements in performance of uncoated and coated cemented carbide tools seem to be possible from existing grades or new alloy compositions. A better understanding of the correlations between microstructural design, the basic properties relevant to cutting performance, and actual performance in practical applications should not only reduce the unreasonably large number of grades offered by the hardmetal manufactures (see, for example, Brookes, 1979) but also promote the prevailing trend of the growing usage of cemented carbides at the expense of high-speed steels (see, for example, Smart, 1982).

CERAMIC CUTTING MATERIALS

It has been long recognized that ceramic materials have the capability for metal cutting at high speeds due to their excellent chemical stability and retention of hardness at high temperatures which makes them resistant towards more usual wear processes. Compared with the metallic hard materials discussed previously, they suffer from low toughness (Fig. 1) and fail readily when subjected to mechanical impact or thermal shock.

Until recently, alumina has been the only ceramic tool material exploited commercially. Its success compared with other ceramic materials is based on the careful design of a dense and fine microstructure with equiaxed grains achieved by pressureless sintering using small magnesia additions as sintering activators. A commercial alternative to pure alumina is an alumina-titanium carbide composite which apparently owes its better thermal shock resistance to a somewhat increased thermal conductivity. It is, however, more expensive since hot pressing must be used for compaction of mixed powders. Even so, mechanical impacts, thermal shock as well as severe temperature gradients cause drastic mechanical failure which restricts the volume of ceramic tools used in cutting to less than 2 % of that of cemented carbides (Lardner, 1982).

The new concept of microstructural design raises the hope of overcoming the inherent high thermal expansion and low strength of ceramics. Utilising the positive volume change of about 4 vol.% which the tetragonal modification of zirconia undergoes during cooling when transforming to the monoclinic modification, the detrimental thermal contraction of alumina can be reduced in the critical temperature range, and its crack resistance can be decisively improved. The details of the transformation and the strengthening mechanisms involved have been extensively investigated by Claussen and coworkers (for reviews see Claussen and Hasselmann, 1980; Petzow and Claussen, 1977, 1981). Zirconia is admixed in the form of very fine particles up to 30 vol.% during ceramic processing. Figure 6 shows a coarse microstructure obtained by extended annealing. Maximum effects are achieved at particle sizes in the sub-micron range. Preliminary experiments presented by Grewe, Kolaska and Reiter (1979) prove that alumina strengthened by zirconia has distinct advantages compared with a conventional alumina cutting material when cutting ferrous materials (Fig. 7).

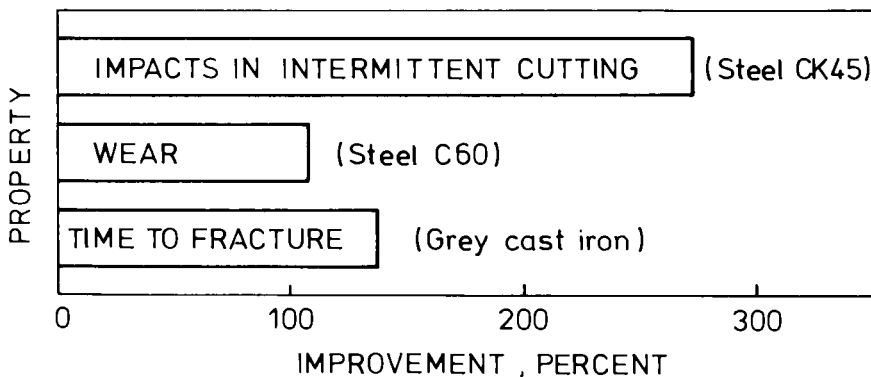


Fig. 7: Comparison of parameters characterizing the cutting behaviour of a conventional alumina grade and a grade containing dispersed zirconia (data from Grewe, Kolaska and Reiter, 1979).

Sophisticated microstructural design is an outstanding feature of this development. Figure 8 shows the particle size dependence of the transformation temperature together with experimental and estimated thermal expansion curves. Thermal contraction during cooling is significantly reduced in the critical temperature range between 300 and 600 °C by adding 13 vol.% ZrO_2 with a size $< 0.5 \mu\text{m}$. The idealized curve indicates how a near zero expansion could be obtained by using carefully selected volume fractions of particles in three size ranges (approx. 0.2, 0.5 and $1.0 \mu\text{m}$ respectively). The particle size effect in the transformation temperature hysteresis also allows the design of alumina based materials with optimized toughness. As discussed by Claussen (1976) and Petzow and Claussen (1977, 1981) the size of the zirconia particles must be large enough to transform during cooling in order to form microcracks which are able to absorb fracture energy by crack opening (microcrack toughening), or small enough to retain the tetragonal structure to room temperature and to transform into the monoclinic structure only in the stress field of a propagating crack (transformation toughening).

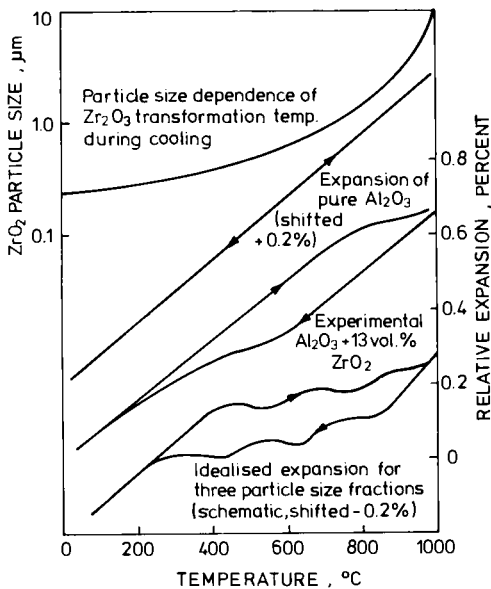


Fig. 8: Particle size dependence of the temperature of tetragonal/monoclinic transformation of zirconia, experimental expansion curves of pure alumina and of an alumina-13 vol.% zirconia composite, and predicted expansion of alumina containing three size fractions of zirconia particles (according to Petzow and Claussen, 1981).

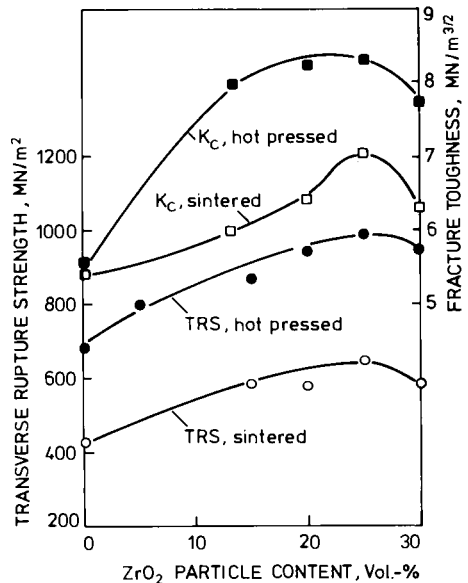


Fig. 9: Strengthening and toughening effect of zirconia additions to hot-pressed and pressureless sintered silicon nitride (according to Claussen and Jahn, 1978).

More recently, silicon nitride has aroused much interest as a potential cutting tool. However, dense materials are only obtained by hot pressing which makes this material expensive and the optimization of microstructure difficult.

Pressureless sintering is possible if alumina is added, and the so-called Sialons (Si-Al-O-N composites) have actually been shown to be superior to cemented carbides as well as to alumina cutting grades for special applications. Extremely high cutting speeds are possible (1000 m/min for cast iron) and superior cutting behaviour for hardened steel and superalloys has been reported (Jack, 1982). No information on microstructural design of these materials is yet available. However, improvement up to 60 % in fracture toughness and 50 % in strength have been reported by Claussen and coworkers (Claussen and Jahn, 1978, Petzow and Claussen, 1981) for silicon nitride based materials by adding up to 30 vol.% zirconia using the same concept as described above for alumina (Fig. 9). Other oxides (e.g. mullite or spinell) can be improved in the same way (Petzow and Claussen, 1981). By increasing the toughness of ceramic tool materials to higher levels than shown in Fig. 1, more of the potentials of ceramic materials for cutting application may be exploited industrially in the future.

SUPERHARD MATERIALS

The extreme hardness of diamond seemed to be the ultimate answer to wear problems. However, the brittleness of diamond crystals, the reaction of diamond with ferrous or nickel alloys and in air at elevated temperature, and the high price places severe restrictions on its use in cutting applications. With the production of man-made diamond and the nearly as hard boron nitride, a group of new superhard materials with microhardness exceeding 100 GN/m², ten times harder than conventional tool materials (see Fig. 1) became available. Both synthetic diamond and cubic boron nitride are expensive as is natural diamond, but they offer possibilities for toughening. By using transition metals as sintering aids and high pressure and high temperatures, polycrystalline materials are produced which have been introduced as cutting materials. Little information on the microstructure of these materials is available due to the fact that metallographic investigations are difficult. Recent investigations by Brookes and Hooper (1982) have shown that bridges are formed between the individual crystals during hot pressing and that the holes between these bridges are filled by the metallic residues used for activating bonding during hot pressing. The random orientation of the crystals inhibits gross cleavage while the high defect density and twin boundaries seem to favour crack propagation. Boron nitride materials have much finer grains (< 10 µm) with a similarly bridged composite structure.

With the little information available, optimization of microstructure will take considerable time. A microstructural design similar to that of conventional cemented carbides, i.e. a metal network interpenetrating a rigid skeleton of the hard phase would seem to be advantageous. Metal bonded diamond and boron nitride based composites have been introduced to the cutting field under various trade names (see, for example Pipkin, Roberts and Wilson, 1982, Diblik, 1981). Bonding is the major problem in these developments and interlayers must be used to get good bonding while brittle layers must be avoided (Bronshtein and coworkers, 1982). Technological know-how as well as scientific understanding are both in a rudimentary stage. Extreme secrecy about compositions and details of production processes prevails.

When the problems of bonding and of microstructural optimization are solved, the success of superhard materials presently restricted to some particular applications, as, for example, cutting of aluminum-silicon alloys or fibre glass (Smart, 1982, Lardner, 1982) is expected to expand into a much larger field to cutting applications.

ACKNOWLEDGEMENT

Thanks are due to Dr. G.J. Rees for critically reading the manuscript and valuable suggestions for improvement.

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Some Reflections on the Competition Between Hard Materials in Industrial Applications

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ABSTRACT

With metal cutting as an appropriate example the competition between the new superhard materials (diamond and cubic boron nitride), ceramics, cemented carbide and high speed steel is discussed. The hardness-toughness relationship of the different materials is presented as is their consumption in industry over the latest few decades.

It is pointed out that new materials are generally only slowly accepted by the market with coated cemented carbide as a conspicuous exception. Application areas for the new superhard materials and ceramics are indicated with emphasis on differences in their characteristic properties in comparison with new coated cemented carbide grades.

As a result of recent development it appears unlikely, at least in the near future, that prices and availability of raw materials will be a very important factor in the choice between the different hard materials.

KEYWORDS

Cutting materials; cemented carbides; ceramics; indexable inserts.

INTRODUCTION

In many recent articles - and in particular those which have served as a basis for discussions about national materials policies and similar general subjects - we have been reminded of the importance that efficient tool materials have for our civilisation. It is often pointed out that the replacement of stone tools by those of bronze and later by those of iron forms a series of markstones in human progress which may not yet have come to an end.

If we limit ourselves to the latest 100 years the first new tool material that should be mentioned is high speed steel, which was introduced at the turn of the century. With tools of this steel, there was a large

increase in the productivity of the manufacturing industry. Even more spectacular were the effects of cemented carbide, which, after a humble start in the late 1920's and the 1930's became a major industrial tool material after World War II. There have been estimations that most goods from the mechanical engineering industry would cost some 25% more, with a concomitant reduction in our standard of living, but, for the cemented carbide tools. These are now well established but have recently been the subject of an increasing competition from the 'old' tool materials, ceramics and diamond (to which we may associate man-made cubic boron nitride) which are showing signs of a 'come-back', as well as from improved high speed steel.

The aim of this paper is to give some comments on how future developments could affect the relative importance of these tool materials in industrial applications. It hardly needs saying that I can only deal with a few aspects of this vast subject in this paper. Quite arbitrarily I shall confine myself to metal cutting materials and start with some more general observations of tool materials for such applications. In this part I have used information from a number of excellent review papers as well as from discussions with many colleagues (Anonymous, 1981; Kalish, 1979; Kono and Ushida, 1982; Lardner, 1978; Lévesque, Leroy and Boisot, 1976; Rüdiger, 1977; Schedler, 1981; Shiratori, 1981; Thümmel, Holleck and Prakash, 1981). It has only exceptionally been possible (or practical) to refer a specific piece of information to a specific source since more or less the same facts are used in all papers although presented in slightly different contexts and with somewhat different emphasis. In the second part of my paper I shall as an appropriate example give a more detailed account of trends in the use of different materials in indexable inserts - one of the most important industrial tool products.

GENERAL REMARKS ON MATERIALS IN METAL CUTTING TOOLS

The various materials used in the edge of metal cutting tools are arranged according to their combination of hardness and toughness in Fig. 1.

The hardest material, diamond, has only limited application as a cutting material, since more than 80% of the material that is cut is iron-based and the chemical reaction between carbon and iron is rather rapid at temperatures reached in high speed cutting. Cubic boron nitride, which is almost as hard as diamond, is much more stable in contact with hot iron-based material and has a considerable potential as a metal cutting material (Wentorf, DeVries and Bundy, 1980; Taeyaerts, 1981).

Next in hardness are the different ceramics (Abel and Gomoll, 1980; Furukawa and Hagio, 1981; Inamori, 1982), which can be divided into those mainly containing oxides (almost exclusively aluminium oxide with minor additions of zirconium dioxide), and those mainly containing nitrides (at present only with silicon nitride as the major constituent). Mixed, or black, ceramics consist of a mixture of aluminium oxide and titanium carbide (often with various other additions) and have properties between those of ceramics and cemented carbide.

The various types of cemented carbide come next in hardness. Among these, those with titanium carbide as the major carbide constituent are often singled out as a special group characterised by high hardness and low toughness. However, by far the largest group of cemented carbide has tungsten carbide as a major ingredient.

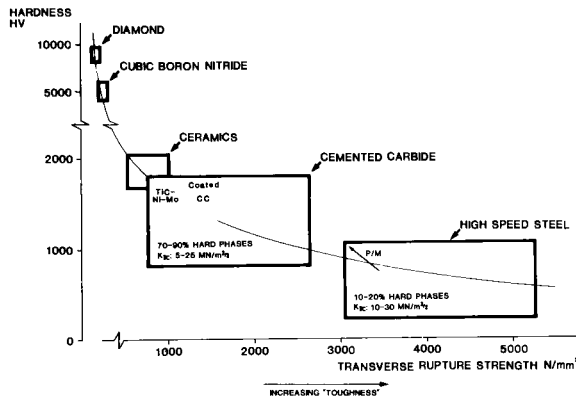


Fig. 1. Hardness (Vickers) and transverse rupture strength of different tool materials.

The classical quasi-binary WC-Co cemented carbide grades are still widely used in particular in mining applications and in cutting of cast iron. Virtually all steel-cutting grades, however, contain two carbide phases; one is tungsten carbide, WC, which always has a composition close to the stoichiometric one, and one is a mixed (Ti,Ta, Nb, W)C cubic carbide. In addition metal cutting grades contain about 10% of the binder cobalt phase, which has variable amounts of tungsten carbide in solid solution. Close to 50% of the most important cemented carbide product for metal cutting, the indexable insert, are now coated by a few micrometers of titanium carbide, titanium nitride and alumina, often in combination. This takes place by CVD processes that operate at around 1000° C. (For a review, see for instance Hintermann, 1979; König and co-workers, 1981; Schintlmeister and co-workers, 1980).

The toughest of the commonly used materials for metal cutting is high speed steel. Through the development of P/M production routes grades with higher contents of carbide forming elements (e.g. ASP 60 with 6 wt% of vanadium) and hence a higher hardness than the classical grades were introduced some 10 years ago. Very recently, tools of high speed steel with coatings of titanium nitride have been developed. These coatings have been made by PVD processes, which operate at substrate temperatures below 500° C and hence do not cause overheating and concomitant deterioration of the properties of the steel.

The consumption of the different tool materials over the last few decades is summarised in Fig. 2. This is based on figures that are only approximate but, I believe, sufficiently accurate for some cautious general comments. An obvious first observation is the long period of time necessary for a more general acceptance of a new tool material. Even 20 years after the introduction of high speed steel the yearly consumption was only a few thousand tons. It took 15 years for cemented carbide to reach

1000 tons and the consumption of ceramics for metal cutting, of which there was much talk already during the 1950's, has only in recent years reached a few dozen tons. Seen in this perspective there would seem to be little hope for the ultra hard materials on this side of 1990.

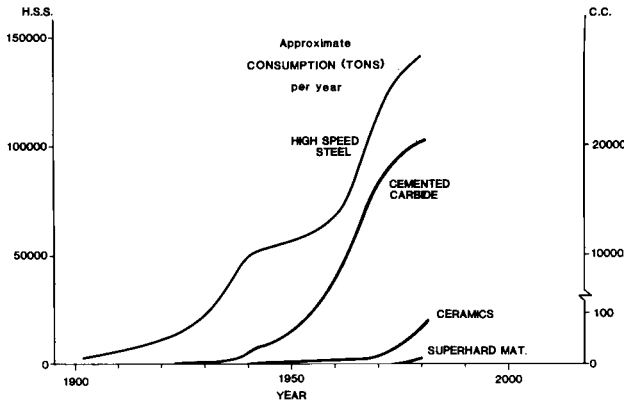


Fig. 2. World consumption of different tool materials.
(For high speed steel and cemented carbide, total consumption per year, for ceramics and superhard materials only consumption for cuttings tools.)

Although somewhat uncertain it appears from Fig. 2 that the establishment of cemented carbide tools before and during the war years had a strong restraining effect on the volume development of high speed steel tools in the 40's and 50's. However, by 1960 the two tool materials seem to have found their respective application areas and the volume development has been nearly the same with an average yearly volume increase of about 4 per cent up to 1980 after which it has flattened out to about zero. Undoubtedly, conclusions based on these crude figures require some qualifications. Firstly, whereas more than 90% of high speed steel has been used in metal cutting ever since the introduction of this steel, the corresponding figure for cemented carbide, being around 50%, has probably increased somewhat during the 1960-1980 period (but not the last few years due to the increase consumption for oil prospection and production). Hence, for this application the volume increase may have been higher than the average increase in cemented carbide consumption given in Fig. 2. Secondly, there has been a large improvement in the efficiency of cemented carbide tools by the introduction of coated grades the amount of chip produced per unit weight of cemented carbide was roughly doubled and this is not reflected in the curves of total consumption. However, even allowing for this we can hardly draw any other conclusion than that high speed steel by and large has maintained its position as a metal cutting tool material over the latest two decades. If successful technical-commercial solutions to the coating of high speed steel tools are found it could do even better in the years to come.

During the last two years or so the consumption of both high speed steel and cemented carbide has been more or less constant. The economic recession has a much higher influence on this than any minor loss of market to other tool materials. However, there is no doubt that ceramics are increasingly used in metal cutting (the volumes indicated in Fig. 2 only refer to consumption for metal cutting). Will this trend continue and have a similar effect on cemented carbide as the latter had on high speed steel in the 1940's and 1950's with the modifications due to a much smaller overall economic growth, or will an 'equilibrium' quickly be established? And what about the ultra-hard materials, in particular cubic boron nitride? With lower production costs these could have a strong impact on the tool material market. Finally, what effects will developments concerning production methods, machines and work materials used in the manufacturing industry as well as fluctuations in price of scarce raw materials, such as tungsten and cobalt, have on the use of the different tool materials?

These are very vast questions which easily inspire many lengthy and inconclusive discussions. In a (probably vain) hope to avoid this and be more specific, I shall confine myself to the most important single type of metal cutting tool products, the indexable insert.

TOOL MATERIALS IN INDEXABLE INSERTS

The introduction of the indexable insert had a large influence on the increased use of cemented carbide. The advantages in comparison with the classical brazed tools are fairly obvious. Regrinding could be abolished at the same time as up to eight corners of the insert could be used by simply turning it around. The mass-produced inserts could easily be given geometries that permitted efficient chipbreaking and they could be coated by just adding another step in the established production line.

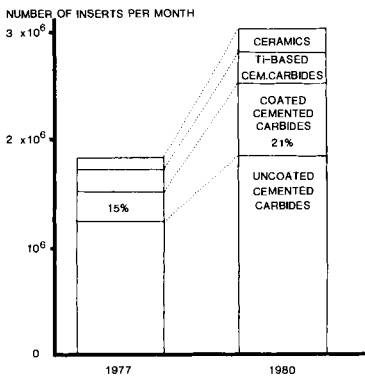


Fig. 3. Monthly consumption of indexable inserts with different cutting materials in Japan (Doi, 1982).

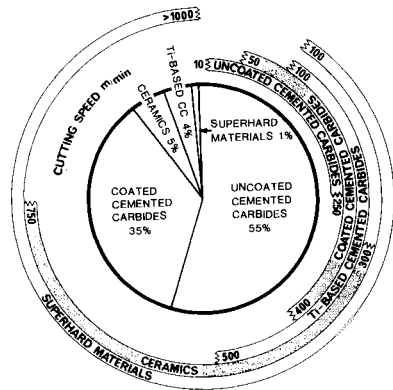


Fig. 4. Use of different hard materials in metal cutting. Mainly after Kalish and August (1980).

As shown in Fig.3, the Japanese market for indexable inserts is at present about 35 million pieces per year (Doi, 1982). It is reasonable to assume this to be about 10% of the world market outside Eastern Europe and China. Hence 300-400 million inserts are yearly consumed in the Western World. The present proportions between the different insert materials are indicated in Fig 4, in which the cutting speed necessary to exploit the potential of the materials are also indicated. This figure illustrates the situation on the whole Western World market, which is somewhat different from that in Japan given in Fig. 3.

As seen from Fig. 4, the ceramic materials require very high cutting speeds (above 200 m/min in cast iron) in order to give an advantageous production economy. One important factor behind the increased use of ceramic cutting material is the development of more rigid and powerful built-in machines permitting high cutting speeds with only small vibrations (which is very important when brittle tools are used) and a good protection of the environment. One other important factor is the improved processes in producing tough ceramic materials, which is a result of the extensive activities in ceramics in many countries often as part of energy-related R&D programs.

It is a reasonable guess that these factors will continue to contribute favourably to the use of ceramic materials in metal cutting in the near future. In addition the new nitrogen-based ceramics (Jack, 1980) may further increase the applications in which ceramics offer economically advantageous solutions. In particular, through the combination of a low thermal expansion and a good thermal conductivity silicon nitride based ceramics are likely to extend the use of ceramics into milling operations. Partly based on studies in this laboratory the applications of the different ceramic cutting materials can be illustrated with the aid of Fig. 5 which refers to about 4% of the total insert market. As we have also indicated in this figure, the use of the expensive CBN cutting tools will be mainly confined to high speed machining of hardened steel. (It should be mentioned in passing that these tools have opened an interesting alternative to grinding (Werner, 1982).)

The future relative importance of the different hard cutting materials mentioned in Fig. 4 - and in particular to which extent they will make further inroads upon the cemented carbide market - will, of course, depend on their price. Raw material costs are very low for the oxide ceramics, and should be modest also for silicon nitride based materials which contain very common elements. With cheaper processing these groups of materials could become even more competitive. The ultra hard materials, in this context mainly cubic boron nitride, are expensive to produce due to the extreme high pressures necessary during processing. If any of the ideas to circumvent this problem (e.g. an inexpensive coating technique) turns out to be successful, this situation could be drastically changed, but at present the prospects for such a development seem very dim indeed.

The future use of ceramics in metal cutting tools will, of course, also depend on the further development of competing materials, that is mainly cemented carbide. The coated variety of this has taken a large part of the potential area of ceramics. Introduced in 1969 it has steadily increased its share of the insert market. There is still scope for improvements as shown by the continued introduction of new grades, in which there are continuously better combinations of the advantageous properties of the hard and inert ceramic phases at the surface and of the tough substrate. A micrograph of a new coated cemented carbide grade is shown in

Fig. 6. A weak point is the limited high temperature strength of the cemented carbide substrate which leads to unacceptable deformation at the highest cutting speeds. It is hard to see how a substrate with much better high temperature strength can be developed but it is premature to exclude the possibility for further improvements, and, in addition, there is still some uncertainty to which extent the highest cutting speeds really can be efficiently exploited.

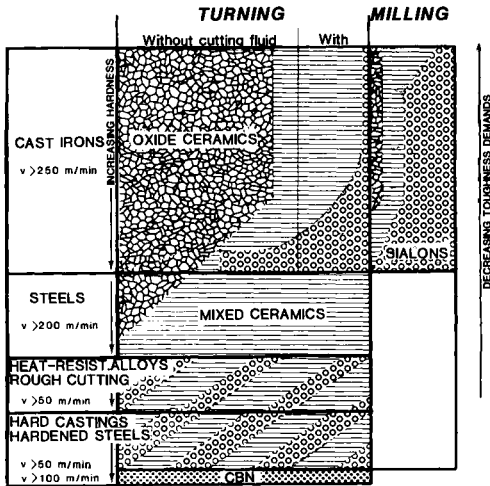


Fig. 5. Approximate use of ceramic materials in different metal cutting operations.

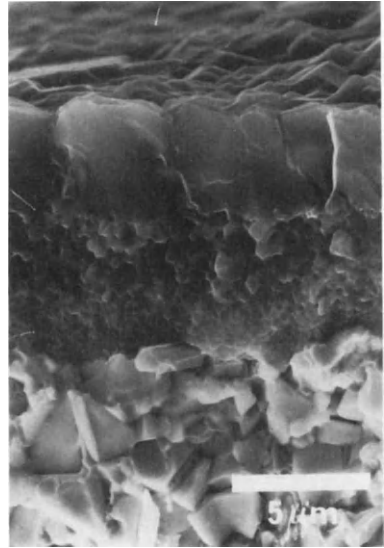


Fig. 6. Micrograph of a modern coated cemented carbide grade (Sandvik GC 415). The three coating layers are titanium carbide, alumina and titanium nitride (5, 3 and $1\mu\text{m}$ respectively).

One argument against cemented carbide is its reliance on scarce raw materials. Without tungsten cemented carbide, the good combination of toughness and wear resistance that characterises present grades cannot be obtained. Although tungsten prices fluctuate there are abundant sources of tungsten spread around the world and at present prices there seems to be little risk of supply problems. Cobalt could be more difficult, but the cemented carbide industry only needs 10% of the yearly production of this metal and is not extremely sensitive to modest price variations. Tantalum gave grave concern a couple of years ago, but by trimming tantalum contents and using more scrap as raw materials, the cemented carbide industry has sharply reduced its requirements of tantalum which has contributed very much to the recent very large drop in tantalum prices. In this context the much extended capacity for using cemented carbide scrap as a raw material should be stressed. This will alleviate any problem due to disturbances in raw material supply. Thus the arguments on this point are considerably weaker at present than just a few years ago and are not likely to influence the competition between cemented carbide and ceramics very much in the foreseeable future.

A further point to add to this discussion is the new grades of titanium carbide-nickel grades (sometimes included under the heading cermet) for which improved methods of production are also being developed. (For a review see e.g. Hara and co-workers, 1982; Kalish and August, 1980; Shiokawa, 1981.) This very hard (and correspondingly less tough) type of cemented carbide will not depend on raw materials supply and could somewhat limit the scope of oxide- and nitride-based ceramic materials.

No certain conclusions can be drawn from the various points discussed above. In the end even a factor not known today may turn out to play the most important role. A reasonable guess is that the new (or reborn) harder cutting materials will somewhat increase their share of the cutting materials market during the 1980's. However, as when cemented carbide was introduced, the established materials will, perhaps after a period of more limited growth, reassert their position, which will also be strengthened through the strong R&D activity that the competition from other hard materials will stimulate.

ACKNOWLEDGEMENTS

I wish to thank many colleagues, in particular Mr B Fredriksson of Fagersta AB and Mr M Lagerquist of Sandvik AB, for valuable discussions, and Sandvik AB for permission to publish this paper.

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The Current Status of Diamond and Cubic Boron Nitride Composites

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ABSTRACT

The development of high pressure technology which has allowed the synthesis of diamond and cubic boron nitride has also resulted in the production of a new and exciting range of ultra-hard ceramic-type materials. These materials, polycrystalline diamond and cubic boron nitride composites, offer distinct advantages over their single crystal counterparts and hold the promise of a fascinating future in all areas connected with material removal and other specialist usages.

KEYWORDS

AMBORITE, SYNDITE, Polycrystalline, Hard Materials, Synthesis

HISTORICAL INTRODUCTION

The production of the SYNDITE and AMBORITE range of synthetic diamond and cubic boron nitride (CBN) composites is a two stage process. The first stage involves the production of the diamond and CBN grit and the second, the compaction of this grit into the required shape. Both these processes involve the use of the same ultra-high pressure chemical technology. In this introduction, a brief account will be given of the relevant aspects of the high pressure synthesis process and earlier attempts to produce composite materials.

Diamonds are synthesised world wide using the same process that was first developed in the 1950's. Basically, this process involves taking a carbonaceous starting material (typically graphite) and subjecting it to extremely high pressures whilst in the presence of a molten solvent-catalyst. The solvent-catalysts used are normally taken from the transition elements - Cr, Mn, Fe, Co and Ni - which, in the presence of carbon, form the so-called intermediate metal carbides. Under the correct thermodynamic conditions, the graphite crystals are intercalated by the molten solvent and subsequently go into solution in the form of modified macro-molecules of graphite. Such macro-molecules are then in a position to spontaneously form diamond nuclei or to grow on to existing diamond nuclei.

Although the basic science of diamond synthesis has not altered over the past 25 years, there have been massive changes in high pressure technology. In the early days of diamond synthesis, the control of the pressure-temperature environment was very imprecise, the reaction volumes small and the lives of the various high pressure components short.

Nowadays, however, high pressure systems are vastly improved, reaction volumes are relatively large and stable, and the whole process can be very accurately controlled. A good measure of this improvement can be seen by reference to Fig. 1 which shows that, over the years, there has been a systematic increase in the maximum diamond size commercially available.

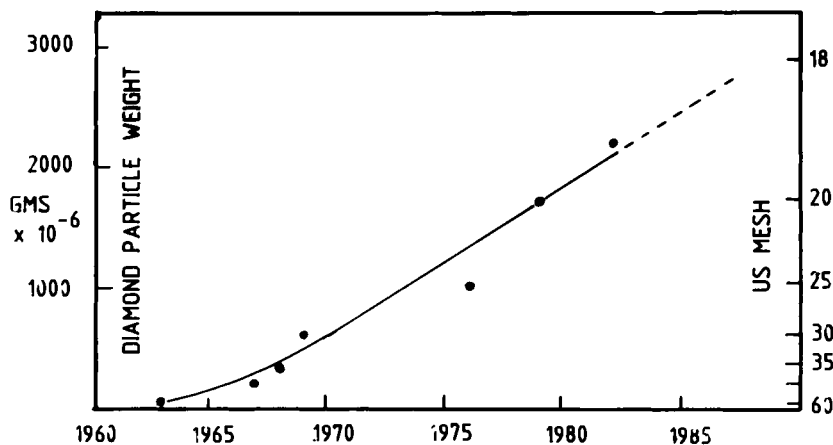


Fig. 1 Maximum commercially available grit size by year

Without this improvement in high pressure systems engineering, the present range of composite products would have been neither technically nor economically feasible. This is because similar conditions of pressure, temperature and time necessary for the synthesis of good quality diamond crystals of the order of 20 US mesh are also required in the production of SYNDITE and AMBORITE composites. The type of apparatus most commonly used today to manufacture diamond and composite materials is based upon the well known 'belt' apparatus. This system is capable of routinely generating pressures in excess of 6 GPa. However, the absolute pressures used will depend upon the type of composite required and the chemical method adopted for its synthesis. An important consideration is that, using the same apparatus and techniques, the synthesis of a good quality one carat diamond can take as long as one week, yet the manufacture of a composite containing, perhaps, tens of carats can be accomplished in only an hour or so.

So far, only the synthesis of diamond has been discussed. However, the synthesis of cubic boron nitride can be regarded as physically similar yet chemically different. Certainly, the pressures and temperatures required for the production of diamond and diamond composites are almost identical to those used in the synthesis of CBN and CBN composites. However, the chemistry of the two processes is quite dissimilar. Instead of graphite as the starting material, hexagonal boron nitride is used, together with a solvent-catalyst chosen from the alkali and alkali earth metals and their nitrides and borides. In addition to the above, alloys of aluminium with Fe, Co and Ni have also been shown to be effective in the production of fine CBN grits. As in the case of diamond, it is possible, by a judicious combination of solvents and conditions, to make various types of grit. These vary from irregular, rough particles for resin bond grinding applications to strong and well-developed crystals for use in vitreous and

metal bonded tools where the cutting forces are high. By using certain chemical additives, the colour of the grit may also be varied and, in the case of CBN, this can be from a clear amber colour to pitch black.

ULTRA HARD MATERIAL COMPOSITES

It is valid to ask the question - just what is an ultra-hard material composite? By virtue of the fact that diamond and CBN are the two hardest substances known, such a composite can, in principle, represent any material which contains either of these components. However, the strength of a composite body as an integral unit will depend largely upon the nature of the bonding mechanism. Four basic categories can be identified and will be discussed below. Here, diamond composites are used to illustrate the basic ideas, but these concepts equally apply to CBN.

(A) (DIAMOND - ORGANIC) COMPOSITES

Within this class of composites fall all the well-known resin bonded grinding wheels which are used for the machining of carbides and hardened steels. Here, the diamond particles are physically (rather than chemically) bonded into the composite. To assist keying of the particles in the bond, the diamonds are purposely made irregular in shape and with many included angles. Electrodeposited coatings of nickel and copper have also been shown to be effective in improving the physical bonding of the particles within the matrix.

(B) (DIAMOND - NON-ACTIVE METAL) COMPOSITES

All the well-established metal bonded grinding wheels, saws and drills fall within this group of composite materials. In this case the diamonds are more strongly and more rigidly held within the metal matrix than in the case of organic resins. Consequently, much stronger diamonds (known commercially as Saw Diamond Abrasives - SDA) having a well-defined crystal morphology can be used. However, the bonding between the diamond and the metal matrix (typically bronze and cobalt) is still weak by chemical bonding standards. This is borne out by the fact that in a deliberately broken composite the fracture often tends to go round the diamond leaving exposed and intact crystals protruding from the surface.

(C) (DIAMOND - ACTIVE METAL) COMPOSITES

Elements that readily form carbides can react to form strong bonds with a diamond surface. Such elements include the transition metals Ti, Ta, W, V, Zr and Cr and the non-metals Si and B, and can be used either alone or in combination with other metals to form the diamond composite.



Fig. 2 A weak, intergrown polycrystal caused by interference during synthesis

Composites of this type were first made by Blainey and Custers (1966) and several firms now market different variations world-wide. Some types of active metal composites require the use of high pressure and temperature techniques whilst others can be made at room pressure in a suitable oxygen-free environment. An example of the latter variety is the product CDA-M in which small diamond particles are strongly bonded together with an active metal coat to produce larger particles suitable for grinding wheels. In these composites, the adherence of the diamonds to the metal is so strong that fracture lines, when the composite particle is broken, tend to run through the crystals rather than around them.

(D) (DIAMOND - DIAMOND) COMPOSITES

In all of the previously discussed groups, the structure and strength of the composite relies on the type of interfacial bonding between the diamond particles and a matrix material. In no case does there exist any direct diamond to diamond bonding. However, this is not so in the case of the SYNDITE range of composites, for example, where this type of bonding is very substantial indeed. The amount of matrix metal in this class of composites is minimal and, in fact, serves little purpose other than the necessity of its presence to form the composite in the first place. This bonding mechanism, which results in a mass of randomly intergrown diamond crystals, accounts for the very remarkable physical properties of SYNDITE shown in Table 1.

The possibility of producing composites containing considerable diamond - diamond bonding has been recognized since the earliest days of diamond synthesis. During the early attempts to produce good quality single crystals, the result was often the production of unwanted intergrown polycrystals of the type illustrated in Fig. 2. These arise from many individual crystals interfering with each other during growth and, as a consequence, are structurally very weak, with limited application. One of the more interesting attempts to use this type of approach to make, for example, a cutting tool is illustrated below.

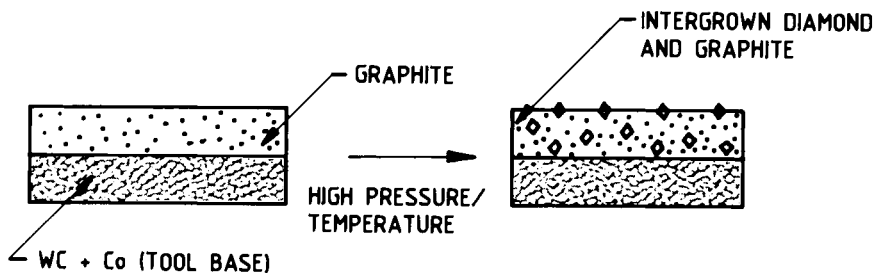


Fig. 3 Synthetic Ballas Tool

Here, graphite is placed in contact with a tungsten carbide substrate and subjected to the high pressure and temperature necessary for diamond synthesis. Under these conditions, cobalt, either from the tungsten carbide or from a separate source sandwiched between the two, is allowed to impregnate the graphite and convert it to a mass of intergrown diamond in intimate contact with the tool base.

The use of graphite as a starting material for the production of this type of diamond composite (sometimes referred to as synthetic ballas) has been studied extensively by Vereshagin and Borovikov (1973). The nature of the composites formed appears to be critically dependent on the type of starting graphite used and the Russians have made substantial claims for these products. However, few of these compacts are available in the West and verification of these claims has been difficult.

Today, composites of the SYNDITE type are made using diamond micron powder as the starting material and two procedures are commonly used.

In the first method, illustrated in Fig. 4, a mixture of micron sized diamond, finely divided cobalt (or any other solvent - catalyst metal) and graphite is placed in a suitable high pressure apparatus and subjected to diamond synthesis conditions. At high pressures and temperatures, the graphite is intercalated by the molten cobalt and converted to new diamond which can act as a cement to bind the old diamond together. The result is a strongly intergrown diamond composite which may, if required, be bonded to a metallurgically compatible base, such as tungsten carbide, during the synthesis cycle.

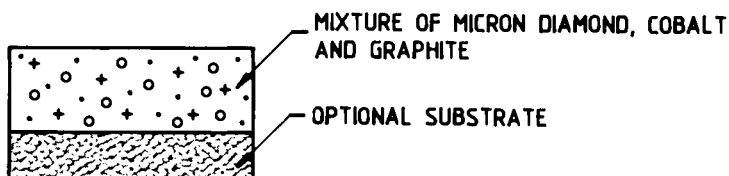


Fig. 4 Composite Reaction Volume (Method 1)

It should be noted, however, that successful diamond sintering in the absence of graphite also relies on the provision of a driving force. However, in a system where the pressure is perfectly hydrostatic and no temperature gradients exist, the only driving force for the reaction would arise from the minimization of surface energies and would be very low. This is, in fact, experimentally verified in the well-known diamond reconstitution experiments Field (1979). In these experiments, micron diamond is blended with cobalt and placed in a high pressure vessel where, under the correct conditions, carbon atoms diffuse from a hot to a cold zone and grow on to a seed diamond to produce a gem quality crystal.

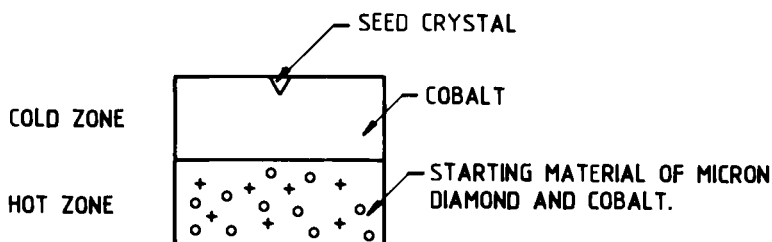


Fig. 5 Diamond Reconstitution Reaction Volume

The high pressure capsule, in these cases, is deliberately designed to minimize pressure and temperature gradients. It is indicative that, even after experiments lasting about a week at synthesis conditions, the physical properties of the micron diamond starting material, extracted from the capsule as an extremely hard and integrated slab, are in no way comparable with those of SYNDITE.

The second commonly used procedure for the manufacture of composites involves the use of infiltration techniques. Here, micron diamond is placed adjacent to a source of cobalt or other suitable metal and subjected to synthesis conditions.

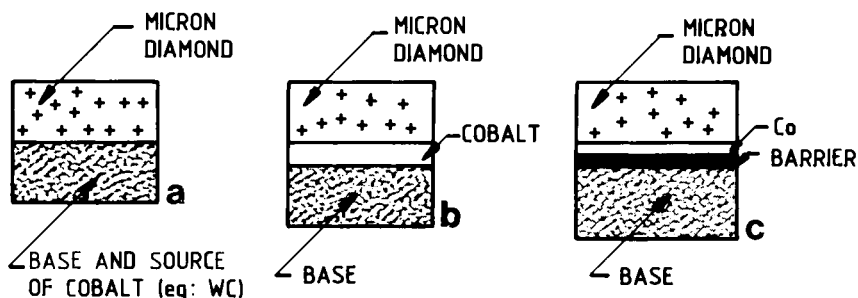


Fig. 6 Typical Composite Reaction Volumes (Method 2)

At these extremely high pressures, substantial plastic deformation of the diamond particles takes place at the contact areas between the crystals. However, at points away from these contact areas - at places which can aptly be described as voids - the diamond surfaces see little, if any of this pressure. Consequently, at the existing high temperature, these surfaces are quickly converted to graphite. As the cobalt melts it begins to infiltrate the voids in the compact and reconvert any graphite present to new diamond, thus completing the cementation process between the existing crystals. The infiltrating cobalt also acts in such a way as to clean the diamond surfaces and sweep any impurities out of the sintering region in a process analogous to zone refining. Variations of this procedure are illustrated in Figs. 6 (b) and (c).

Compacts of the SYNDITE type have many advantages over those produced directly from graphite, not the least of which is that one is able to control the particle size of the diamond in the final composite.

MECHANISM OF COMPOSITE FORMATION

The role of the cobalt matrix during the formation of diamond composite materials has been extensively studied by Pipkin and Wilson (1977) using X-ray diffraction techniques. In a series of experiments covering a range of synthesis conditions - from grossly underheating to severely over-heating, the high pressure capsule - the presence of the 002 graphite peak and relative positions of 111 cobalt and diamond peaks of the partially completed composite were examined. Normally, the cobalt and diamond X-ray reflections overlap but in the presence of dissolved carbon, the cobalt peak will show a shift to smaller Bragg angles. By observing these line shifts, Pipkin and Wilson were able to identify six stages of composite formation.

During the first stage of the synthesis cycle, and whilst temperature is increasing, the single, broad diamond reflection indicates that plastic deformation and hence densification of the diamond particles takes place below the melting point of the cobalt metal. However, within the voids between the diamond grains, where pressure is low, graphitization is occurring and a relatively large graphite peak is detected at this stage (Figs. 7 (a) and 8 (a)).

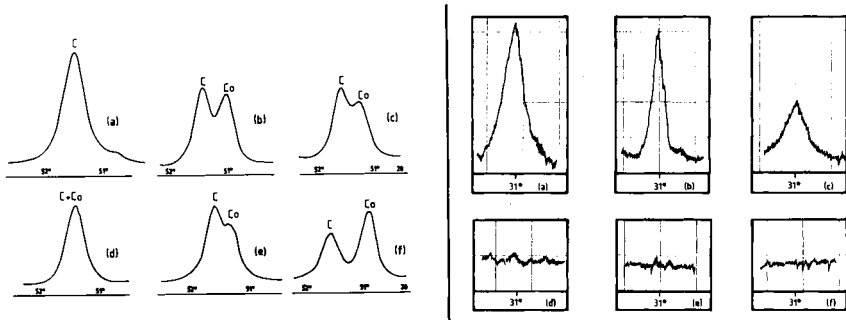


Fig. 7 & 8 Effect of increasing synthesis temperature on the relative positions of the diamond and cobalt 111 peaks and extent of graphitization

Above the cobalt melting temperature, molten cobalt begins to sweep between the diamond grains, dissolving graphite as it does so. This stage in the process is indicated in Figs. 7 (b) and 8 (b) where the shift in the cobalt peak to a Bragg angle of 51.02° corresponds to a theoretical carbon solubility of 3.6 percent atomic. Since in no samples was a greater carbon solubility noted at this stage of the cycle, it is likely, therefore, that the cobalt is completely saturated with carbon at this point and hence excess graphite will still remain. Further increases in temperature result in a shift of the cobalt peak back to larger Bragg angles. This is indicative of a lower carbon content and the precipitation of carbon, therefore, in the form of diamond. Some graphite still remains, however, and it is likely that a stable situation persists at this stage between the rate of carbon precipitation and graphite solution (Figs. 7 (c) and 8 (c)).

At higher temperatures, the precipitation process is completed and no graphite remains. When this stage is reached, the cobalt reflection interferes with that of diamond and a single composite peak is observed (Figs. 7 (d) and 8 (d)). It is at this stage that the maximum intergrowth and hardness of the composite are achieved.

During the last two stages where the temperature is increased still further, but which is not normally permitted to occur, the cobalt peak shifts yet again to lower Bragg angles. This suggests that diamond is re-dissolving into the cobalt as the conditions move out of the diamond stable region and the solubility of carbon in cobalt increases.

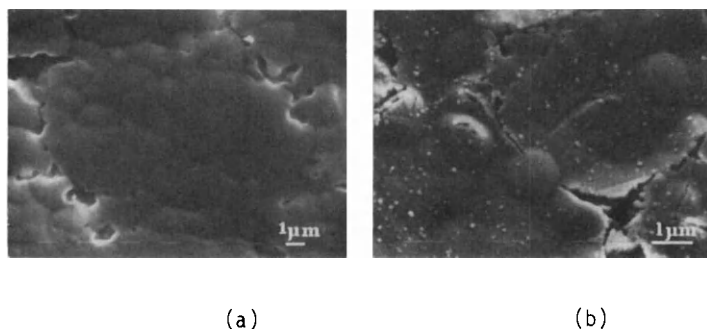


Fig. 9 Sub-grain structure caused by plastic deformation observed in SYNDITE (a) and AMBORITE (b)

It has also been determined that the plastic deformation of the crystals which takes place during the early stages of the synthesis cycle also results in the formation of a mosaic substructure. For example, using diamond particles of 1-3 microns as the starting crystallite size, a mean sub-grain diameter of 0.1 microns has been measured. This type of sub-structure is also observed in AMBORITE, the cubic boron nitride composite, which is manufactured in much the same way as its diamond counterpart (Figs. 9 (a) and (b)). In some cases the sub-grains can even be seen to be crossing the grain boundaries between the original starting crystals. The presence of a sub-structure is considered to be an important element in the remarkable toughness of composite materials.

AMBORITE is thermally stable and can be heated to extremely high temperatures with impunity. This is due to the type of solvent-catalyst metal used during synthesis manufacture. The residual binder phase in the AMBORITE range of products is aluminium nitride and/or aluminium di-boride. Since these are both stable compounds, no dissolution of boron and nitrogen from the composite takes place. CBN composites are used mainly for the machining of extremely hard steels where tool tip temperatures are necessarily very high and such a property obviously has enormous advantages.

PROPERTIES AND APPLICATIONS

The trouble with most materials that are very hard is that they also tend to be extremely brittle and have low tensile strengths. When tungsten carbide was first commercially developed in the 1920's, it represented a considerable advance in materials development and was of major significance to the machine tool business. Because of its relatively high hardness compared with other materials of the day, coupled with reasonable levels of strength and fracture toughness, tungsten carbide rapidly gained acceptance in many facets of industry and without it, of course, diamond synthesis would not even have been possible. In a similar vein, the introduction of diamond and CBN composites a few years ago represented another distinct leap forward. Composites possess characteristics of strength and fracture toughness which are similar, if not better than those of tungsten carbide, yet are significantly harder (Table 1).

Table 1

PROPERTY (in GPa)	DIAMOND	SYNDITE	AMBORITE	WC
Knoop Hardness	56 - 102	50	41	18
Young's Modulus	964	841	680	630
Modulus of Rigidity	401	345	279	258
Bulk Modulus	541	501	405	375
Ultimate Tensile Strength	2.6	1.3	0.5	1.0
Transverse Rupture Strength	-	1.1	0.6	1.7
Compression Strength	8.7	7.6	3.8	4.5
Thermal conductivity (W m ⁻¹ K ⁻¹)	900	560	135	50-80

The hardnesses of SYNDITE and AMBORITE composites are, in fact, very close to those of diamond and CBN respectively. However, unlike their single crystal counterparts, both materials are perfectly isotropic and thus are equally hard and abrasion resistant in all directions and less prone to cleavage fracture. It is this feature, combined with versatility in shape and size, that has virtually revolutionized some aspects of the cutting

tool market and generated such wide spread interest in many other areas of industry.

Currently, composite materials are generally synthesised in the form of discs or cylinders and are available with or without a supporting substrate or backing layer. From these simple forms, other shapes can be cut, using laser or spark erosion techniques, to produce triangles, squares, rectangles and cubes depending on the type of tool required. Some of the varieties which are commercially available are illustrated in Fig. 10.

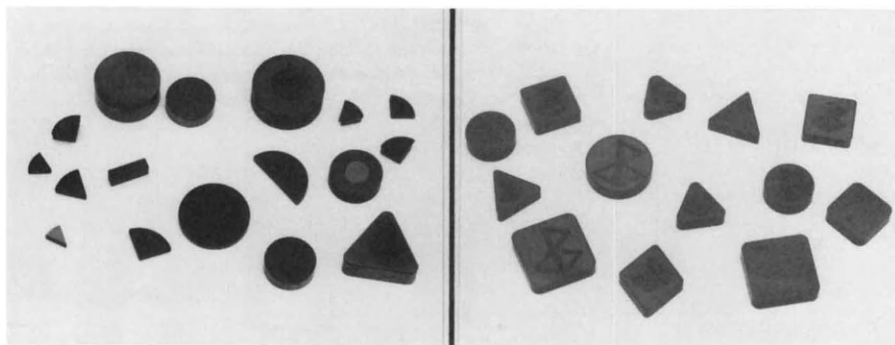


Fig. 10 Some of the various product shapes offered in the SYNDITE and AMBORITE range of composite materials

The unusual properties of diamond and CBN composites are currently being exploited in three major areas for use as cutting tools, wire drawing dies and rock drilling crowns. The literature is already well documented with these subjects and it will suffice here to briefly summarize these three categories.

As cutting tools for the machining of extremely hard or abrasive metals, both AMBORITE and SYNDITE have demonstrated that, despite their relatively high cost compared with some of the more conventional tools, massive savings in time and cost can be achieved. Indeed, some materials have proved almost impossible to cut at all, other than with composite tools and, previously, such materials could only be machined by the slow and arduous task of grinding. AMBORITE is used mainly for turning ferrous metals such as tool steels, Ni-hards and other alloys where the chemical affinity of iron and carbon would otherwise preclude the use of a diamond composite. A particular advantage of AMBORITE is its ability to withstand the repeated shocks of interrupted cuts, even when working at high speeds and heavy infeeds. Furthermore, all of these operations can be performed dry without affecting the workpiece or the tool tip. SYNDITE tools have shown to be efficient in the cutting of highly abrasive materials such as aluminium/ silicon alloys, unfired porcelain, epoxys and asbestos cements. Even tungsten carbide, in either its green or sintered state, can be machined with ease using SYNDITE products.

Already, diamond composites have made a considerable penetration into the wire drawing industry, where their remarkable resistance to abrasion has enabled die lives to be achieved which are up to two orders of magnitude

better than those obtained with tungsten carbide. There are many cases, too, where SYNDITE dies are reported to be far superior to natural diamond. The reason for this is that, because of its structural anisotropy, natural diamond tends to wear preferentially at fixed angular positions around the hole, leading eventually to a general out-of-roundness of the wire.

The use of diamond composites in rock drilling applications is still a relatively new field, but even so, some major success stories have been reported and the potential for further development is vast indeed. Radically new bit designs, which incorporate diamond composites attached to long carbide support studs have been developed. This arrangement enables the rock to be broken by shearing rather than compression and faster, truer holes can often be drilled. Drilling with composites is generally limited at present to the softer formations such as limestones and shales but it is predictable that, as experience grows and a greater expertise is gathered, a much wider variety of drilling applications will be found. In fact, it is expected that it is in this area that the greatest volumetric use of composites will be made.

THE FUTURE

Over the next 10 years or so, the future of diamond composites in which there is no direct inter-crystal bonding is likely to remain sound but technically uninspiring. The reason for this is that such products, as may be represented by the well-known resin and metal bonded systems, are already well established and mature. However, the one area that may yet stimulate further research is that involving composites with active metal bonding. Here, relatively inexpensive products, manufactured by conventional (non-high pressure) techniques, are possible. Whether such composites would ever seriously compete with SYNDITE type products would naturally be determined by considerations of performance and cost effectiveness.

Cubic boron nitride, as a crystalline abrasive, is still in its commercial infancy despite the fact that its laboratory synthesis followed shortly after that of diamond. Unlike synthetic diamond which had, of course, its own natural equivalent and could blend into the existing network of applications, CBN has had to find entirely new markets and levels of acceptance in industry. Consequently, considerable activity in the CBN composite area where there is no direct crystal bonding is likely. Systems such as resin, vitreous and metal bonds all seem ripe for further development.

Diamond and CBN composites with direct crystal to crystal bonding have only been commercially available for about 5 years and have already reached a very high standard of quality and reproducibility. Composites of this type are already well established in a broad range of industrial sectors and new applications for these materials are continuously being found. This market penetration is also likely to be enhanced over the years by a steady increase in the range of shapes and sizes offered. In principle, composites can be cut to any shape, and if a significant market need can be defined a

new configuration will be launched. Other variations will most certainly include different substrate materials, unbacked types (as is the case with AMBORITE), thermally stable composites and products which can be easily brazed to other materials by conventional methods.

A further development and utilization of composite materials is likely to occur over the next few years in non-cutting applications. For example, the excellent thermal conductivities of diamond and CBN could lead to them being used as heat sinks in the electronic or space industries. Wear resistant surfaces is another important potential area. Here, large surfaces could be created by joining several composite pieces together. Additionally, the high values of Young's Modulus and Compressive Strength for diamond composites make them ideally suited for components in high pressure studies.

The composites available world-wide already comprise a range of different chemistries where various sintering aids have been added to the original mixtures of diamond or CBN. These aids do have an effect on the final properties of the composites, allowing them to be used with great efficiency in some areas but sometimes falling short in others. Thus, it is likely that future research will also be directed towards the chemistry of composite synthesis, leading to an increase in the range of materials that can be economically machined.

Much further down the line, it may eventually be possible to produce a composite without the use of a binder phase and which would be similar to that occurring in nature in the form of carbonado or framesite. Natural carbonado is a rare polycrystalline diamond found generally in only the upper levels of a kimberlite deposit. It is extremely hard with no regular cleavage and, because it is virtually impossible to shape by cutting or polishing, it has fairly limited uses. A synthetic equivalent with similar properties of toughness and abrasion resistance, but which could be moulded to a specific shape, would have tremendous benefits and would represent just about the ultimate in composite materials.

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Development and Performance of CVD-coatings on Cutting Tools

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ABSTRACT

Coatings of refractory hard substances on cemented carbide substrates during the past decade have resulted in a dramatic increase in performance of cemented carbide cutting tools. The thermodynamic fundamentals of the chemical vapour deposition of TiN, TiC, HfN, Al₂O₃ and of combinations of carbides, nitrides and carbonitrides on cemented carbide substrates are discussed, along with the practical implementation in larger scale industrial coating facilities.

The improved performance of coated, in comparison with uncoated, tools is primarily due to the increased cratering resistance provided by coatings. The relative merits of different coating systems are strongly dependent on work material properties and chosen cutting parameters: Coatings of Al₂O₃ have excellent performance at higher cutting speeds and harder steels, but are generally inferior to nitride - and carbide - based (TiN, TiC, HfN) coatings when cutting softer steels at intermediate and low cutting speeds. The combined effect of work material properties, and cutting parameters (principally feed and speed), and tool geometry on cutting performance can be characterized through a single quantity, the cutting shear angle.

Thus, Al₂O₃ coatings generally provide superior performance under high shear angle conditions (harder steels, high speeds, negative rake geometry), where the principal mode of failure is cratering; while at low shear angles (soft steels, low speeds, positive rake geometry) the nitride and carbide based coatings tend to show better performance.

Multiphase coatings, such as TiC/Al₂O₃ combine the benefits of TiC and Al₂O₃ in the low cutting speed range, but are generally inferior to single layer Al₂O₃ coatings in the range of higher shear angles at the same total coating thickness.

KEYWORDS

Machining; cutting; CVD coatings; shear angle; aluminium oxide; hafnium nitride.

COATINGS ON CEMENTED CARBIDE

Since the first appearance of coated cemented carbide inserts in the late 1960's the market share of coated cutting tools has steadily increased to the current level of about 30-35 percent worldwide.

The initial coatings consisted primarily of 5-10 μm layers of TiC and TiN on substrates of P- and M-class cemented carbides and permitted increases in cutting speeds at equivalent tool life, in the order of 30-50% with respect to uncoated carbide tools. Further, substantial performance increases in certain cutting ranges were achieved in subsequent developments of coating systems on the basis of HfN and Al_2O_3 , the latter predominantly in connection with a sub-layer of TiC .

A large number of publications have been devoted to the description and analysis of the mechanisms of the chemical vapour deposition processes (Powell, Oxley and Blocker, 1966; Ellis, 1968; Van Houten, White and Bodie, 1961; Johannesson and Linstrom, 1975; Graham and Hale, 1982; Hara and co-workers, 1982) used in applying wear-resistant coatings to carbide substrates, and it is not the object of this paper to elaborate on these by now well-established processes. The proliferation of coating systems and extensive performance testing carried out by companies and laboratories of coated cemented carbide tool materials have generated a wealth of data reported in the literature; but, owing to the complexity of the cutting process itself, the often poorly analysed effect of different work material on the test results, as well as other variables, such as choice of carbide substrate and cutting geometry, coating material structure and thickness, and carbide/coating interface structure, it becomes very difficult to define application boundaries and find a common denominator for the observed behaviour of the different coating materials.

From field experience, it appears now fairly well established that Al_2O_3 and HfN coatings are superior to other coatings when cutting harder steels and at high cutting speeds, whereas TiN and TiC coatings as well as HfN coatings, are generally preferable to aluminium oxide in the range of lower cutting speeds and on softer work materials. Al_2O_3 also has a definite performance advantage over nitride and carbide based coatings in machining abrasive materials such as cast iron. These findings are in agreement with data reported by Graham and Hale (1982) and Hara and co-workers (1982). Thermodynamic stability and hot hardness (Graham and Hale 1982) may provide a guide for explaining crater resistance, such analyses have validity however only if interaction with the work material to form intermediate phases or extensive solid solution ranges is taken into consideration; thus, for example, in spite of considerably higher thermodynamic stability and wear resistance than TiC , TiB_2 fails as a potential coating candidate for machining steel by its known tendency to form higher borides of comparatively low melting point.

In an extensive cutting programme carried out at the laboratories of Teledyne and Sintex to study the fundamental aspects of metal-cutting processes for the purpose of optimizing tool geometries in metal cutting, coated tools from commercial sources, as well as experimental coated tools prepared in our own laboratories, were included.

Although the work is still in progress, a fairly consistent picture concerning the optimum application range of various coating classes is beginning to emerge. The functional relationships linking cutting shear angle, cutting parameters (speed and feed), the work material properties, principally shear strength and fracture toughness, and cutting tool geometry, as well as the

pressure distribution on the rake surface of the tools are now well understood and will be reported elsewhere (Rudy, 1983). Although the mathematical details are quite complex, these relationships, when applied to steel, can be generalized as follows:

(a) Metal cutting is a step process proceeding via an incremental propagation of a crack in the cutting direction; the incremental crack advance is a function of speed, feed, and material properties, principally fracture toughness.

(b) Secondary, or "packet" shear, resulting in the characteristic serrations of turning chips occurs within defined ranges of cutting shear angles and is the product of an imbalance between fracture toughness and shear strength of the work material. The lamellae spacings of these shear packets decreases with increasing cutting speed, and increases with increasing shear strength of the steel and the feed rate (Fig. 1).

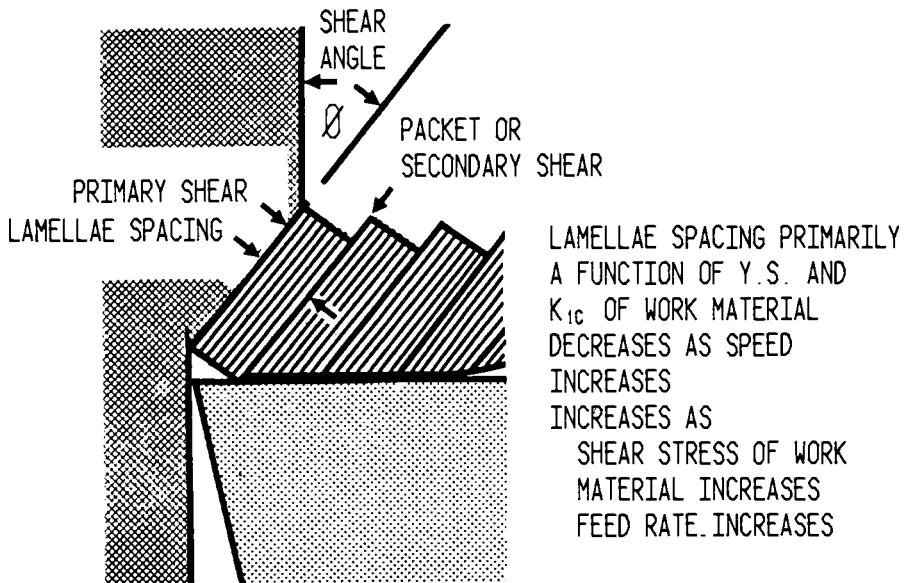


Fig. 1. Chip formation nomenclature

(c) Within the range of "packet" shear, the average cutting shear angle remains practically unaffected by the cutting parameters (speed, feed, geometry).

(d) Within the region where only primary shear occurs, the cutting shear angle is a single-valued function of the cutting parameters and material properties; since the fracture toughness of ordinary steels can be reasonably well related to the yield point (Knott, 1973).

The cutting shear angle (Fig. 2) increases with increasing hardness, speed, and feed rate; it also increases with increasing tool rake angle, until it reaches its natural cutting shear angle. At still higher tool rakes the

cutting shear angle coincides with the rake angle of the tool, a condition that usually exists when machining with high speed steel tools.

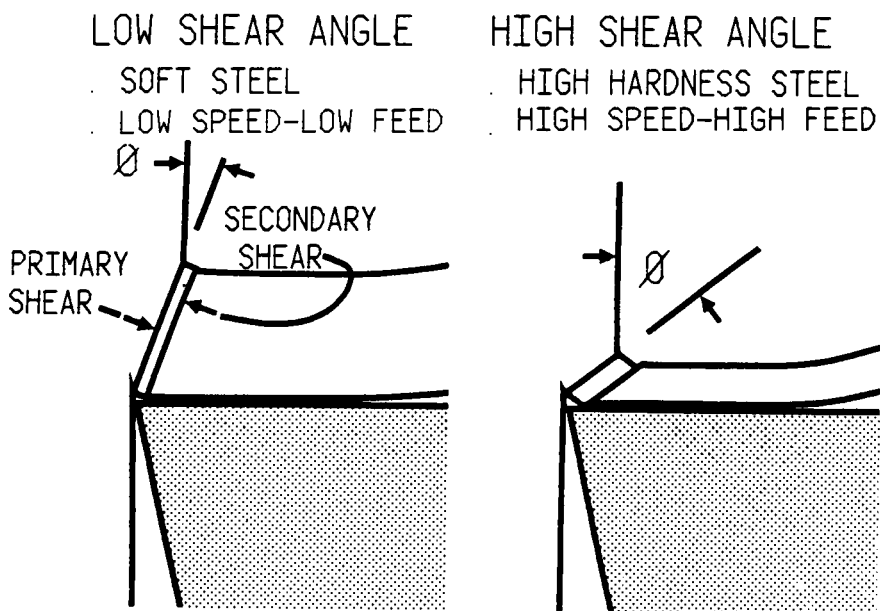


Fig. 2. Chip formation at low and high shear angles

In relating typical cutting conditions currently used in the industry (Fig. 3) we can determine that hardened steels ($R_C > 45$) are cut with appropriate carbide cutting tools at cutting shear angles between 36 and 50° ($46\text{--}122\text{ m min}^{-1}$ ($150\text{--}400\text{ sfm}$), $0.076\text{--}0.254\text{ mmPR}$ ($0.003\text{--}0.010\text{ IPR}$ feed rate)), steels in the intermediate hardness range (HRC 25-30) at shear angles between 32 and 37° , and mild steels with low yield points at shear angles between 15 and 30° , the latter angle (30°) corresponding to speeds in the order of 488 m min^{-1} (1600 sfm) at feed rates around 0.254 mmPR (0.010 IPR).

In the context of these discussions concerning cutting shear angles, cast iron can be regarded as a hard steel with low effective yield point.

Analysis of tool wear graphs such as the example shown in Fig. 4, and of representative data from the literature (Graham and Hale, 1982; Hara and co-workers, 1982), indicates that at cutting shear angles exceeding about 27 to 28° coatings of Al_2O_3 increasingly exceed in performance those based on TiC and TiN , while at lower shear angles the reverse is true. It is

interesting to note that the range of usable cutting shear angles is considerably extended upwards by HfN-coatings, especially when applied in heavier thicknesses of 12 to 15 μm ; it is readily apparent that HfN coatings offer a considerable improvement over TiN- or TiC-coated carbide tools in the upper cutting speed ranges.

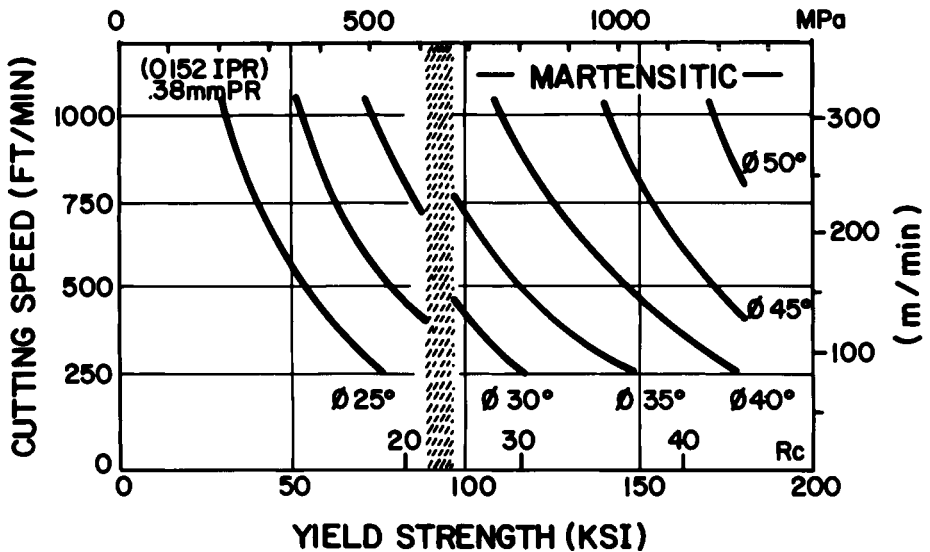


Fig. 3. Shear Angle vs cutting speed and yield strength

TABLE 1 Cutting Shear Angle

Steel	1045	4340	4340	4340	4340
Condition	Hot Rolled	Annealed	Heat Treat	Heat Treat	Heat Treat
Hardness Rc	-	16-20	22-25	28	40-45
Yield Strength MPa (KSI)	275.8 (40)	413.7 (60)	586 (85)	758.5 (110)	1241 (180)
Speed m min^{-1} (sfm)					
91.5 (300)	19.3	22.9	27.7	29.7	41.3
182.9 (600)	23.4	27.4	32.9	35.3	47.0
228.6 (750)	24.9	29.5	34.7	37.0	48.7
304.8 (1000)	26.8	31.5	37.8	39.7	52.0

Tool Geometry : BR-5; SR-5; SCEA 15, Feed 0.386 mmPR (0.0152 IPR).

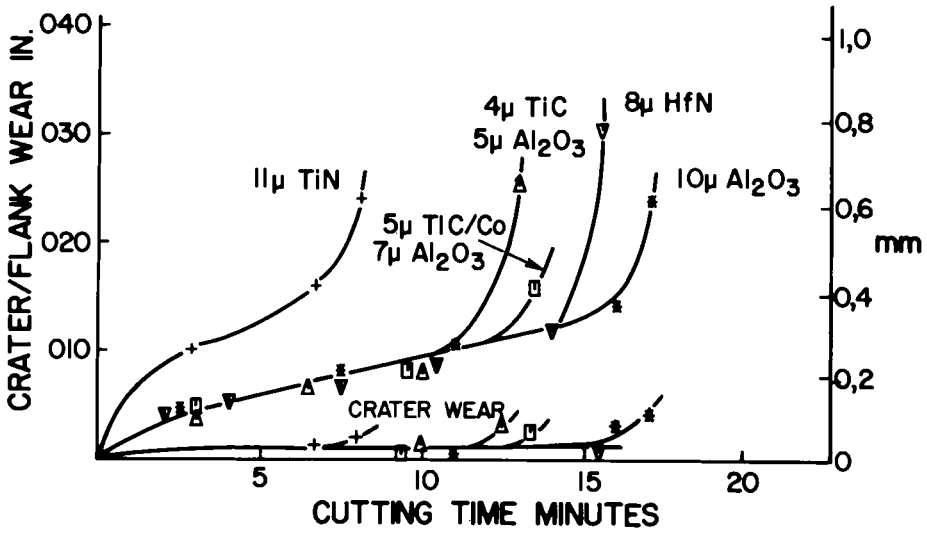


Fig. 4. Wear curves for shear angle 39°

Tool: SNG-432 Material 4340 Cutting Speed (500 sfm) 152.4m min⁻¹
BR -5° Condition HT.TR. Conditions Feed (.0101 IPR) 0.25 mmPR
SCEA
15° SR -5° Hardness RC 37/39 Dry DOC (.080 Inch) 2.03 mm

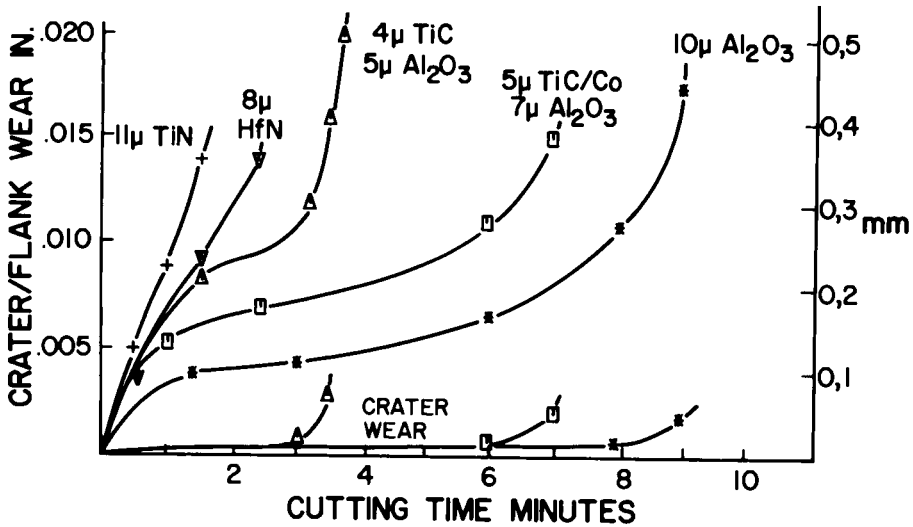


Fig. 5. Wear curves for shear angle 37°

Tool: SNG-432 Material 4340 Cutting Speed (1000 sfm) 304.8 m min⁻¹
BR -5° Condition HT.TR. Conditions Feed (.0152 IPR) 0.38 mmPR
SCEA
15° SR -5° Hardness RC 22/24 Dry DOC (.080 Inch) 2.03 mm

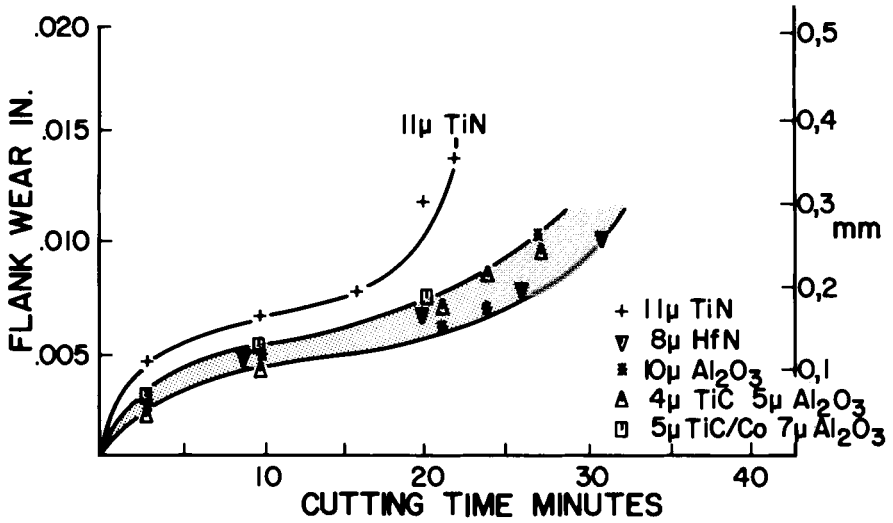


Fig. 6. Wear curves for shear angle 32°

Tool:	SNG-432	Material	4340	Cutting	Speed (600 sfm) 182.9 m min ⁻¹
BR	-5°	Condition	HT.TR.	Conditions	Feed (.0152 IPR) 0.38 mmPR
SCEA	15°	SR	-5°	Hardness	RC 22
				Dry	DOC (.080 Inch) 2.03mm

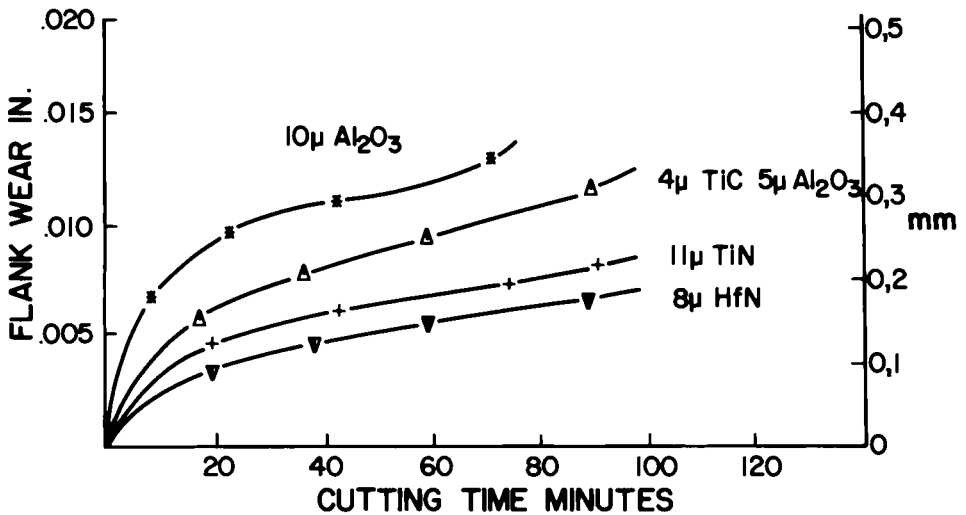


Fig. 7. Wear curves for shear angle 27°

Tool:	SNG-432	Material	4340	Cutting	Speed (300 sfm) 91.4 m min ⁻¹
BR	-5°	Condition	HT. TR.	Conditions	Feed (.0152 IPR) 0.38 mmPR
SCEA	15°	SR	-5°	Hardness	RC 22/24
				Dry	DOC (.080 Inch) 2.03 mm

Comparison between different families of Al_2O_3 coated tools, namely substrates coated with a single layer of Al_2O_3 (Fig. 8), or cobalt-diffused TiC and Al_2O_3 , (Fig. 9) or double layered TiC - Al_2O_3 (Fig. 10) coatings showed that in the upper speed ranges (shear angles $> 35^\circ$) and at comparable total coating thicknesses, monolithic Al_2O_3 coatings consistently out performed double-layered tools, while at shear angles less than about 32° , tools with single Al_2O_3 layers failed earlier than TiC/ Al_2O_3 -coated tools as a result of higher flank wear. However, a closer examination of the test data reveals that the improved performance of the monolithic Al_2O_3 at high cutting speeds is mainly due to the increased coating thickness with respect to that of the Al_2O_3 layer in double-layered tools.

It can be observed that the higher the shear angle the preponderance of work done is shifted to the tool surface where crater resistance will determine tool life. In the case of low shear angles more work is done in primary shear and tool loads move closer to the cutting edge.

It is usual practice to remove extreme sharpness of the cutting edge by applying a small negative chamfer (K Land) or a small radius. This reduces the tendency of edge chipping on entering the cut. It does not change the basic geometry of the tool itself, for instance the chamfer does not simulate a more negative cutting geometry.

Improper honing procedures, especially hones which extend downward toward the flank, can lead to excessive compressive loading on the tool during the beginning of the cut and can be the cause of coating and catastrophic tool substrate failure.

At high speeds the better thermal insulation of the tool substrate by the aluminium coatings seems to be the reason for lower thermal deformation when compared with that experienced with TiC intermediate coatings.

In connection with the above discussions, it should be noted that for cutting in the upper speed ranges (shear angle $> 35^\circ$), in all cases adequate coating thickness becomes of paramount importance if the tool is not to fail prematurely by thermal deformation as a result of inadequate heat insulation of the substrate. Presence of eta-carbide at the substrate-coating interface invariably causes a drastic reduction of cutting performance as a result of shear failure of the coatings. Similarly, the presence of impurities in the alumina layer such as iron group metals, which may co-deposit from materials of construction of the reactor, adversely affects high speed performance.

CONCLUSIONS

Evaluation of performance of coated inserts is generally defined for fixed material and machining parameters. It is shown that a single parameter, shear angle, combines a number of significant variables in machining and thus can be used to effectively characterize the performance envelope of tools.

The performance range for various coatings is more clearly defined by reference to shear angle. It is shown that Al_2O_3 or TiC/ Al_2O_3 layers perform best at high shear angles whereas tools coated with TiC or TiN have better performance at low shear angles. The surprising result is that HfN (and possibly also HfC coatings) show exceptional performance over the entire range of cutting shear angles.

Fig. 8.

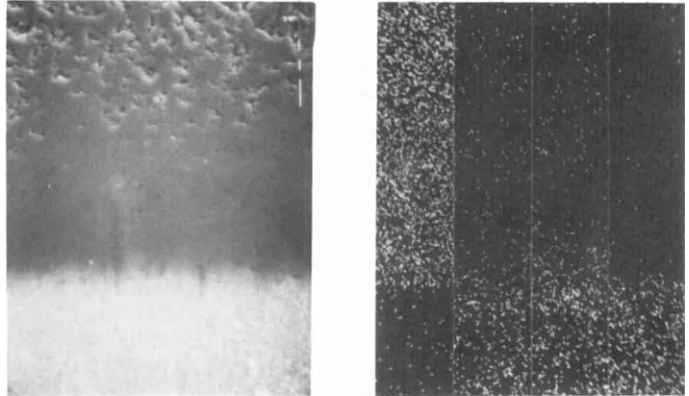
Coating Structure
Monolithic Al_2O_3 

Fig. 9.

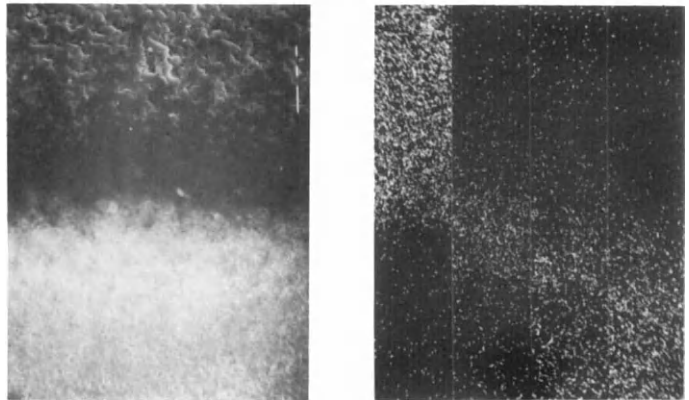
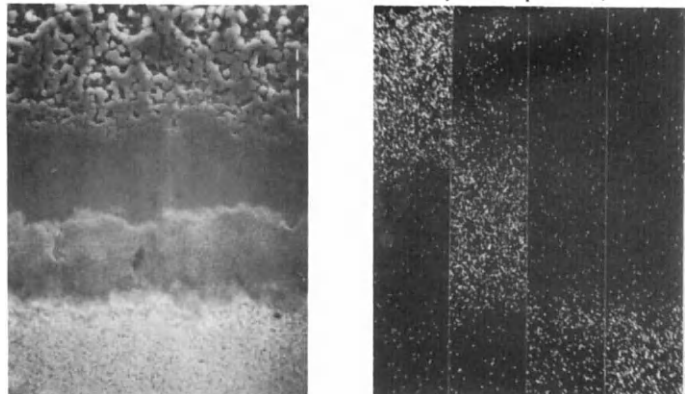
Coating Structure:
 $\text{TiC-Co}/\text{Al}_2\text{O}_3$ 

Fig. 10.

Coating Structure:
 $\text{TiC}/\text{Al}_2\text{O}_3$ Low Angle Sections
S.E.M. 500x

	Al		Ti		Co		W	
X-Ray Maps								

Our experiments have also shown that monolithic Al_2O_3 coatings can be prepared with comparable bonding quality and performance to the more usual Al_2O_3 coatings over TiC intermediate layers.

Both monolithic and TiC/ Al_2O_3 , as well as hafnium nitride coatings, can be successfully produced and have good performance up to a total coating thickness of $15\mu\text{m}$. Increased coating thickness enhances tool life considerably.

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Copper-Boron Low Alloy High Strength Steels

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ABSTRACT

The use of boron and copper additions in low carbon high strength steels is discussed. The properties of steels containing 1.8% Cu and 9 ppm boron are detailed for various processing schedules. Particularly outstanding properties with yield strength in excess of 700 MPa and a transition temperature of less than -80°C are obtainable in controlled rolled and aged material.

KEYWORDS

Steel; copper additions; boron additions; controlled rolling; mechanical properties.

INTRODUCTION

A number of high strength, low alloy (HSLA) steels for service at low temperatures have been developed in recent years. In particular, Cu-containing HSLA steels have shown good tensile and fracture toughness properties, together with good weldability and excellent corrosion and fatigue resistance. An alloying element which is potentially attractive from economic and metallurgical considerations is boron, as small additions of this can increase substantially the hardenability of steel and suppress the austenite to ferrite transformation, thus reducing the precipitation of solute atoms.

This paper reports on an investigation of the use of boron as an alloying element in Cu-containing steels in terms of its effect on mechanical properties and on the transformation and precipitation kinetics.

BORON AS AN ALLOYING ELEMENT

Minute additions of boron in the range 0.0005 to 0.003% impart substantial hardenability to steel and, hence, can replace more costly hardenability

promoters such as Cr, Mn, Ni and Mo (Koul and McVicker, 1976). Boron has this effect because of its retardation of the $\gamma \rightarrow \alpha$ transformation by delaying the formation of proeutectoid ferrite (Irvine and co-workers, 1957; Pickering, 1965). Thus, non-polygonal, high dislocation density microstructures can be produced, enabling a greater strength to be obtained on subsequent aging. In Cu-containing steels Cr and Mo are normally used to inhibit auto-aging (Hydrear, Chard and Shelton, 1972); however boron could be utilized in their place.

It is known that boron has a synergistic effect with Mo on transformation, and low carbon-Mo-B steels utilizing this effect have been developed (Irvine and co-workers, 1957; Pickering, 1965). More recently it has been reported that boron has a similar effect when used together with niobium (Maitrepierre and co-workers, 1978), while some preliminary studies have indicated that a synergistic effect exists between boron and copper (Sojka, Krishnadev and Banerji, 1980). Such synergistic effects can be utilized to achieve higher section capability in HSLA steels and also to increase strength levels in thinner sections.

EXPERIMENTAL

Preliminary investigations showed that, for extra-low carbon HSLA steels containing $\sim 1.8\%$ Cu and 9 ppm B, it was possible to obtain yield strengths of 450-800 MPa with a transition temperature below 0°C , depending on the rolling and the reheat and quenching practice (Krishnadev, 1980; Sojka, Krishnadev and Banerji, 1980). Subsequently, controlled rolling has been used to process Nb-Cu-B steels, and Table 1 details the compositions of the alloys studied, together with their processing schedules (Sojka, 1982). The mechanical properties of the various steels in the as-rolled, as-rolled and aged, and re-austenitized, quenched and aged conditions are given in Table 2.

DISCUSSION

The data given in Table 2 demonstrate the excellent strength and toughness combination produced in the as-rolled condition for the Nb-Cu-B steels. Even after aging to produce higher yield strength, good toughness and ductility are maintained. The strengths obtained are greater than are normally obtainable in commercial HSLA steels.

The synergistic effect of the boron and copper additions on the resulting mechanical properties is demonstrated in Fig. 1, while their effect on the transformation kinetics is illustrated in Table 3.

The reason for the synergistic effect is not clear. It may be related to copper delaying the growth of segregated boron carbides. If the growth of these carbides is delayed, that is, if there is a delay in the formation of an incoherent interface between the carbide and the matrix, ferrite nucleation will be retarded (Maitrepierre and co-workers, 1976). Another way of interpreting the synergistic effect is in terms of the influence of the alloying elements, i.e., copper and boron, on the activation energy for ferrite nucleation. It has been suggested that boron in solution can increase the activation energy for ferrite nucleation, which partly depends on the activation energy for carbon diffusion (Maitrepierre and co-workers, 1976). Probably when boron and copper coexist, the activation energy requirement for ferrite nucleation is also synergistically increased.

TABLE 1 Chemical Composition and Processing Schedule of Steels

Steel	IA	VA	12	13	14
C(wt %)	0.053	0.039	0.047	0.039	0.042
Mn(wt %)	1.62	1.52	1.30	1.29	1.23
P(wt %)	0.002	0.004	0.004	0.004	0.004
S(wt %)	0.014	0.019	0.015	0.016	0.015
Si(wt %)	0.26	0.25	0.01	0.01	0.01
Al(wt %)	0.023	0.018	0.014	0.010	0.009
Ti(wt %)	0.037	0.035	0.027	0.025	0.028
Nb(wt %)	--	--	0.070	0.060	0.003
Cu(wt %)	--	1.79	1.84	1.85	1.81
Ni(wt %)	--	--	1.04	1.02	1.02
B(ppm)	10	9	2	9	23
Zr(ppm)	50	20	50	70	60
N(ppm)	70	60	56	61	51
Processing	HR	HR	CR	CR	CR

HR: Austenitized 1250°C; hot rolled with finish rolling temperature (FRT) 1020°C; air cooled.

CR: Austenitized 1250°C; controlled rolled in 9 passes with FRT of 760, 820 or 830°C; water quenched.

TABLE 2 Mechanical Properties of the Experimental Steels

Steel	Treatment	Final Thickness (mm)	FRT (°C)	YS (MPa)	UTS (MPa)	E1 (%)	RA (%)	DBTT (°C)
IA	AR	12.7	1000	307	431	46	81	-34
	R, Q+A, 600°C, 1h	12.7	950	627	659	21	72	<-100
VA	AR	12.7	1000	483	706	27	68	-23
	R, Q+A, 600°C, 1h	12.7	950	755	784	25	65	-46
12	AR	12.7	760	502	693	28	69	-110
	AR+A, 550°C, 90 min	12.7	760	730	782	28	68	-75
	AR+A, 550°C, 3h	12.7	760	723	775	28	68	-65
	R, Q+A, 600°C, 1h	12.7	760	576	627	20	77	-85
	AR	25.4	830	628	718	22	67	-110
	AR+A, 550°C, 3h	25.4	830	744	789	26	72	-20
	AR+A, 550°C, 5h	25.4	830	726	771	25	69	-28
	AR+A, 600°C, 1h	25.4	830	716	760	27	73	-28
	AR	12.7	820	494	695	28	69	-115
	AR+A, 550°C, 3h	12.7	820	769	811	27	70	-50
	AR+A, 700°C, 1h	12.7	820	541	676	27	70	-110

TABLE 2 (Cont'd.)

Steel	Treatment	Final thick- ness	Thick- (mm)	FRT (°C)	YS (MPa)	UTS (MPa)	EI (%)	RA (%)	DBTT (°C)
13	AR	12.7		760	522	704	26	67	<-115
	AR+A, 550°C, 90 min	12.7		760	729	782	26	70	-75
	AR+A, 550°C, 3h	12.7		760	758	806	29	69	-78
	R, Q+A, 600°C, 1h	12.7		760	620	672	26	76	-98
	AR	25.4		830	552	740	25	67	-117
	AR+A, 550°C, 3h	25.4		830	773	817	25	70	-70
	AR+A, 550°C, 5h	25.4		830	745	786	26	69	-60
	AR+A, 600°C, 1h	25.4		830	767	809	25	69	-85
	AR	12.7		820	549	737	20	66	<-115
	AR+A, 550°C, 45 min	12.7		820	812	831	25	67	-88
	AR+A, 550°C, 3h	12.7		820	787	831	25	67	-110
	AR+A, 700°C, 1h	12.7		820	556	713	26	69	-105
14	AR	12.7		760	447	606	35	65	-95
	AR+A, 550°C, 45 min	12.7		760	683	749	28	70	-75
	AR+A, 550°C, 3h	12.7		760	600	657	27	68	-98
	R, Q+A, 600°C, 1h	12.7		760	617	670	20	74	-120
	AR	25.4		830	511	611	27	68	-120
	AR+A, 550°C, 3h	25.4		830	636	692	27	70	-100
	AR+A, 550°C, 5h	25.4		830	597	646	27	72	-93
	AR+A, 600°C, 1h	25.4		830	616	672	30	71	-100
	AR	12.7		820	429	638	20	69	<-115
	AR+A, 550°C, 45 min	12.7		820	702	769	27	66	-95
	AR+A, 550°C, 3h	12.7		820	645	690	28	68	-110
	AR+A, 700°C, 1h	12.7		820	408	622	31	70	-95

AR: As-rolled and water quenched.

AR+A: As-rolled, water quenched and aged.

R, Q+A: Reaustenitized 950°C, water quenched and aged.

FRT: Finish rolling temperature.

DBTT: Ductile-brittle transition temperature.

It is well known that copper has only a mild effect on the transformation behaviour of steels (Grange, Lambert and Harrington, 1959). However, when added in conjunction with boron, the transformation temperature range is lowered considerably even under moderately slow cooling rates (see Table 3). The extent of the lowering is comparable to that observed in other HSLA steels. Lowering the transformation temperature results in higher dislocation density microstructures of acicular ferritic or bainitic type being produced even at moderate cooling rates. It also retards the precipitation of copper in the as-rolled condition, permitting increased strengthening upon aging.

The results obtained indicate that the Cu-B steels are extremely promising structural materials, and they have the additional advantage of being relatively soft in the as-rolled condition. Hence they can be formed into pipe or other shapes and aged subsequently to obtain higher strength levels while maintaining adequate toughness. The problem of hot shortness, often considered to be serious in Cu-containing steels in the past, is readily avoided by proper control of alloy content, furnace atmosphere and processing

conditions (Habraken and Lecomte-Beckers, 1982).

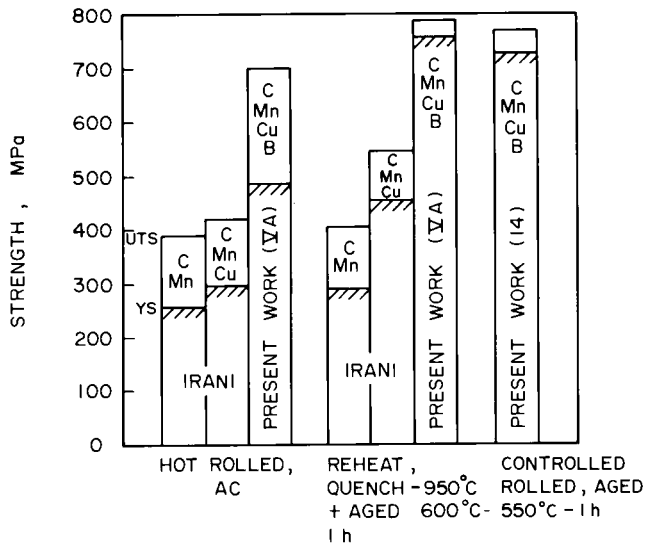


Fig. 1. Effect of boron on the mechanical properties of Cu-containing steels, including data from Irani, Dulieu and Tither (1968).

TABLE 3 Effect of Copper and Boron Additions on Transformation Kinetics

Steel	Cooling Rate (°C/min)	A_r (°C)
IA	250	700-628
VA	250	616-556
1/2 Mo-B ^a	250	660-560
IN-787 ^b	214	602-579
Nb-Mo ^c	200	626-508

a: 0.1% C, 0.52% Mn, 0.52% Mo, 0.0022% B.

b: Commercial steel with 0.04% C, 0.6% Mn, 0.73% Cr, 1.0% Ni, 0.18% Mo, 1.2% Cu, 0.04% Nb.

c: Commercial steel with 0.04% C, 1.8% Mn, 0.09% Nb, 0.25% Mo.

CONCLUSIONS

The initial studies reported here demonstrate clearly the excellent properties obtainable in HSLA steels containing boron and copper. The strengthening obtained is greater than the sum of the individual strengthening effects from copper and boron, and the synergistic effect of the two alloying elements has been identified.

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Microalloyed Hot Rolled Bars for Hot Forging Applications

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ABSTRACT

Energy conservation and cost savings can be realized by elimination of the heat treatment of forgings by the use of hot rolled microalloyed steel bars.

KEYWORDS

Microalloyed steels; hot rolled bars; heat treatment; energy conservation; forging.

INTRODUCTION

The benefits to be obtained by microalloying additions to low carbon steels hot rolled into sheet and plate have been known and utilized for some time (Pickering, 1975). The process of hot forging is one of thermal-mechanical treatment and therefore the properties of the as-received hot rolled bars are significantly altered during forming. Traditionally, the desired properties in most critical automotive parts have been obtained by heat treatment. However, microalloying medium carbon steels for forging applications has permitted the elimination of heat treatment in some cases (Bucher, Held and Butler, 1979). Forgings receive more variable deformation and cooling than are experienced during the hot rolling of sheet and plate. In addition, specific property requirements of forgings prevent the application of certain advances in metallurgy such as dual-phase steels (Butler and Bucher, 1979). However, the concerns appropriate to the hot rolling of microalloyed steels are the same to be considered in forging microalloyed steels. Due to space limitations, the basic metallurgy will be presented in limited fashion and successful application of these principles to industrial practice will be stressed.

BASIC METALLURGY

Niobium and vanadium singly or in combination in amounts ranging from about 0.02% to 0.15% are the elements used for microalloying sometimes with re-

nitrogenized steels. Typical base steel compositions are SAE 1045, SAE 1541 and SAE 1141. The strength of the hot rolled bar is a good indication of the potential achievable in the forged part. Figure 1 (Bucher, 1981) shows that an addition of .05% Nb to plain-C steel is more effective in increasing the strength at lower carbon levels but, more importantly for our interests here, a significant effect persists in the 0.4% to 0.6% C range. The means of strengthening is structural refinement in combination with precipitation strengthening. Figure 2 shows the fine ferrite-pearlite microstructure typical for SAE 1141 + .04% Nb in an air-cooled connecting rod. Lower transformation products, such as acicular ferrite and bainite are also sometimes obtained.

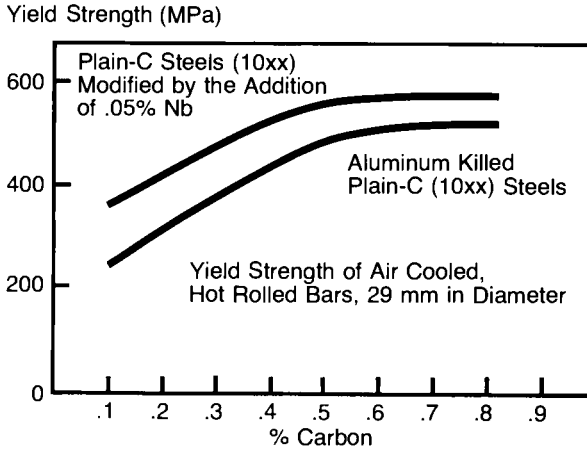


Fig. 1. Strengthening of plain-C steels by 0.05% Nb.

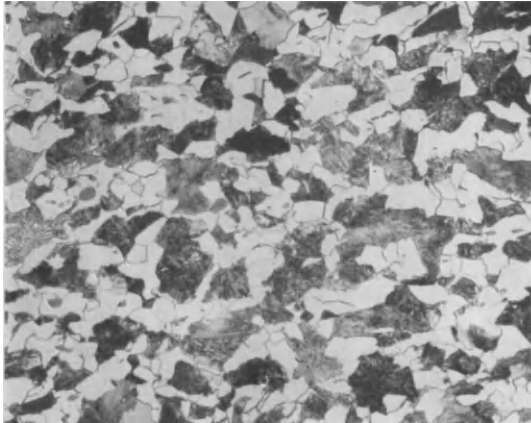


Fig. 2. Microstructure typical of air-cooled connecting rod made from SAE 1141 + 0.05% Nb, 400X.

The soak temperature before forging should be adequate to render the niobium and/or vanadium in solution but not so high as to promote grain growth. Cooling of the forgings should be as uniform as is practical and controlled at a rate sufficient to achieve the desired properties. Comparable hardness, tensile properties and fatigue resistance have been achieved in air-cooled microalloyed forgings vs heat treated parts. However, achievement of toughness comparable with quenched and tempered parts is not always a practical possibility. For best results, a soak temperature of 1200–1300°C and a cooling rate of about 100°C/min. or slightly faster are recommended for maximum strengthening – Figs. 3 and 4 (Niwa and colleagues, 1981).

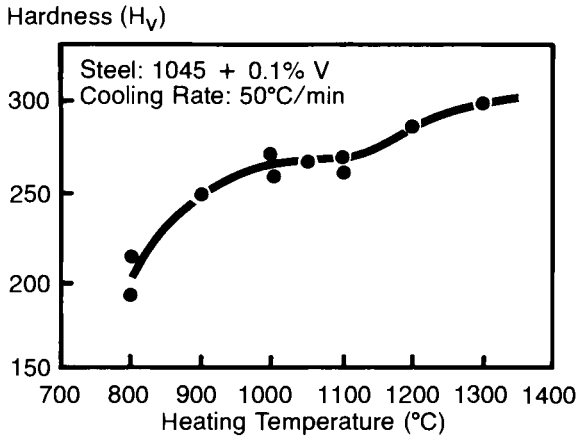


Fig. 3. Effect of heating temperature on the hardness of forgings.

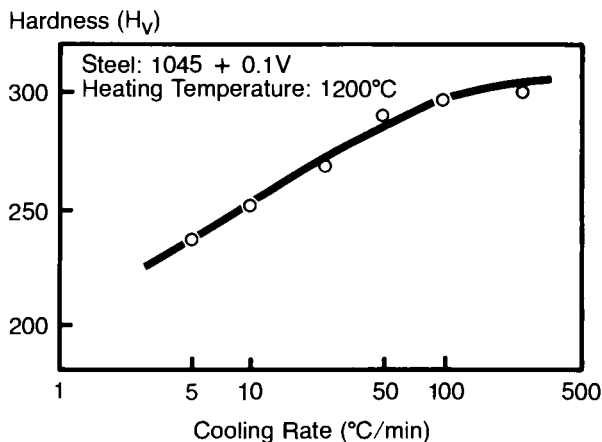


Fig. 4. Effect of cooling rate on the hardness of forgings.

V(CN) goes into solution at somewhat lower temperatures than Nb(CN). Nb has a greater hardenability effect than V as well as a greater restraint on austenite recrystallization, so that all things being equal Nb-modified steels will be finer grained than V-modified steels with the latter having more precipitation strengthening. However, the same general processing guidelines pertain for all microalloyed steels.

Part geometry and size will be important factors in determining the suitability of the microalloying approach. Steel chemistry should be adjusted in accordance with the microalloying additions in order to achieve the desired properties. Figure 5 shows the carbon equivalent selected for various parts to achieve the desired hardness using air cooling and a temperature range of 1200–1300°C during reheating (Nippon Steel Corporation, 1982).

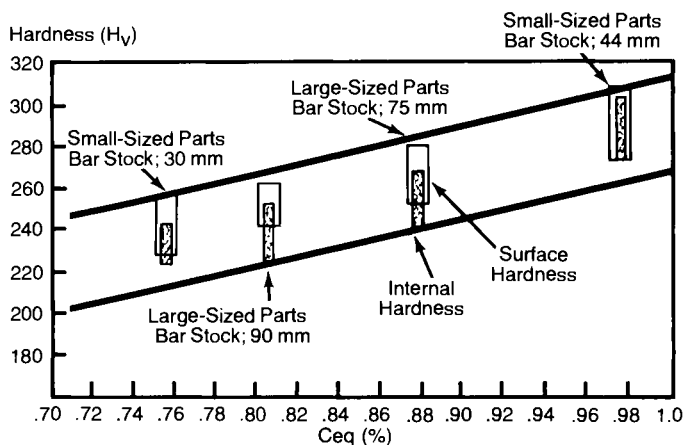


Fig. 5. Carbon equivalent is adjusted appropriately.

APPLICATIONS

For many applications, fatigue is the property of primary interest so that any deficiencies in the toughness for these ferrite-pearlite steels vs a quenched and tempered part are not of significance. However, there is a practical limit placed upon how far this approach can be taken by the degradation in ductility and toughness associated with increasing hardness. An upper limit of about 300 Hv for forged parts seems appropriate. In other words, if the desired hardness in the forging is greater than 300 Hv, quenching and tempering is recommended rather than controlled air cooling of microalloyed steel.

Table 1 lists four examples of the use of microalloying to eliminate quenching and tempering. Connecting rods and caps, universal joint couplings (Bucher, 1981), crankshafts (Razim, 1981 and Hashimoto and colleagues, 1982) and miscellaneous suspension components (Niwa, 1981) are included.

Table 1 Examples of the Elimination of Quenching and Tempering

PART	STEEL CHEMISTRY							
	%C	%Mn	%Si	%Cr	%S	%Pb	%Nb	%V
Connecting Rods and Caps	.37/.45	1.35/1.65	.15/.30		.08/.13		.03/.05	
Universal Joint Coupling	.37/.45	1.35/1.65	.15/.30		.08/.13		.03/.05	
Crankshaft	.47/.53	.70/1.10	.15/35		.04/.07			.05/.10
Misc. Suspension Components	.44	.81	.55	.22	.003	.12		.17

Crankshafts made from microalloyed steel offer: reduced primary cost, improved production technology and lower energy requirements (Razim, 1981). Cooperative work done by Honda Motors and Daido Steel (Niwa, 1981) has dealt with various suspension system components as well as connecting rods. The examples in Table 1 were selected in part because they illustrate the use of specific variations in steel chemistry to achieve the desired overall result: both resulfurized and leaded steels are used to enhance machinability, both Nb and V have been used, hardenability has been adjusted to fit the part primarily by varying Mn, Si and Cr.

In summary, the actual cost savings by elimination of heat treatment will depend on the particular situation. In general, energy savings, reduced labour, time and space requirements, and improved machinability can be realized leading to a significant reduction in total cost. Microalloying with Nb and V of medium carbon often resulfurized steels has been used for connecting rods and caps, weld yokes, crankshafts, suspension components and other automotive parts. Reasonable control of the forging process is necessary to achieve the desired results and these requirements have been outlined.

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Developmental 2.25Cr-1Mo Steels for Coal Conversion Vessels

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ABSTRACT

First generation (coal liquefaction) vessels will be fabricated from 400 mm thick 2.25Cr-1Mo steel ring forgings or plates, which may develop surface to center variations in microstructures and mechanical properties on quenching due to limited rates of heat transfer. Alloy modifications based on minor additions of Mn, Ni and Cr have eliminated polygonal ferrite from the center location giving, on tempering, bainitic microstructures with more uniform mechanical properties throughout the 400 mm sections. The presence of additional Cr (0.75%) accelerated the formation of the alloy carbides $(\text{FeCr})_7\text{C}_3$ and M_{23}C_6 at 650°C, giving improved resistance to hydrogen attack but reduced creep rupture strength. The relationship between carbide precipitation kinetics and mechanical properties is presented for a series of Cr-Mo steels currently being developed for second generation liquefaction vessels.

KEYWORDS

2.25Cr-1Mo steel; thick section pressure vessel steel; hydrogen attack; creep; alloy development; microstructure-mechanical property relationships; coal liquefaction systems; carbides.

INTRODUCTION

The rapidly developing technology for economical utilization and conversion of coal demands materials capable of satisfactory performance in environments which are both more chemically and mechanically hostile than those experienced commercially (Scott, 1979; King and Judkins, 1980; McNeese, 1981). Coal conversion processes may require massive steel pressure vessels (as large as 40 m high, 6 m in diameter and with 300-400 mm wall thicknesses) to contain process streams including hydrogen and hydrogen sulphide gases at pressures up to 20 MPa and temperatures of 450°C-900°C). These structures must be fabricated from tough, weldable steels having yield strengths greater than 310 MPa, with good resistance to creep, fatigue, fracture and environmental degradation due to hydrogen embrittlement and hydrogen attack. 2.25Cr-1Mo steels have been selected for first generation vessels but alloy modifications, which have

improved thick section hardenability, hydrogen attack resistance and elevated temperature properties, must now be developed for future applications. Empirical data collected by Nelson (1951) have shown that low alloy steels containing Cr and Mo are immune from hydrogen attack in temperature-pressure regimes more severe than those required for plain carbon steels. Considerable interest has, therefore, arisen in alloy modifications of 2.25Cr-1Mo steel containing additional Cr to promote the formation of chromium-rich carbides, e.g. M_7C_3 , $M_{23}C_6$ which are thought to reduce susceptibility to attack.

This paper describes research studies on a series of developmental 2.25Cr-1Mo steels containing minor amounts of Mn, Ni and Cr for improved hardenability and hydrogen attack resistance. It is well known (Kar, 1979; Kar and Todd, 1981; Baker and Nutting, 1959; Ishiguro and co-workers, 1981; Wada and Eldis, 1981) that the cooling rates at the quarter and center thickness locations of 400 mm commercial 2.25Cr-1Mo steel plate (approximately 8°C/min) result in microstructures containing up to 40% polygonal ferrite and upper bainite. Combined additions of Ni, Mn and Cr have been investigated for improvements in thick section (400 mm) hardenability and mechanical properties.

The relationships between alloy composition, microstructure and mechanical properties including hydrogen attack susceptibility and elevated temperature properties, are discussed in this paper.

EXPERIMENTAL PROCEDURE

The compositions of the alloys used in this investigation are given in Table 1. Samples were austenitized at 1000°C for 1 hour and either oil quenched (surface microstructures) or cooled at 8°C/min to simulate the quarter thickness location of 400 mm plate. The specimens were tempered for 4 hours at 650°C and thin foils were prepared for transmission electron microscopy.

TABLE 1 Compositions of Commercial Alloys (alloy addition wt%)

Type	C	Mn	Ni	Cr	Mo	Si	P	S	V	Al
2.25Cr-1Mo(A)	0.15	0.42	0.10	2.18	0.91	0.30	0.015	0.009	-	0.019
A+1Mn	0.15	0.50	0.13	2.25	0.96	0.33	0.012	0.007	-	0.021
A+0.5Mn										
+0.5Ni	0.16	0.92	0.51	2.27	1.03	0.28	0.013	0.008	-	0.021
A+0.5Mn										
+0.5Ni(GR)*	0.16	0.92	0.50	2.25	1.03	0.28	0.013	0.008	0.022	0.035
A+0.5Mn										
+1.0Ni	0.16	0.95	1.02	2.29	1.02	0.29	0.014	0.007	-	0.014
A+0.5Mn										
+1.0Ni+0.75Cr	0.15	0.94	0.97	2.96	0.98	0.28	0.010	0.008	-	0.014

*GR - Grain refined with 0.02%V and 0.01%Al

Tensile specimens (25.4 mm gauge length, 6.3 mm diameter) and Charpy V-notch samples (L-T orientation) were tested at room temperature. Tensile and Charpy blanks of quenched and tempered alloy modifications were exposed to hydrogen at 10 MPa pressure and 550°C for 1000 hours. Simulated cooled and tempered modifications were exposed at 13.8 MPa hydrogen and 550°C for 1000 hours. Constant load creep rupture tests were conducted on smooth round bar specimens (25.4 mm gauge length, 6.3 mm diameter) of simulated cooled and tempered 2.25Cr-1Mo steels at 500°C, 560°C and 600°C for durations up to 2000 hours.

RESULTS AND DISCUSSION

The effects of chemical composition on the mechanical properties of unmodified and developmental 2.25Cr-1Mo steels after tempering for 4 hours at 650°C and also after exposure to hydrogen are shown in Table 2. The cooling rate from the austenitizing temperature had a marked effect on the unexposed 2.25Cr-1Mo steel. The yield strength decreased from 656 MPa (oil quenched and tempered) to 410 MPa (simulated cooled and tempered) as the microstructure changed from tempered martensite to upper bainite with 40% polygonal ferrite. When the ferrite was eliminated by the alloy modifications, the yield strengths were similar, with the quenched and tempered steels being only 8% higher than the simulated cooled and tempered materials, despite the fact that the carbide structures vary with alloy composition. For example Fe_3C and Mo_2C were observed in 2.25Cr-1Mo and the Ni-Mn modifications, whereas predominantly $(\text{FeCr})_7\text{C}_3$ (with traces of M_{23}C_6 and Mo_2C) were observed in the 3Cr-1Mo-1Mn-1Ni steel (Todd and co-workers, 1982).

TABLE 2 Mechanical Properties of Tempered and Hydrogen Exposed Steels

Alloy		σ_{YS} (MPa)	σ_{UTS} (MPa)	% ϵ	%RA	67J TT°C	Time (hrs)	H ₂ (MPa)
2.25Cr-1Mo	OQ	656	743	26.0	73.4	-60 ^a	-	-
+1Mn	OQ	643	733	27.0	72.8	-48 ^a	-	-
+0.5Mn+0.5Ni	OQ	657	738	26.0	71.8	-70 ^a	-	-
+0.5Mn+1Ni+								
0.75Cr	OQ	642	762	26.7	72.0	-38	-	-
2.25Cr-1Mo	SC	410	706	21.5	69.5	-12	-	-
+1Mn	SC	592	711	25.0	72.8	-50	-	-
+0.5Mn+0.5Ni	SC	615	737	24.1	70.0	-45	-	-
+0.5Mn+1Ni+								
0.75Cr	SC	593	745	25.0	73.8	-53	-	-
<u>OQ*, 4 hrs 650°C</u>								
2.25Cr-1Mo		656	743	26.0	73.4		0	0
		604	687	27.0	75.0		500	10
		515	605	30.0	75.1		1000	10
+1Mn		643	733	27.0	72.8		0	0
		623	716	25.0	67.5		500	10
		534	620	28.0	71.5		1000	10
+0.5+0.5Ni		656	738	26.0	71.8		0	0
		632	716	26.0	79.9		500	10
		569	654	26.0	68.4		1000	10
<u>SC†, 4 hrs 650°C</u>								
+0.5Mn+0.5Ni		631	743	25.9	69.8		0	0
+0.02V		656	779	24.0	65.9		1000	13.8
+0.75Cr+0.5Mn+		615	713	26.0	72.3		0	0
1.0Ni		505	663	23.0	68.6		1000	13.8

*OQ = oil quench; †SC = simulated cooled; ^aCourtesy R. J. Kar

Tensile properties for the alloy modifications are compared after exposure to hydrogen at either 10 MPa or 13.8 MPa and 550°C for 500 and 1000 hours. The yield strength after 1000 hours had decreased by 21.5% for the quenched and tempered 2.25Cr-1Mo steel and by 17% and 13% for the 1Mn and 0.5Mn+0.5Ni modifications respectively. An 18% decrease was observed for the simulated cooled and tempered 3Cr-1Mo-1Mn-1Ni alloy. No microscopic evidence of hydrogen attack (e.g. blisters, microvoids) were observed and there were no significant changes in ductility for any of the alloys.

The effects of hydrogen at elevated temperatures and pressures are seen more

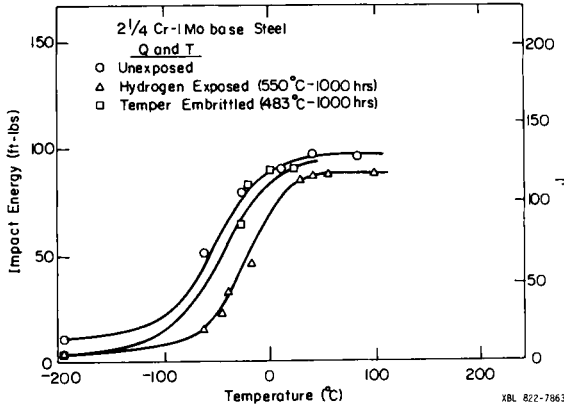


Fig. 1 Comparison of Charpy impact transition curves for unexposed, hydrogen exposed (10MPa) and isothermally aged 2.25Cr-1Mo steel.

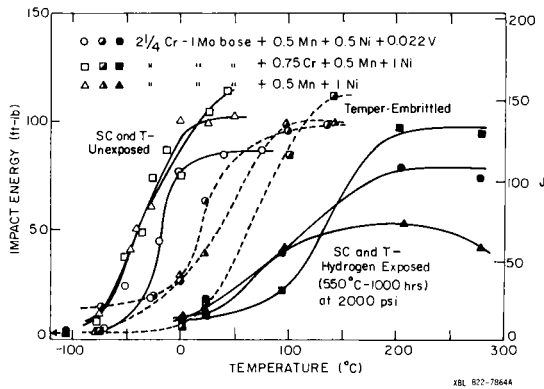
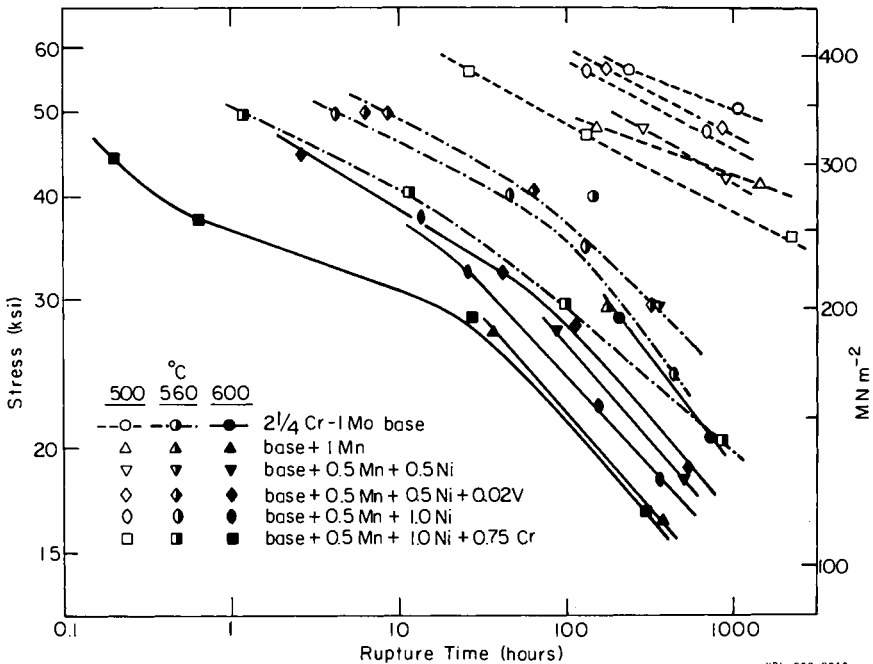


Fig. 2 Comparison of Charpy impact transition curves for unexposed, hydrogen exposed (13.8MPa) and isothermally aged alloy modifications (13.8MPa).

clearly when the Charpy impact transition temperature curves are plotted in Figs. 1-2. The unexposed, hydrogen attacked (550°C, 1000 hours, 10 MPa) and temper embrittled (isothermally aged 483°C for 1000 hrs) impact transition curves for quenched and tempered 2.25Cr-1Mo steel are compared in Fig. 1. The shift in 67J (50 ft-lb) impact transition temperature for the hydrogen exposed steel (40°C) was greater than that for the temper embrittled samples (12°C). Scanning electron micrographs of 2.25Cr-1Mo steel and Ni, Mn modifications fractured at -196°C revealed mixed cleavage and intergranular fractures but no methane bubbles were observed at prior austenite grain boundaries. The changes in tensile and impact properties could not, therefore, be attributed specifically to hydrogen attack, but also reflected changes due to tempering and segregation of impurities during isothermal aging. The incubation period required for methane formation with catastrophic decreases in ductility and toughness is clearly greater than 1000 hours at 10 MPa.

When the pressure was increased to 13.8 MPa, upper shelf toughness levels decreased and the 67 J impact transition temperature for the simulated cooled developmental alloys shifted 130-170°C (Fig. 2) indicating that significant hydrogen damage occurred. Methane bubble formation was observed on grain boundary facets of all the specimens fractured at 0°C. Before exposure the carbide structure of the 0.5Mn+1Ni steel was $\text{Fe}_3\text{C}+\text{Mo}_2\text{C}$ whereas the 0.75Cr+0.5Mn+1Ni steel contained predominantly $(\text{FeCr})_7\text{C}_3$ and M_{23}C_6 . The elimination of Fe_3C from the microstructure has contributed to improved hydrogen attack resistance of the Cr-Mn-Ni alloy and additions of vanadium also appear to improve stability (Chung, Todd and co-workers, 1982).

Elevated temperature creep rupture properties are presented in Fig. 3 for test temperatures of 500°C, 560°C and 600°C. At all three temperatures the creep rupture strengths of the simulated cooled and tempered developmental alloys are lower than those of the unmodified 2.25Cr-1Mo steel. The greatest reductions in creep strength and highest creep ductilities were observed for the 1Mn and 0.75Cr+0.5Mn+1Ni modifications. The poor properties of the 0.75Cr+0.5Mn+1Ni modification reflect the presence and rapid coarsening of the precipitate $(\text{FeCr})_7\text{C}_3$ (Kuo, 1953) and the lower volume fraction of Mo_2C than observed in the 2.25Cr-1Mo steel.



XBL 823-8340

Fig. 3 Creep rupture data for 2.25Cr-1Mo steel and alloy modifications tested at 500°C, 560°C and 600°C.

The steels examined in this work have been subjected to short term tempering treatment at 650°C. The preliminary results indicate that improved resistance to hydrogen attack could be achieved by longer tempering times to replace Fe_3C in the microstructure with a stable alloy carbide distribution, which may also be beneficial for creep strength. Although the elements Cr and V appeared to improve the hydrogen attack resistance, the M_7C_3 precipitates were

coarser than the Mo_2C carbides observed in 2.25Cr-1Mo steel and insufficient V was present to dispersion strengthen the bainite against creep. The effects of higher V additions to 3Cr-1Mo steel are now being investigated to determine the improvements in creep rupture properties due to a stable VC distribution.

CONCLUSIONS

1. Minor alloy additions of Ni, Mn and Cr to 2.25Cr-1Mo steel improve thick section hardenability and reduce surface to center variations in the microstructures and mechanical properties of 400 mm plate.
2. The incubation period for methane bubble formation is greater than 1000 hours at 10 MPa pressure and 550°C for quenched and tempered 2.25Cr-1Mo steel but was less than 1000 hours at 13.8 MPa pressure and 550°C for the simulated cooled and tempered samples.
3. Hydrogen attack resistance is promoted by the elimination of Fe_3C from the microstructure and the presence of alloying elements Cr and V.
4. All the developmental alloys exhibited lower creep rupture stresses than 2.25Cr-1Mo steel at 500°C, 550°C and 600°C. Further compositional modifications and optimized heat treatments are required to produce both hydrogen attack and creep resistant microstructures.

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ACKNOWLEDGEMENTS

This work was funded by the United States Department of Energy through Oak Ridge National Laboratory under Union Carbide Subcontract. This research was performed whilst the authors were Research Engineers in the Department of Materials Science and Mineral Engineering at U.C. Berkeley. The authors wish to thank Professor E. R. Parker for many helpful discussions.

Rapid Solidification of Steels: Model and Commercial Alloys

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ABSTRACT

Rapid solidification processing is already being applied commercially to the production of high alloy steels and superalloys. However, the fundamental effects of such techniques on phase equilibria and microstructure have not as yet been fully investigated. The purpose of this paper is to present the results of a detailed study of commercial tool steels and model Fe-Ni and Fe-Mn based alloys produced by melt spinning and pendant drop melt extraction. The as-quenched microstructures are described for the industrial alloys. In the model steels, the effects of vanadium and carbon additions to the base compositions are considered in terms of both the as-quenched structures and their response to simple heat treatments.

KEYWORDS

Rapid Solidification. High Speed Steels. Fe-Ni. Fe-Mn.

INTRODUCTION

A decade ago, the term 'rapid solidification' was reserved for an area of academic interest relating to the quenching of a few milligrams of liquid material at quench rates in excess of 10^5 Ks^{-1} . The results of intensive research on a wide range of materials demonstrated that several advantages could be gained by this process. The most important benefits can be summarised as: (i) the stabilisation of amorphous (non-crystalline) phases at room temperature, (ii) the production of new metastable crystalline phases and (iii) the extension of solubility limits.

Although there was considerable interest in the bulk production of aluminium alloys (Jacobs, Doggett and Stowell, 1974) most of the early work concentrated on more exotic alloys. In particular, the major emphasis was on rapidly solidified transition metal-metalloid (P, C, B, Si, etc.) alloys which could be quenched to form metallic glasses. Most commercially available amorphous alloys are iron-based and they display remarkably high

specific strengths, excellent corrosion resistance (in alloys with more than 7 at. % Cr) and above all very good magnetic properties.

The number of investigations into microcrystalline iron alloys and steels was initially small (e.g. Ruhl and Cohen, 1967, 1969; Wood and Honeycombe, 1974). However, during the first study of plain Fe-C alloys the only 'new' crystalline phase (ϵ -phase) to be found in rapidly quenched steels was reported (Ruhl and Cohen, 1967). This is an hexagonal phase which is formed directly from the melt and not by the decomposition of austenite.

Large increases in carbon and boron solubility have been reported for a variety of steels (Ruhl and Cohen, 1969; Wood and Honeycombe, 1978) in addition to modifications in carbide/boride precipitate morphology after subsequent ageing. The initial solidification structure, ranging from dendritic to planar front growth, was shown to be an important factor in the kinetics and morphology of precipitation.

The requirement for rapidly solidified materials in a larger form led to the development of many new techniques. These range from melt-spinning/planar flow casting to laser beam melting and high velocity atomisation. These methods and their variables have been described elsewhere (Jones, 1981). In all cases one dimension is small to allow rapid heat removal, and products are limited to thin sheet (up to $\sim 100\mu\text{m}$), powders, wires, etc. However, techniques such as hot extrusion and hot isostatic processing are suitable for making larger components.

With the large range of techniques now available, the emphasis has changed from a preoccupation with cooling rate to the development of desired final microstructures. This has been demonstrated in high speed steels, where conventional production routes lead to banding of carbides and inefficient usage of expensive alloying elements. Continuous spray deposition (CSD) has been developed as a process to build up bar stock by the splatting of individual droplets emanating from an atomising nozzle (Rickinson, Kirk and Davies, 1982). In addition to longer cutting times for continuous turning or drilling, CSD high speed steel displays superior grindability and increased resistance to chipping compared with material made by conventional means. Concurrent with these new bulk production techniques and commercial exploitation, there has been an increase in the volume of underlying work on structures and properties of rapidly solidified crystalline steels, and these have been reviewed recently by Wood and Honeycombe (1981).

The purpose of this paper is to report on a structural study of a number of model iron-based alloys and commercial high speed steels carried out in order to gain some insight into how the composition of commercial steels might be modified to take best advantage of the rapid solidification processing route.

EXPERIMENTAL TECHNIQUES

Model alloys were prepared by melting pure elements in an argon arc furnace. Commercial steels were provided by Aurora Steels, Sheffield, U.K. The compositions of these materials, and others referred to in the text, are given in Table I.

TABLE I Compositions of Model and Commercial Alloys (wt %) : (balance Fe)

Designation	C	Mn	Ni	V	Cr	Mo	Co	W
1	-	-	16.0	-	-	-	-	-
2	0.57	-	21.3	-	-	-	-	-
3	-	-	22.5	5.0	-	-	-	-
4	0.1	-	20.4	5.0	-	-	-	-
5	0.67	-	20.1	5.0	-	-	-	-
6	-	18.7	-	-	-	-	-	-
7	0.50	19.5	-	-	-	-	-	-
8	-	19.3	-	5.3	-	-	-	-
9	0.1	19.4	-	6.0	-	-	-	-
10	0.5	18.8	-	5.6	-	-	-	-
M2	0.8	-	-	1.9	4.0	5.0	-	6.3
M15	1.55	-	-	5.0	4.7	3.0	5.0	6.5
M42	1.07	-	-	1.1	3.8	9.7	8.3	1.5

All alloys were rapidly solidified, using both melt spinning (MS) and pendant drop melt extraction (PDME), in an enclosed chamber evacuated to a pressure of 10^{-2} Pa prior to admittance of a pure helium atmosphere. The details of the apparatus have been described elsewhere (Wood, 1978). Melt spinning resulted in a ribbon of width 3 - 5 mm, while melt extraction produced fibres of 30 - 80 μ m diameter. Although it is possible to use a notched wheel to generate particulate material by melt extraction, in the present study lengths of fibre were chopped to 0.5 - 2 mm in length prior to compaction.

The melt spun ribbon was used for structural investigations. Samples back-etched in nital or mixed acids in glycerol were examined in a Philips 501B scanning electron microscope. Discs of 3 mm dia. were twin-jet electro-polished in a perchloric/glycerol/ethanol solution for observation in a Philips 301 transmission electron microscope.

RESULTS AND DISCUSSION

a) Commercial High Speed Steels

Rapidly solidified M2, M15 and M42 steels all displayed a dendritic solidification morphology (Fig. 1). The secondary dendrite arm spacing was of the order of 0.5 μ m (corresponding to a cooling rate during the liquid to solid transformation of $\sim 10^6$ Ks $^{-1}$). The final grain size varied between 5 and 15 μ m, and since the dendrites grow along $\langle 100 \rangle$ directions, it can be seen that the grain orientation appears completely random.

Transmission electron microscopy revealed that networks of carbides precipitate along the interdendritic boundaries during solidification (Fig. 2). At higher magnifications (Fig. 3) fine matrix dispersions of MC-type carbides in an austenitic matrix were observed, which probably came out of solution during subsequent solid-state cooling. Although the fine scale of precipitation produced hardness values in excess of 700 Hv in the

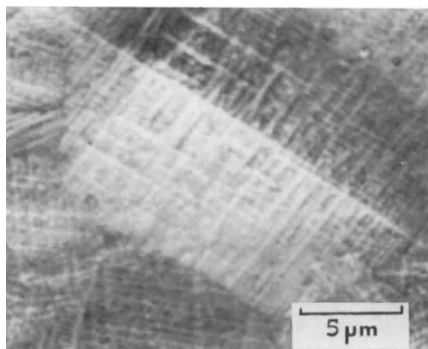


Fig. 1. As-quenched M42 (SEM)

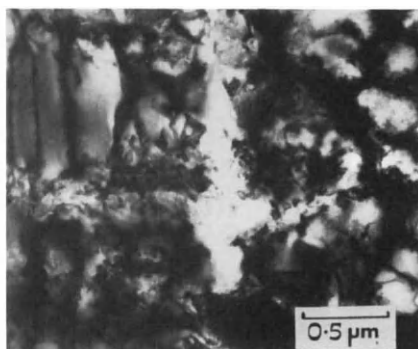


Fig. 2. As-quenched M15 (CTEM)

as-quenched condition, the continuous networks of brittle carbides could lead to low crack growth resistance without further heat treatment (Wood and Bee, 1979). However, similar structures have been reported in CSD H.S. steel bar (Rickinson, Kirk and Davies, 1982), which even though two orders of magnitude coarser still exhibit (after forging) superior hardness and unnotched Izod values than conventionally produced M15 and M42.

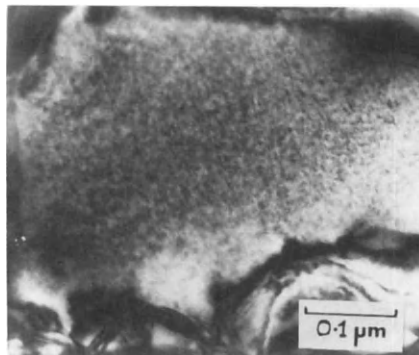


Fig. 3. As-quenched M15 (CTEM)

Initial tests on the consolidation characteristics of particulate made from PDME fibres demonstrated that a prior anneal is necessary to reduce the hardness before consolidation, and that a fully dense product can only be achieved using a combination of heat and deformation (e.g. hot extrusion or hot isostatic pressing). The consolidation temperature must also be carefully controlled if liquid phase sintering is to be avoided. Although carbides have precipitated during solidification, excess carbon still in solution stabilises the austenite and lowers the solidus temperature. This effect has been observed in a 12Cr - 2Mo - 0.3C steel after consolidation

at 1150°C. Liquid phase sintering occurred quite extensively here although the phase diagram indicates that this temperature should be well below the solidus. This results in a dramatic fall in hardness properties (from 724 Hvin in the as-quenched state to only 190 Hv in the sintered condition). A similar effect has been observed in M1 high speed steel (Sare and Honeycombe, 1979). This suggests that further work is necessary to optimise the consolidation parameters for RS steels if the benefits of this production technique are to be fully realised in the final component.

b) Model Steels

In view of the complexity of commercial steel compositions, many model alloys have been investigated, and these studies have been reviewed elsewhere (Wood and Honeycombe, 1981). In the present paper, the effects of vanadium and carbon additions on Fe - Ni and Fe - Mn base systems are described. Alloy compositions are given in Table I, and the constituent phases of the as-quenched products are listed in Table II.

TABLE II

Alloy designation	Phases present
1	Polygonal ferrite
2	Austenite + martensite (twinned and dislocated)
3	martensite (dislocated) + austenite
4	" "
5	Austenite + VC
6	Austenite + martensite
7	Austenite
8	Austenite + ferrite
9	Austenite + ferrite + VC
10	Austenite + VC

The major aim of this project was to characterise the structures obtained by the RSP of two important binary systems related to the production of stainless steels. In addition, further alloying with vanadium and carbon provided information on the precipitation of a simple alloy carbide (MC) during heat treatment of RS alloys. A detailed report of this investigation is outside the scope of this paper and the following discussion presents a summary of the results obtained.

(i) Iron-nickel alloys. Although massive ferrite may form at lower quench rates, recent work on the nature of RS Fe - Ni binary alloys (Inokuti and Cantor, 1982) indicated that for additions up to 20 wt % Ni fully martensitic structures are produced. In the present study, a form of polygonal ferrite was found in alloy 1 : Fe - 16% Ni (Fig. 4). However, this is not thought to be due to a lower quench rate. The apparent anomaly may arise from the difference in quenching technique. PDME and MS provide undeformed specimens, and it is not certain that the lath martensite observed after splat quenching is not caused by high strain rate

deformation, which would give an M_d temperature above ambient.

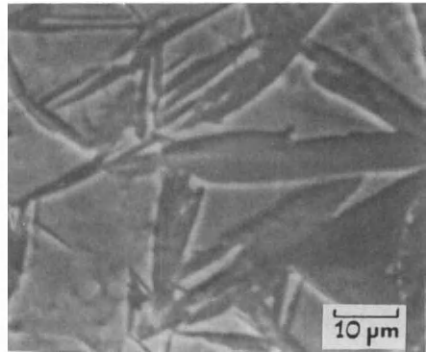
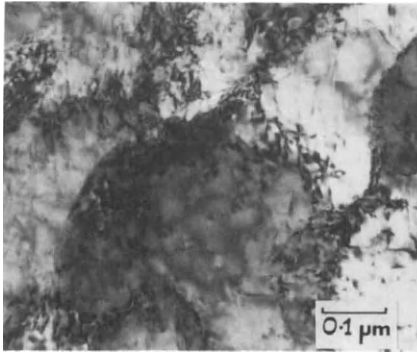


Fig. 4. As-quenched Fe-16Ni (CTEM) Fig. 5. As-quenched Fe-20Ni-0.6C (SEM)

The addition of 0.57 wt % C (alloy 2) produced a mixed austenite/martensite structure (Fig. 5). Both finely twinned and dislocated martensite were observed. The retained austenite displayed a fine modulated structure and evidence of superlattice formation, which are commonly taken as pre-martensitic phenomena.

Increasing the vanadium content would be expected to reduce the stability of austenite and also depress the M_s temperature. A binary Fe - 22% Ni alloy is ferritic after annealing, but martensitic if quenched in the solid state (Kaufmann and Cohen, 1956). However, on splat quenching a duplex ($\alpha' + \gamma$) structure is produced. This regime is only slightly displaced by the addition of 5% vanadium (alloy 3): the amount of retained austenite being reduced from 50% in the binary alloy to 10%. Assuming an $M_s - M_f$ range of 200 K, then these results suggest an M_s of 393 K for the binary alloy with the addition of 5% V lowering the M_s to 313 K. Thus the effect of vanadium is to depress the M_s temperature by 20 K for each weight % addition (which is consistent with its influence on other conventional alloys steels). No twinned martensite was observed, the structure consisting of heavily dislocated lath martensite (Fig. 6).

Vanadium also changes the nature of the solidification structure from a planar to dendritic form. The cell size and secondary dendrite arm spacing are between 1 - 2 μm (Fig. 7), which is relatively coarse (cf. Fig. 1). It can also be concluded that the boundaries visible in Fig. 6 are low-angle cell or interdendritic boundaries rather than high-angle grain boundaries.

Increasing the carbon content of vanadium-bearing steels (alloys 4 and 5) stabilised austenite, and the dendritic structure was retained. At the higher carbon level (0.67%), VC precipitates were observed on cell walls. After heat treatment at 973 K, excess carbon in solid solution reacted to form a dense array of fine MC-type precipitates and the matrix transformed to ferrite on subsequent cooling (Fig. 8).

(ii) Iron-manganese alloys. Iron-manganese alloys do not form lath

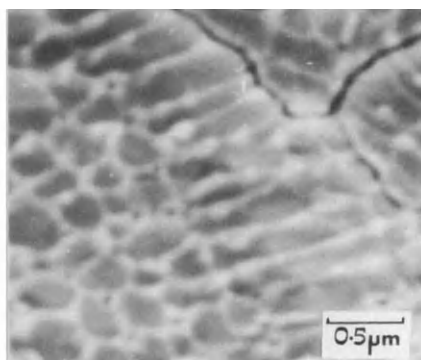
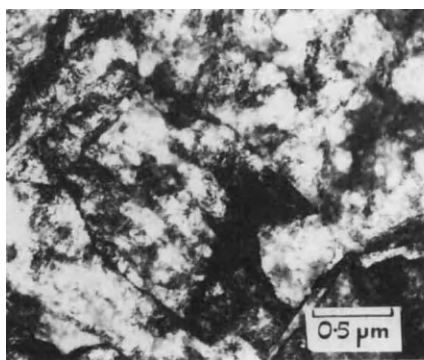


Fig. 6. As-quenched Fe-22Ni-5V (CTEM) Fig. 7. The same alloy. (SEM)

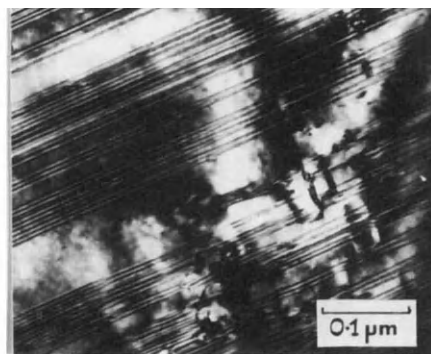
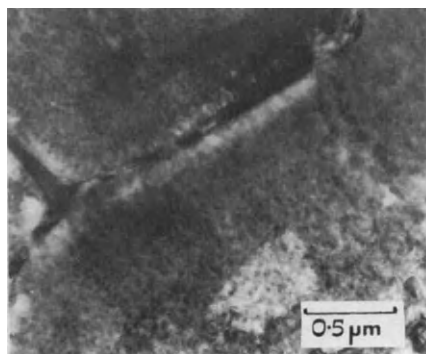


Fig. 8. Heat-treated Fe-20Ni-5V-0.7C (CTEM) Fig. 9. As-quenched Fe-19Mn (CTEM)

martensite after rapid solidification. In the binary Fe - 18.7% Mn (alloy 6) a mixture of austenite and hexagonal ϵ -martensite was observed (Fig. 9). The latter phase has been shown to develop from the overlapping of stacking faults in austenite (Bee and Wood, 1980). This alloy also exhibited a large reversible memory effect. However, its potential as a shape memory metal was found to be limited. The $\epsilon \rightleftharpoons \gamma$ reaction was reversible for only three cycles, with the volume of martensite transformed decreasing with each cycle and the M_s/A_s temperatures increasing.

The addition of carbon (alloy 7) stabilises austenite and no ϵ -martensite is found even after subsequent quenching to 77 K. Evidence of segregation was observed in lightly-etched thin foils (Fig. 10), although the grain boundaries do not seem to be affected by this phenomenon. It appears therefore that this alloy solidified as δ -ferrite and transformed to γ without bulk diffusion. This sample had also been heat treated at 973 K and precipitates of cementite can be seen with the grains. The effect of vanadium (alloy 8) is to stabilise ferrite as predicted, and this resulted

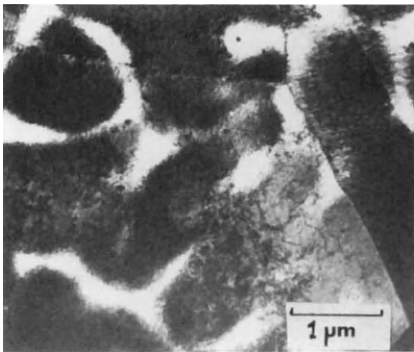


Fig. 10. As-quenched Fe-20Mn-0.5C (CTEM)

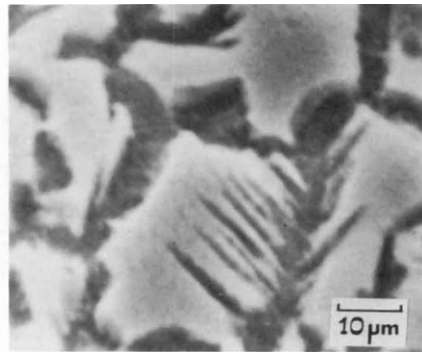


Fig. 11. As-quenched Fe-20Mn-6V-0.1C (SEM)

in a two-phase ($\alpha + \gamma$) microstructure. Small carbon additions (alloy 9) did not affect this equilibrium to any extent and gave rise to similar structures (Fig. 11).

As for the Fe-Ni alloys, the addition of more carbon (alloy 10) produced a solidification structure consisting of austenite with VC particles along the interdendritic boundaries. This alloy responded to heat treatment at 973 K in the same way as alloy 5, to produce a fine matrix dispersion of VC precipitates (see Fig. 8).

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Strain Hardening and Strain Aging in Fe-Al-Mn Alloys

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ABSTRACT

Four Fe-Al-Mn alloys were selected for this study of strain aging and post-quench aging. Various temperatures and aging times were used in the experiments. Specimens were subjected to different pre-strain cold working treatments during the strain aging process. Microstructural examinations were mostly done by optical means, results were compared and related to the mechanical properties of the materials which had been subjected to different treatments. The appearance of a β -Mn phase is suggested to be the main reason for the hardening phenomenon.

KEYWORDS

Fe-Al-Mn; poor man's stainless steel; β -Mn phase; strain aging; post-quench aging.

INTRODUCTION

The Fe-Al-Mn alloys have recently been considered to be a new family of alloys which holds particular promise as an austenitic stainless steel which may be of long-term strategic advantage. Koster and Tonn (1933-34) had established a partial phase diagram for this ternary system. This was later generally confirmed and slightly modified (Chakrabarti, 1977; Schmatz, 1959). Dean and Andenson (1943) had already patented a series of complex Fe-Al-Mn alloys and outlined a rough composition range. Ham and Cairns (1958) reported the development of a promising candidate in the new Fe-Al-Mn alloy group: 10.2 wt% Al, 34.4 wt% Mn, 0.76 wt% C, bal Fe. They called it the "poor man's stainless steel". Schmatz (1960) reported another composition range of 8-9 wt% Al, 30-35 wt% Mn, 0.75-1 wt% C, 1-2 wt% Si, bal Fe. He especially recommended a combination of 8Al, 30Mn, 1C, 1.5Si, bal Fe. Following Schmatz's work, studies on the effect of other alloying elements and the oxidation resistance of the Fe-Al-Mn alloy system were carried out in detail by Gibson (1961), Perkins (1976), Xiao-jimeil (1979), Sauer (1979) and others.

Strain aging of the Fe-Al-Mn system was first investigated by Ham and Cairns

(1958). They observed that the 10 wt% Al + 34 wt% Mn alloy had a remarkable strengthening effect due to work hardening and strain aging. As a result, a tensile strength approaching 1725 MPa (250 000 psi) could be obtained. On the other hand, the Ni-Cr austenitic stainless steels are usually stress-relieved and softened when heated after cold working.

Schmatz (1959) also noted that the strength of the Fe-Al-Mn alloy could be improved if quenched and aged afterwards. He suggested that strengthening and embrittlement of these aged alloys might be due to the precipitation of a β -manganese phase. However, his work was incomplete and warrants further investigation. In this paper results of strain hardening, strain aging and post-quench aging of some Fe-Al-Mn alloys are reported.

EXPERIMENTAL PROCEDURE

A. Sample preparation

Four Fe-Al-Mn alloys were prepared in a L-H IS 8/III vacuum induction furnace with argon protective atmosphere. The chemical compositions are listed in Table I. The following thermomechanical treatment was adopted to eliminate material coring: hot forging at 1200°C, homogenization treatment for 24 hours at 1100°C, air cooling, cold rolling (50% reduction in thickness) followed by recrystallization at 950°C for 1 hour. As a result, after air cooling a grain size of 4-6 according to ASTM was obtained.

B. Prestrain and aging processes

Cold working of 20, 40, 60 and 80 per cent reduction in thickness were carried out before the aging process. Strain aging experiments were divided into two series. The first series was treated for one hour, as for all prestrained specimens, by varying the aging temperature from 300°C to 900°C. The second series was kept at a constant temperature of 700°C for various aging times ranging from 15 min to 10⁴ min (166.7 hours).

Specimens for post-quench aging were oil-quenched from 950°C and then aged at temperatures and times as before.

TABLE I Chemical Composition Analysis Results of Alloy A, B, C and D.

Alloy	wt(%)						
	Al	Mn	C	Si	P	S	Fe
A	8.96	33.2	0.01	0.09	0.005	0.014	bal
B	7.76	26.6	0.22	0.11	0.013	0.025	bal
C	7.15	27.5	0.51	0.20	0.011	0.023	bal
D	7.37	28.0	0.50	1.08	0.010	0.024	bal

C. Mechanical properties and metallography

Tensile properties at room temperature were obtained with an Instron tensile machine model 1115 (cross head speed of 0.1 cm/min). The gauge length of the tensile specimen is 25 mm. All hardness results are expressed by an R_A scale.

The usual optical microscopic examinations were supplemented with the colour etching method. The ferrite volume fraction was obtained by linear analysis. The internal structure and the tensile fractured surface were examined by TEM and SEM respectively. Furthermore, all the phase structures were identified with TEM diffraction patterns as well as with X-ray diffraction techniques.

RESULTS AND DISCUSSIONS

A. Structural and mechanical properties of the alloys before the aging process

In all four alloys A, B, C and D, a dendritic structure was observed in the as-cast condition. Some ferritic regions were observed between the austenitic dendrite arms. As the carbon content was increased, from alloy A to D, the volume fraction of the ferrite phase decreased.

After hot forging, homogenization, cold rolling and annealing at 950°C for one hour, the microstructure of the four alloys was found to be either austenitic mixing with ferritic or fully austenitic. Details are given in Table II.

Table II - Phases and ASTM Grain-Size Number of Alloy A, B, C and D in the Annealed Condition

Alloy	Phase	ASTM grain-size number
A	$\gamma + \alpha(25\%)$	4-5
B	$\gamma + \alpha(<5\%)$	4-5
C	γ	5-6
D	γ	5-6

All four alloys showed good workability at room temperature in the annealed condition. Tensile and hardness test results of specimens in the annealed condition and after being cold reduced by from 20% to 80% are listed in Table III.

B. Results obtained from the post-quench aged specimens

Figures 1 and 2 show the changes in hardness of the four alloys during aging with different times and temperatures. Alloy A showed a drastic increase in hardness when aged between 500 and 800°C for one hour (Fig. 1). When the aging temperature was kept constant at 700°C, the hardness of the same alloy increased from 51 R_A to about 73 R_A after 10^4 minutes (Fig. 2).

Compared with alloy A, alloy B shows only a very slight increase in hardness in both instances (Figs. 1 and 2). Alloys C and D show no evidence of any age hardening. Optical microscopy (see Fig. 3) indicates that as a result of post-quench aging, the second phase precipitates are in lamellar form within the ferrite. No precipitated particle was observed within the austenite except for the presence of some precipitates along the α/γ phase boundaries. Therefore, no age hardening was observed in the fully austenitic alloys C and D and only very limited age hardening would be discerned in alloy B.

The precipitates in alloys A and B are suggested to be a β -Mn phase by

Table III - Mechanical Properties of Alloy A, B, C and D

Alloy	Cold rolled, Reduction in thickness, %	Tensile Strength MPa(ksi)	Yield Strength MPa(ksi)	Elongation %	Reduction of area %	Hardness R _A
A	0	564(81.8)	273(39.6)	38	50	50
	20	717(104)	407(59.1)	14	47	63
	40	876(127)	522(75.7)	7	41	66
	60	1000(145)	624(90.5)	6	40	68
	80	1080(157)	710(103)	6	40	69
B	0	578(83.8)	247(35.9)	48	57	47
	20	738(107)	443(64.2)	22	52	63
	40	917(133)	573(83.1)	8	43	67
	60	1050(152)	654(94.8)	7	39	69
	80	1130(164)	724(105)	6	36	70
C	0	703(102)	301(43.7)	47	56	54
	20	903(131)	473(68.7)	19	52	66
	40	1100(160)	620(89.9)	8	40	69
	60	1260(183)	744(108)	8	34	72
	80	1360(197)	814(118)	6	29	73
D	0	696(101)	304(44.1)	48	57	56
	20	910(132)	500(72.5)	21	48	69
	40	1150(167)	646(93.8)	7	44	70
	60	1280(185)	779(113)	7	40	72
	80	1390(202)	855(124)	6	35	73

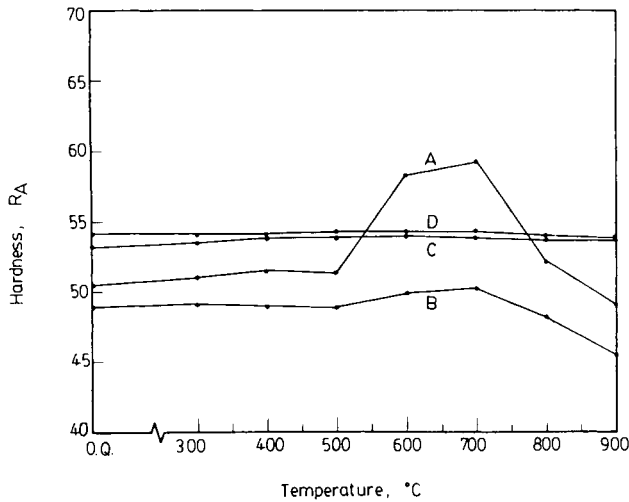


Fig. 1 Hardness vs various quench aging temperatures. The alloys were heat treated at 950°C for 1 h, oil quenched, then aged at various temperatures. The aging time was 1h.

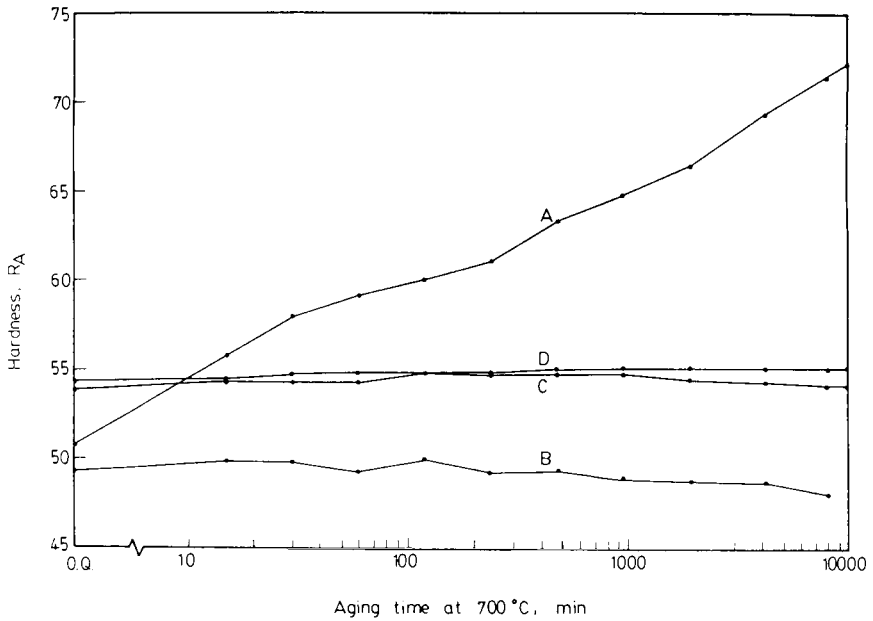
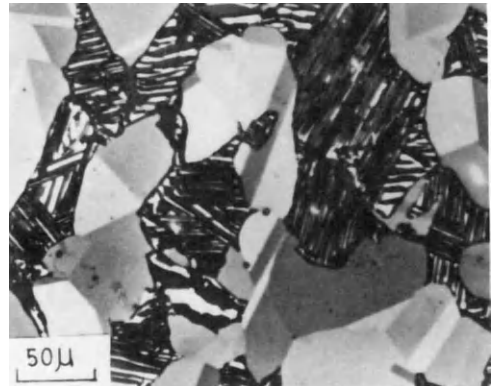


Fig. 2 Hardness vs. various post-quench aging times at a constant aging temperature of 700°C.

Fig.3. Microstructure of alloy A (9Al, 33.2Mn, bal Fe) after quench aged (700°C, 1h.) Austenite grains and twins are tinted various colours according to their crystallographic orientations; the dark lamellar layer structure is β -Mn phase which precipitated in the ferrite region (white).



Schmatz's work (1959). In his equilibrium phase diagram, the four alloys have a possibility of falling into the three phases ($\gamma + \alpha + \beta$) region. X-ray diffraction examinations were carried out on both alloy A and a pure manganese sample which had been quenched from 900°C to room temperature to transform to β -Mn phase. The results are in good agreement, especially the peaks of 310β , 311β , 321β , 331β , 510β , 432β , 520β which are obviously consistent. The TEM selected area diffraction pattern (SADP) experiments were also performed on the precipitates of alloys A and B. Both results of X-ray diffraction and SADP indicate that the precipitated particles are complex cubic with 6.3Å lattice parameter and about 20 atoms per unit cell. It is concluded that the structure of precipitates in alloys A and B is β -Mn phase.

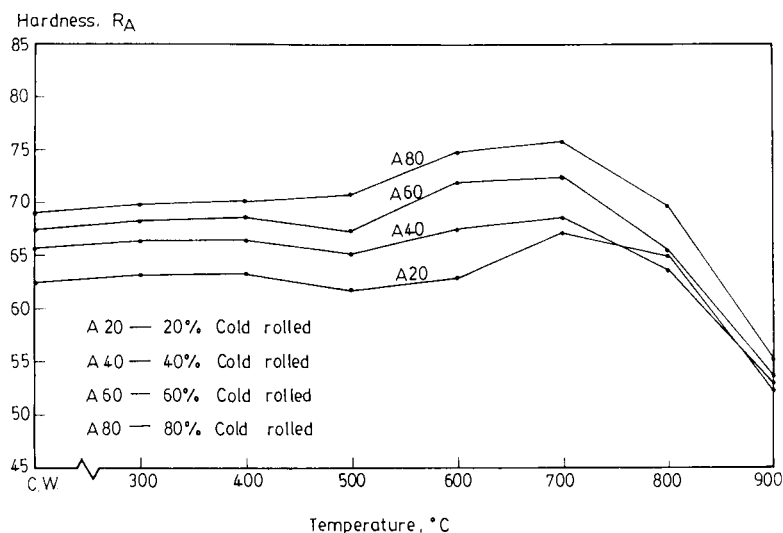


Fig. 4 Hardness vs. various aging temperatures of alloy A prestrained to different degrees of reduction in cold rolling, aging time constant for 1 h .

C. Studies of materials after strain aging

Figure 4 shows the changes in hardness of alloy A, having been cold rolled to different degrees of reduction and aged for one hour at temperatures ranging from 300 to 900°C. The more severe the cold working, the more drastic was the increase in age hardening. It was also observed that the heavier prestrained specimens always recovered and recrystallized at the lower temperatures probably due to a lower recrystallization activation energy. Only a limited degree of age hardening was observed for alloy B and no hardening for alloys C and D which were subjected to a similar experimental procedure.

Alloy A, aged at a constant temperature of 700°C and prestrained to 80%, showed an increase in hardness up to 79 RA after an aging time of 10^4 minutes. Alloys B, C and D were subjected to a similar experiment. A decrease in hardness was observed during the first stages of aging, probably due to recrystallization, but an increase was evident with aging time.

Hardening during the strain aging process can also be attributed to the precipitation of β -Mn. Specially, some small β -Mn particles precipitated in the γ phase as well as in the α phase in the course of the aging process. As can be seen from Figures 5 and 6, the volume fraction of β -Mn in the α phase is much larger than that in the γ phase. Besides, the total volume fraction of β -Mn increases with aging time. The preferred sites of β -Mn precipitates in the γ phase are the recrystallized grain boundaries.

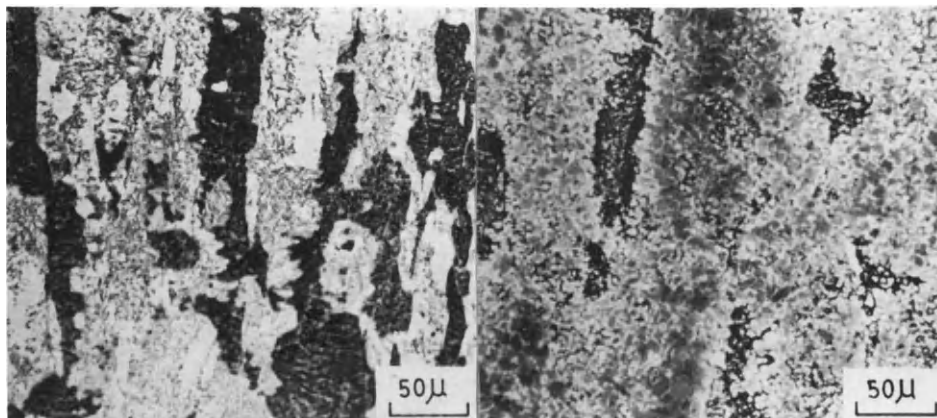


Fig.5. Microstructure of alloy A (9Al, 33.2Mn, bal Fe) after strain aged (80% cold rolled, 700°C, 1h). The tiny β -Mn particles precipitated in both the austenite region (bright) and the ferrite region (dark).

Fig.6. Microstructure of alloy B (7.8Al, 26.6Mn, 0.22C, 0.11Si, bal Fe) after strain aged (80% cold rolled, 700°C, 1h). The tiny β -Mn particles (gray to black) also precipitated in both the austenite region (bright) and the ferrite region (dark).

CONCLUSIONS

1. An increase in carbon content in the Fe-Al-Mn alloys (about 8% aluminium, 30% manganese, bal. iron) from 0.01% to 0.5% results in the complete disappearance of the ferritic phase and only the austenitic phase is observed in the fully annealed condition.
2. During post-quench aging, β -Mn precipitated in the ferrite and it is suggested that this precipitation is responsible for the hardening effect. No hardening was observed in fully austenitic alloys.
3. Post-quench aging of alloy A or B in the temperature range 500 to 800°C causes lamellar precipitation of β -Mn in the ferritic phase.
4. In the strain aging process, the β -Mn particles precipitated inside the γ phase as well as in the ferrite phase. The more severe the prestrain, the stronger the strain age hardening effect was observed to be in the temperature range from 500 to 800°C.
5. In the fully austenitic alloys C and D, a limited precipitation of β -Mn particles was observed in the strain aging course and the hardening process was therefore retarded. The softening in the primary stages of aging is probably due to recrystallization processes.
6. A reduction in thickness of 80% by cold rolling of alloy A led to an increase in hardness to about 79 R_A by applying a suitable combination of aging time and temperature.

ACKNOWLEDGEMENTS

We are grateful to Mr. Chuen-Rong Lin and his staff for their help in the material melting, casting and hot forging. This research was sponsored by the R.O.C. National Science Council under Contract No. NSC 71-0405-E007-02.

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An Investigation into the Superhardening Effect in Molybdenum-free Steel with Specific Reference to Alloy Substitution

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ABSTRACT

The influence which the superheating of a steel melt has on its hardenability has been determined using a combination of three hardenability tests. It is shown that the hardenability of some alloy steels can be drastically increased if the melt is superheated to a minimum of 1650°C combined with a high deoxidant level ($Al \geq 0.05\%$). It is proposed that the ideal critical diameter of steel treated by this superhardening treatment may be calculated by the equation

$$D_{I\text{superhardening}} = (D_{I\text{base}})^{2/55} \text{ mm, for } D_{I\text{base}} \geq 55 \text{ mm.}$$

Isothermal transformation diagrams indicate that the superhardening treatment causes the pearlite and bainite noses to be strongly displaced to longer times. The possibility of using the superhardening effect to extend the properties of conventional low-alloy steel qualities into markets traditionally served by higher alloyed steels is reviewed, and it is concluded that serious attention should be given to alloying element conservation by means of this treatment.

KEYWORDS

Hardenability; low-alloy steel; alloy substitution; isothermal transformation diagrams.

INTRODUCTION

Due to the limited worldwide resources, the conservation of alloying elements is a strategic problem which is receiving earnest attention internationally. Long-term national research programmes aimed at reducing the need for strategic metals have recently been launched both in the U.S.A. (Gray, 1982) and locally. Specifically in low-alloy steels, alloying elements are primarily added for improvement of the fracture toughness and hardenability properties. Since the time of the classic work of Grossmann (1942), Crafts and Lamont (1944) and Kramer, Siegel and Brooks (1946), it has been accepted that the hardenability of low-alloy steels is uniquely related to the chemical composition and austenite grain size. The only way to substitute one alloying element, was by increasing the quantity of another. Due to the interactive multiplication effect of most alloying elements, some conservation has been found possible by using a variety of alloying elements rather than

just a single element. Recently, however, Brown and James (1980) have upset this classic concept by reporting a dramatic increase in the hardenability of some low-alloy steels by superheating of the melt. This phenomenon was termed the superhardening effect.

Brown and James (1980) reported that for the 150M36 (En15) casts investigated, a combination of superheating the melt to 1650°C plus high aluminium content ($Al \geq 0.05$ mass percent) resulted in such an increase in hardenability that the Jominy test, due to the relatively high cooling rates present even at the air-cooled end, was insufficient to assess the hardenability. They also showed that the superhardening effect was only obtained when a certain threshold level of base hardenability had been exceeded. The conditions necessary for achieving superhardenability in the laboratory melts were confirmed by making twenty production casts. The initial results were verified by a group of research workers at Cambridge (Sachs, Ralph and Slater, 1980) by conducting a detailed study of the transformation kinetics of such a production cast.

In the present work the following aspects of the superhardening effect are considered:

1. A quantitative assessment of the hardenability increase due to superhardening. In the original work of Brown and James, Jominy tests were used exclusively and due to the flat Jominy curve observed, the hardenability increase could not be quantified. In this work, use was made of Jominy, extended Jominy and air hardenability tests to quantify the increase in hardenability.
2. The establishment of a formula for calculating the hardenability of a superhardenability treated steel from an analysis of the experimental work.
3. The influence of steel chemistry. The steels investigated by Brown and James were limited to casts corresponding to 150M36 (En15) with a very small variation in base hardenability and steel chemistry. It was considered important that the superhardening effect should be studied in a range of steels of widely different chemistry and base hardenabilities, including steels with a much higher base hardenability than those studied previously.
4. The transformation kinetics of superhardenability studied by the construction of isothermal transformation diagrams.
5. The influence of prolonged holding times at high austenitising temperatures on the superhardening effect.

EXPERIMENTAL PROCEDURE

Laboratory casts

Three series of casts were prepared. Series A was made in an air induction furnace using commercial 530A40 (En18D) base material with manganese and aluminium additions; Series B was prepared in an inert gas (Argon) induction furnace with the same base material and additions as previously, while in series C a low carbon higher manganese steel prepared in an inert gas unit was studied (see Table 1 for compositions). In all three series some of the casts were made with (1650°C) and some without (1550°C) superheat. Alloying additions were made to the melt at 1550°C. In all instances superheated melts were held at 1650°C for a minimum time of two minutes.

Altogether forty-nine casts were prepared. All of the superheated steels were cooled to 1550°C before casting. Temperature measurements of the bath were made by an optical pyrometer as well as thermocouples (Pt-Pt 10 % Rh). The casts were forged into 30 mm rounds prior to machining. The mass of most of the casts were 10 kg, but some 2 kg casts were also produced.

TABLE 1 Chemical Composition Ranges of Casts

Series	Chemical composition (mass per cent)												ASTM grain size
	C	Mn	P	S	Si	Ni	Cu	Cr	Mo	V	Nb	Al	
A	0.46-0.50	0.83-1.64	0.02	0.03	0.15-0.29	0.13-0.14	0.15-0.16	0.93-0.95	0.05-0.06	0.04	0.01-0.02	0.01-0.21	7-9
B	0.43-0.52	0.69-1.10	0.02	0.03	0.23-0.31	0.15-0.20	0.15-0.17	0.94-0.98	0.05-0.06	0.04	0.01-0.02	0.01-0.11	7-9
C	0.26-0.40	1.81-2.55	0.01-0.02	0.03-0.05	0.28-0.39	0.10-0.24	0.04-0.07	0.08-0.59	0.01-0.04	0.01-0.03	0.01	0.05-0.12	8-9

Hardenability Testing and Prediction

Due to the large range of hardenabilities studied three hardenability tests were used. The standard ASTM Jominy test was used for the relatively fast cooling rates. For slower cooling rates the extended Jominy test devised by Rose and Rademacher (1956) was used. For even slower cooling rates, Jatzack's (1978) air hardenability bar was employed. The combination of these three tests resulted in a continuous range of cooling rates from 330°C/s to 0.1°C/s in the temperature interval 704 - 538°C.

Vickers (30 kgf/294 N) hardness measurements were made and the positions on the test bars corresponding to a 50 % martensitic transformation product were determined. For this purpose the carbon content - hardness of 50 % martensite relationship according to Hodge and Orehoski (1946) was used. The flats ground along the hardenability bars were also polished and etched for metallographical confirmation of the 50 % martensite position. These positions were converted to the corresponding ideal critical diameter (D_I) values by using the relationship developed by Grossmann (1942) in the case of the Jominy test and those developed by Rose and Rademacher (1956) and Jatzack (1978) for the other two tests. The experimental technique employed is dealt with in more detail elsewhere. (Mostert, 1982).

For an accurate evaluation of the increase in hardenability obtained by superhardening, it was necessary to have a prediction system which would perform satisfactorily for the 1550°C melts of the three experimental series in question. Alloying element interactions occur (Fostini and Schoen, 1967) which can cause large errors for a particular steel quality. For this reason a number of prediction systems was evaluated, viz: ASTM A255-67 (1981); Crafts and Lamont (1944); Grossman (1942); Just (1968); and Kramer, Siegel and Brooks (1946). In each case the predicted hardenability was compared with that actually measured in a normal cast. The ASTM prediction system together with the Kramer, Siegel and Brooks (1946) values for the minor alloying elements P, S, V and Al resulted in a good correlation for the series A and B casts (see 1550°C casts in Fig. 1). The prediction system of Crafts and Lamont proved accurate for the series C casts mainly due to their corrected multiplication factors for high manganese values.

The following abbreviations for hardenability terminology will be used throughout:

$D_{I\text{base}}$: The ideal critical diameter calculated using the prediction system mentioned.

$D_{I\text{actual}}$: The ideal critical diameter experimentally determined by hardenability testing.

In all instances ideal critical diameter values refer to positions where 50 % martensite has formed.

EXPERIMENTAL RESULTS

Hardenability Testing

Figure 1 compares typical Jominy curves for superhardening and normal casts of the same composition, illustrating the great increase in hardenability obtained by superhardening.

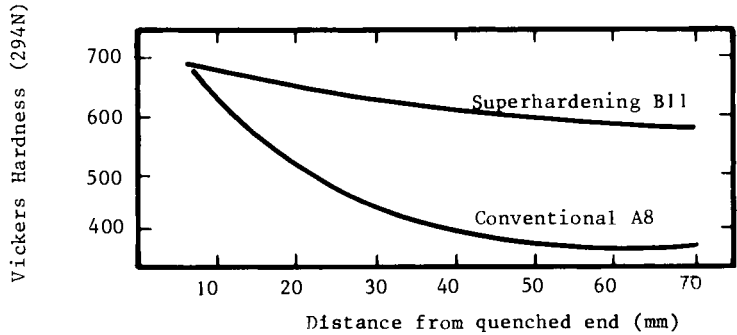


Fig.1 Typical Jominy curves for superhardening and conventional casts. (For compositions see Table 2)

TABLE 2 Chemical Composition of Casts A8, B11, C9 and C11(mass percent)

	Melt														
Cast	temp.	C	Mn	P	S	Si	Ni	Cu	Cr	Mo	V	Nb	Al	ASTM	
	°C													grain	size
A8	1550	0.46	1.09	0.02	0.03	0.19	0.13	0.16	0.94	0.06	0.04	0.01	0.03	8	
B11	1650	0.44	1.08	0.02	0.03	0.28	0.16	0.15	0.94	0.06	0.04	0.02	0.08	8	
C11	1550	0.31	2.26	0.01	0.02	0.33	0.15	0.02	0.55	-	0.01	0.02	0.03	8	
C9	1650	0.30	2.21	0.02	0.04	0.29	0.11	0.04	0.57	0.01	0.01	0.02	0.09	9	

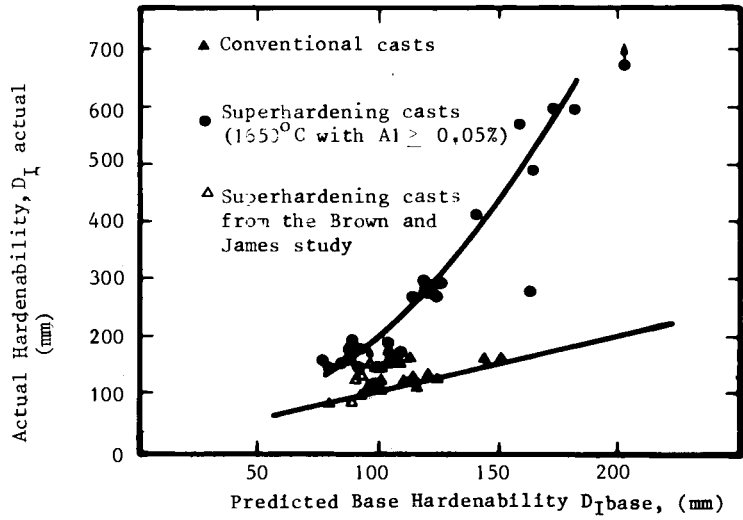


Fig. 2 Hardenability test results of superhardening and conventional casts.

Figure 2 summarises the hardenability test results of superhardenability treated (melt temperature 1650°C and aluminium 0.05 %) and conventional (1550°C) casts by comparing the actual hardenability values to the predicted base hardenabilities. The superhardening points from the Brown and James study were converted to approximate D_I -values and included for comparison. From this figure a number of conclusions can be drawn:

1. The hardenability prediction system for the 1550°C melts is accurate, since the actual hardenability values are near the predicted values for most of the 1550°C casts (see Fig. 2).
2. In all cases the actual hardenability values of the superhardening casts were much higher than the predicted values.
3. The hardenability increase is dependent on the base hardenability. The actual hardenability of superhardening casts with a base ideal critical diameter of 100 mm (En18D without manganese additions) was twice as high as predicted. Increasing the $D_{I\text{-base}}$ -value to 175 mm resulted in superhardening D_I -values of 595 mm (3.4 times the predicted D_I). The hardenability increase is thus much more pronounced in high-base hardenability steels than in leaner alloyed steels. This is a novel finding. The studies of Brown and James (1980) were limited to base hardenabilities (D_I) around 100 mm and this is the first study known to the authors employing casts with much higher base hardenabilities.
4. Casts with similar base hardenabilities but widely different chemical compositions (e.g. some casts in series B and C), showed similar hardenabilities when superhardened. This implies that for steels with the same base hardenability, precise steel chemistry is not important when the hardenability increase is considered. Furthermore it suggests that a wide range of steel qualities would probably respond to a superhardening treatment.

It should be noted that although straight lines could be drawn through the superhardening points in Fig 2, the straight line in Fig 3 actually implies parabolic behaviour in Fig 2.

Calculating the Hardenability of Superhardening Steels

The hardenability test results suggest that the influence of alloying element additions during superhardening is in effect through the influence it has on the base hardenability.

For the purpose of calculating the hardenability of superhardening steels, new multiplication factors for the various alloys employed are not required. The experimental results rather suggest that it can be calculated from the base hardenability by using a superhardening multiplying factor, dependent only on the base hardenability. For this purpose experimental results were evaluated by presenting the $D_{I\text{actual}}/D_{I\text{base}}$ ratio's (the Superhardening Factor) for the superhardening casts as a function of base hardenability as shown in Fig 3.

Mathematical analysis of these values led to the following equation:

Ideal critical diameter of a superhardening steel

$$D_{I\text{superhardening}} = (D_{I\text{base}})^2 / 55 \text{ mm, when } D_{I\text{base}} \text{ is greater than } 55 \text{ mm.}$$

For calculating $D_{I\text{base}}$ for steels similar to 530A40(En18D), the ASTM prediction system together with the Kramer, Siegel and Brooks (1946) factors for the minor alloys P, S, V and Al, is recommended.

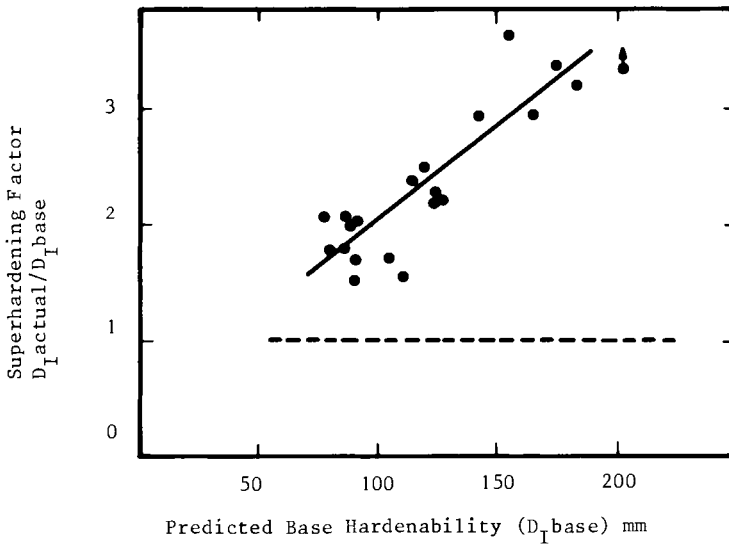


Fig. 3 The Superhardening Factor as a function of base hardenability

The Influence of Aluminium Additions

Brown and James reported that a minimum aluminium content of 0.03 - 0.05% was required to induce superhardening. Results from this study are consistent with these values. Figure 4 shows the hardenability increase of a number of superheated (1650°C) casts with similar $D_{I\text{base}}$ values as a function of the total aluminium content (mass percent). This figure indicates that the aluminium content has to be in excess of 0.05% to obtain full superhardening.

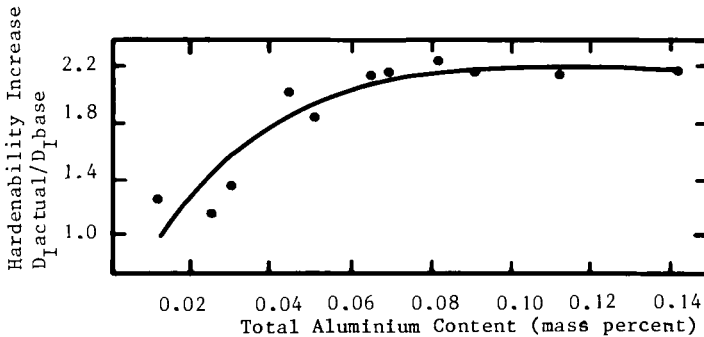


Fig. 4 Hardenability increase of superhardening steels with similar base hardenabilities as a function of total aluminium content

The Influence of Prolonged Holding at High Austenitising Temperatures

Since it was thought that prolonged holding at high austenitising temperatures might result in a loss of superhardenability, equivalent to the so-called boron fade effect, some of the casts of the C series were subjected to such austenitising treatments. Jominy bars were held at 1200°C for 2 hours and thereafter transferred to an oven at 900°C for 1 hour. After quenching the ASTM grain sizes were in the range of 2 - 5. Thereafter the Jominy samples were end-quenched from normal austenitising temperatures resulting in fine-grained structures (ASTM 7 - 9). The Jominy curves before and after the grain growth treatment coincided and it was concluded that holding at high austenitising temperatures did not result in a loss of hardenability.

Mechanical Properties

The tensile and impact properties of some superhardenability treated casts were determined after various heat treatments and no detrimental effects were detected.

Isothermal Transformation Diagrams

The influence of a superhardenability treatment on the transformation characteristics was also evaluated. Isothermal transformation diagrams for a superhardening and control cast were obtained dilatometrically using a quartz dilatometer with cylindrical samples 30 mm long and 3 mm wide. The samples were austenitised in a neutral salt bath at 890°C for 15 minutes, followed by quenching in an isothermal lead bath.

Figures 5a and 5b respectively show the displacement of the beginning and the end of isothermal transformation caused by a superhardenability treatment. In this particular case, superhardenability caused a displacement of the 1 % ferrite start nose from 80 s (600°C) to 350 s (600°C). The pearlite end curve was also drastically retarded. The 1 % bainite start nose was similarly displaced from 12 s (460°C) in the control cast to 59 s (460°C) in the superhardening cast with a shift to longer times at the end of transformation as well.

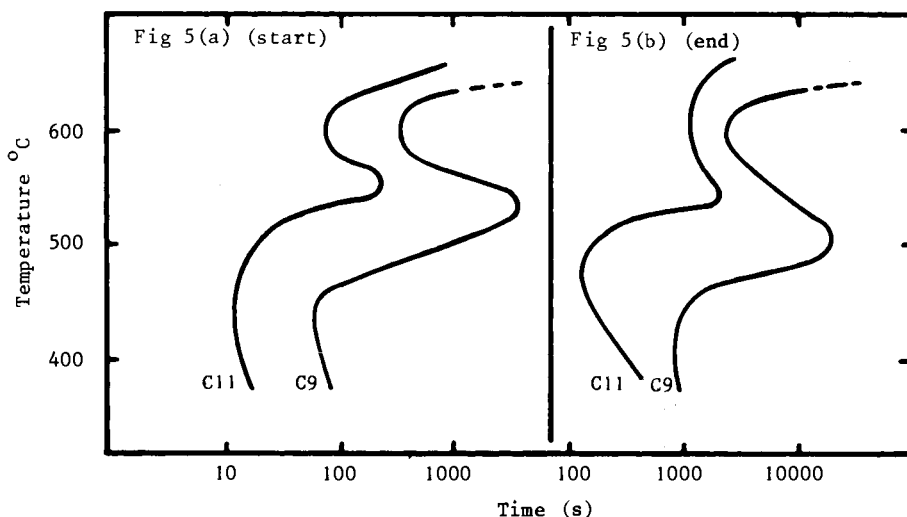


Fig. 5 Transformation start (Fig. 5(a)) and transformation end (Fig. 5(b)) curves for a superhardening and control cast. (See Table 2 for composition)

It appears that superhardening does not basically alter the shape of the isothermal transformation diagram, the main effect being a displacement of the curve to longer times.

THE SUPERHARDENING MECHANISM

The proposed theories concerning the mechanism of superhardening are still speculative in nature. A study of the transformation kinetics of superhardening (Sachs, Ralph and Slater 1980) indicated that a retardation of the ferrite growth rate is primarily responsible for the hardenability increase. It was proposed that the superheat causes a destruction of alloying element clustering in the melt, leading to a more homogeneous distribution of alloy atoms in the solidified steel. A random distribution of carbide forming elements would then more effectively retard carbon diffusion. Alternatively, a homogeneous distribution of austenite stabilizers could enhance the segregation of these elements to austenite grain boundaries, thus retarding austenite decomposition. The role of the aluminium was thought to be as scavenger of nitrogen and oxygen, eliminating the competitive interstitial diffusion of nitrogen and oxygen to austenite grain boundaries.

These postulations were offered without experimental verification. Recent studies on the structure of liquid iron have shown indications of an atomic redistribution in iron melts in the temperature range between 1600°C and 1700°C (Abdel-Aziz, 1981). The specific temperature was found to be influenced by alloying additions (Kisun'ko, Arkharov and Belov, 1975). At this temperature a distinct discontinuity or change of slope was observed in the viscosity-, electrical resistivity- and magnetic susceptibility polytherms. The proposed structural change in iron melts was also supported by X-ray structural analysis (Vatrolin and Pastuchov, 1973).

Results from the present study indicate that steels superheated under inert gas cover had consistently a higher hardenability than air induction casts. Furthermore, a number of 1550°C inert gas casts with high aluminium content superhardened while the same behaviour was not observed for the 1550°C air melts. These observations seem to indicate that a reduction of the active oxygen and nitrogen content through high deoxidant additions, inert gas melting and high melting temperatures is the most important aspect of the superhardening mechanism. It should be noted that inert gas conditions with aluminium additions to the melt was used in the original study.

Much further work is however needed before a conclusive mechanism of superhardening, or for that matter even conventional hardenability, can be proposed.

SUPERHARDENING STEEL QUALITIES AS ALTERNATIVES TO EXISTING STEEL QUALITIES

The foregoing results demonstrate clearly that superhardening steel qualities could provide a very cost-effective alternative to expensive higher alloyed steels and so reduce the Republic's consumption of expensive alloys as well as reducing the country's dependence on strategic imported alloys.

Table 5 compares the measured hardenabilities (D_1) of four superhardening casts with the hardenabilities (calculated according to ASTM) of some commercial qualities. The total alloying element costs (calculated using local prices in December 1981) per 160 ton cast is also tabulated. This table illustrates the ease with which superhardening steel qualities based on En18D plus manganese additions, can adequately replace a wide range of highly alloyed commercial steels. The enormous cost savings possible are obvious. Recently, this concept has been mentioned in the literature (McBroom and MacQuarrie, 1982) and it has been concluded that the

superhardening treatment can extend the properties of conventional alloy steels such as 605M36 (En16) into markets previously served by steels in the 817M40 (En24) to 835M30 (En30) range.

TABLE 3 Comparison of Cost and Hardenability of Conventional and Superhardening Steels

Cast	Melting Practice °C	Composition (mass percent)							ASTM grain D_I (mm)	Alloying element cost per 160 ton cast
		C	Mn	Si	Cr	Ni	Mo	size		
A4	1650	0.43	0.69	0.28	0.97	0.14	0.05	8	145	R 5 800
817M40(En24)	1550	0.43	0.69	0.28	0.97	1.80	0.14	8	150	R 25 000
B4	1650	0.44	1.08	0.28	0.96	0.14	0.05	8	267	R 6 500
826M40(En26)	1550	0.43	0.73	0.28	0.60	2.60	0.50	8	264	R 39 000
V6	1650	0.47	1.52	0.28	0.96	0.16	0.06	9	483	R 7 600
830M31(En27)	1550	0.35	0.70	0.28	1.22	3.00	0.65	8	510	R 47 800

From the experimental results it is, therefore, clear that serious consideration should be given to the superhardening effect as a possible substitute for imported alloying elements (such as molybdenum) in low-alloy steels.

CONCLUSIONS

1. Hardenability tests and dilatometrical studies confirmed that the hardenability of some low-alloy steels can be increased dramatically if the melt is superheated to a minimum temperature of 1650°C. This increase in hardenability as a result of superheating (the superhardening effect) only occurs when the deoxidant level is high ($Al \geq 0.05$ wt %). The magnitude of this hardenability increase seems to be primarily dependent on the base hardenability of the steel, irrespective of the precise chemical composition which gives rise to that base hardenability.
2. The ideal critical diameter of a superhardening steel can be calculated from the base hardenability by the equation $D_{I\text{superhardening}} = (D_{I\text{base}})^2/55$ mm, when $D_{I\text{base}}$ is greater than 55 mm.
3. Impact and tensile properties were not adversely affected by the treatment and prolonged holding at high austenitising temperatures did not result in a loss of the superhardening effect.
4. The superhardening treatment can be used to extend the properties of molybdenum-free low-alloy steels into markets previously served by highly alloyed commercial steels.

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The Influence of Rare Earth Elements on the Temper Embrittlement Behaviour and Mechanical Properties of a Low Alloy Steel

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ABSTRACT

As a potential replacement for molybdenum, the influence of rare earth metal (REM) additions on the temper embrittlement characteristics of a low alloy steel has been determined. REM's were found to effectively inhibit this phenomenon, mainly through chemical fixation of residual impurities by compound formation. Detailed analysis of inclusion size and volume fraction revealed that these parameters also have a major effect on the Charpy impact test 'upper shelf' energy.

KEYWORDS

Temper embrittlement; ductile-brittle transition temperature; rare earth metals; molybdenum.

INTRODUCTION

In alloy steels, temper embrittlement is manifest by a progressive loss of toughness after heating in the approximate range 350-600°C. This has been shown to arise from the segregation of metalloid impurities (P, Sn, S, Sb and As) to prior austenite grain boundaries (McMahon, 1968; Ohtani and co-workers 1976), which weakens the boundaries and leads to intergranular failure.

Until recently, molybdenum appeared unique in preventing temper embrittlement, although the precise mechanism by which this is achieved is still the subject of considerable controversy. It has been suggested (Jin Yu and C.J. McMahon Jnr. 1980) that its principal role is to scavenge phosphorus, thus reducing the bulk chemical activity of the impurity and so reducing segregation to grain boundaries. Alternatively, segregation of Mo itself may lead to increased cohesion of the grain boundaries (Dumoulin and co-workers 1980).

In the search for an alternative means for the elimination of the

embrittling effects of impurities, two approaches are immediately evident.

The simplest method is to reduce the residual impurity content in the primary production process. However this is both difficult and costly. Alternatively, active impurities can be effectively eliminated through chemical fixation.

Using thermodynamic data, it has been predicted (Seah, Spencer and Hondros 1977) that P-induced embrittlement in a pressure vessel steel can be minimised through additions of lanthanum, and this has been confirmed experimentally. Other harmful species are also removed from solid solution, and the optimum La-content can be calculated from the stoichiometry of the precipitates using the equation (Seah, Spencer and Hondros 1977).

$$\text{La} = 8,7 \text{ S} + 2,3 \text{ Sn} + 4,5 \text{ P}$$

Rare earth additions are generally made in the form of mischmetall. The other constituent elements (e.g. Ce, Nd, Pr and Sm) are thought to behave in a similar way to La with respect to S, Sn and P, as well as to scavenge other prevalent residuals (i.e. As and Sb).

The purpose of the present paper is to report further on the effects of rare earth metals on the embrittlement characteristics of a low-alloy steel, and to compare these results with the influence of molybdenum on the same steel.

EXPERIMENTAL PROCEDURE

The control alloy was an En 18 D steel doped with phosphorus. Experimental alloys were prepared through controlled additions to this base steel to the compositions listed in Table I. Ingots were forged to 13 mm thick plate, and from these Charpy impact and notched slow-bend specimens were machined. The specimens were austenitised at 850°C for 0,5 hr and oil quenched. The resulting martensitic structure was tempered at 650°C and then isothermally aged at 510°C for 96 hours (to induce embrittlement).

To determine the relation between the ductile-to-brittle transition temperature (DBTT) and strength, slow-bend specimens from the same alloys were tempered to different strengths (measured by hardness) by changing the tempering time at 650°C. The samples were subsequently embrittled for 96 hours at 510°C and their respective DBTT's determined.

TABLE I COMPOSITION OF ALLOYS USED

	C	Mn	P	S	Si	Ni	Cu	Cr	Mo	V	Al	MM*
En 18D	0,42	0,76	0,021	0,030	0,26	0,14	0,16	0,99	0,060	0,040	0,010	
W ₄	0,46	0,75	0,050	0,030	0,28	0,15	0,16	0,97	0,880	0,040	0,015	
W ₆	0,41	0,72	0,040	0,029	0,26	0,14	0,16	0,97	0,350	0,038	0,007	
W ₇	0,44	0,73	0,041	0,029	0,27	0,14	0,16	0,97	0,580	0,038	0,016	
W ₈	0,43	0,73	0,041	0,031	0,28	0,15	0,16	0,97	1,090	0,040	0,019	
W ₉	0,38	0,72	0,040	0,028	0,27	0,14	0,16	0,97	0,054	0,037	0,010	0,20
W ₁₀	0,40	0,71	0,038	0,004	0,26	0,14	0,15	0,93	0,053	0,038	0,050	0,50
W ₁₁	0,37	0,71	0,030	0,003	0,26	0,14	0,15	0,94	0,051	0,036	0,030	0,87
W ₁₂	0,41	0,73	0,040	0,014	0,27	0,14	0,16	0,97	0,051	0,036	0,030	

*Mischmetall (52% Ce, 24% La, 15% Nd, 7% Pr, 1% Sm, plus 1% other rare earth elements)
W₁₂ control alloy.

RESULTS AND DISCUSSION

Embrittlement Characteristics

The DBTT, as measured by either the Charpy impact or slow-bend test, is considered the most suitable method for characterising temper embrittlement in steels. Both test methods indicate precisely the same trends (Fig. 1). However, the slow-bend test is experimentally more convenient and comparison between the embrittlement characteristics of different alloys is more accurate because of the very sharp transitions obtained by this method.

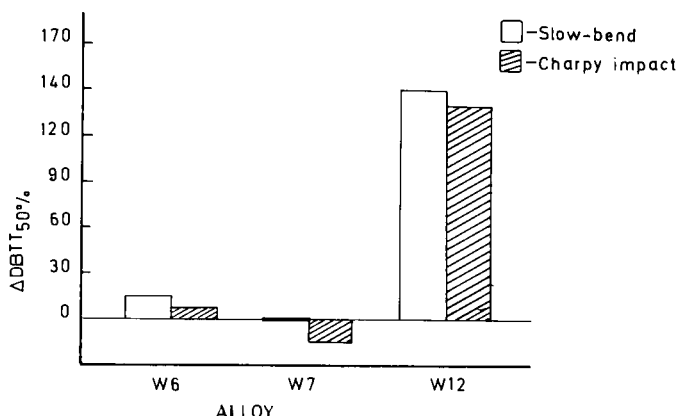


Fig. 1 Barchart showing the DBTT_{50%} for both the slow-bend and Charpy impact tests for some of the alloys tested.

It is well established that the DBTT of a steel is directly proportional to its strength. In this study, the hardness of the different alloys varied due to their different tempering characteristics. In order to make valid comparisons between the extent of embrittlement in two steels, it was necessary to determine the exact relationship between these two variables. This dependency was found to be linear in the area of interest, with an average temperature shift of 4K per Rockwell C. For useful comparative purposes, therefore, all the results were reduced to a specific hardness (strength) level of 30 Rockwell C.

The measured DBTT values for all the alloys studied have been presented previously (Barrett, Bee and Garrett 1981). On the basis of these results an anomalous optimum Mo content (0,3%) was found, together with a linear decrease in DBTT with REM content.

The variation of DBTT as a function of Mo and REM content, when corrected for hardness is shown in Fig. 2. It should be noted that the Mo curve in this case shows a minimum (optimum) value at 0,6 - 0,7 wt%, which compares favourably with other results (e.g. Dumoulin and co-workers 1980). For the REM alloys, the shape of the curve is no longer linear, but suggests that an optimum alloy addition may exist. Such a minimum value of DBTT is anticipated from the analysis by Seah (1980) which is based on predictions of the influence of any segregant atom on the grain boundary cohesion of iron (Fig. 3).

For small mischmetall additions, rare earth sulphides were detected, which replaced the MnS inclusions of the control steel. However, at higher REM concentrations, complete removal of sulphur was effected (see Table I). In these alloys, the inclusions were found to be rich in rare earth elements, phosphorus, tin, arsenic and magnesium.

It appears therefore that the rare earth elements can have two major effects: complete removal of impurities such as sulphur from the steel into the slag during melting, while other impurities are rendered harmless by the formation of chemical compounds. The net result is a drastic reduction of residuals in solid solution and hence the elimination of their potential to induce temper embrittlement in the steel.

Size and Distribution Analysis.

TABLE 2

Alloy		Charpy Upper Shelf Energy (J)	Impact
		(J)	
W12	control	70	
W6	(0,35%)	43	
W7	(0,58%)	35	
W9	(0,22% REM)	47	
W10	(0,60% REM)	50	
W11	(0,87% REM)	35	

It has been reported (Seah, Spencer and Hondros 1977) that increasing the REM content of a steel leads to a reduction in the Charpy impact test 'upper shelf' energy. In the present study, no consistent decrease in this parameter was observed, although both REM- and Mo-containing alloys did exhibit much lower values than the control steel (W₁₂) (Table 2).

Although other workers (Seah, Spencer and Hondros 1977) have reported that this effect could be associated with a size scale phenomenon, it was considered rather that it could be related to the inclusion content of the steels. Thus detailed determinations were made of inclusion size distribution and volume fraction using an image analysing computer. This hypothesis finds support in the results presented in Fig. 4. Thus, increasing either the volume fraction of inclusions or the mean inclusion size in a steel causes a decrease in the measured upper shelf energy.

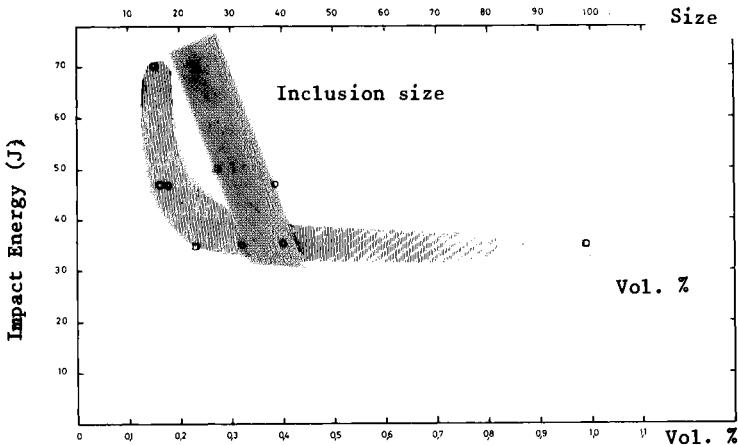


Fig. 4 Graph showing both the mean inclusion size and volume percent as a function of impact energy.

CONCLUSIONS

Rare earth metal additions are a simple and effective means of inhibiting temper embrittlement in alloy steels. Their major influence is in the chemical fixation of residual impurities through compound formation. The observed decrease in Charpy upper shelf energy is undesirable, but correct steel-making practice should eliminate this problem.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Council for Scientific and Industrial Research (Co-operative Scientific Programmes) and the University of the Witwatersrand for one of the authors (WB).

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The Determination of Soluble and Insoluble Boron in Steel by Emission Spectrometry Using an Inductively Coupled Plasma and a Scanning Monochromator

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ABSTRACT

Small amounts of boron improve the hardenability of low carbon, low alloy steels and evidence is mounting that only the boron in solid austenitic solution is responsible for this effect. Analytical methods were therefore investigated to determine soluble and insoluble boron in steel.

Three independent methods were used. The total boron content is determined by dissolving the sample in a phosphoric-sulphuric acid mixture. Insoluble boron is determined on the insoluble residue after leaching samples in an iodine-methanol solution for forty eight hours. The difference represents the soluble boron content. Soluble boron is also determined directly by electrolytic dissolution in diluted hydrochloric acid and the residue analysed for insoluble boron.

The analytical measurements were carried out with an inductively coupled plasma emission source run at 2 kW. A computer-controlled scanning monochromator with dispersion of ca. 0.3 nm/mm and a spectral slit width of 0.008 nm was used for measuring the intensity of the 249.68 B line. High resolution is essential for excluding interference.

A detection limit of approximately 2 $\mu\text{g/g}$ of boron in steel samples was obtained when using 1% steel solutions. Thus the effective and ineffective boron content in the 5-50 $\mu\text{g/g}$ range could be accurately determined. The results correlate well with hardenability tests.

KEYWORDS

Soluble boron in steel; phosphoric acid dissolution; iodine-methanol extraction; electrolytic separation; inductively coupled plasma measurement.

INTRODUCTION

It has been known for more than forty years that minute additions of boron have a pronounced effect in increasing the hardenability of low and medium

carbon, low alloy steels. The addition of 10-20 ppm of boron to medium carbon steels can be as effective as 0.3% Mo, 0.4% Cr or 1.25% Ni for increasing the hardenability. Thus small amounts of boron are used to substitute much larger amounts of more expensive elements such as Mo, Cr and Ni. The importance of boron has been emphasized in a recent paper by Irving (1982) with the spectacular title "Boron is proving to be a diamond in the rough".

Boron is a very reactive element and if it is introduced into the molten steel unprotected, it will combine preferentially with oxygen and nitrogen to form insoluble boron compounds. Therefore it is important to control the manufacture of boron steels very carefully. The steel is usually completely deoxidized by the addition of silicon and aluminium, or other strong deoxidizers which adequately protect the boron from oxidation.

In addition, one or more elements, such as titanium or zirconium are added, either separately or combined with boron, in the form of complex ferroalloys, to protect the boron from combining with nitrogen in the steel.

Various terms are used to describe the amount of boron effective in improving the hardenability of low and medium carbon steels, e.g. "boron in austenitic solid solution", "acid soluble boron", "effective boron", "free boron", etc. These terms refer to the amount of boron that is not combined with oxygen or nitrogen.

The accurate determination of the amount of boron in solid solution which is effective with respect to hardenability is important from two points of view: the practical - to assess the efficiency of the steel manufacturing process the theoretical - to determine the hardening mechanism involved.

The aim of this investigation is to obtain a simple and accurate method of determining the soluble boron in steel.

Several chemical methods have been suggested. Most of these involve a photometric measurement and soluble (effective) boron is calculated by the difference between total boron and insoluble boron.

The four extraction methods for soluble boron

- a) sulphuric acid extraction
- b) nitric acid extraction
- c) iodine-methanol extraction
- d) sodium citrate electrolysis

were discussed in a paper by Kawamura, Otsubo and Furukawa (1976). In general, the results obtained from the iodine-methanol and electrolytic methods were higher and more accurate than those obtained by the other extractions. The lower results shown by the nitric and sulphuric acid extractions appeared to be due to the microstructure of the different boron compounds in the residue.

Where very fine particles were present and partial dissolution of fine precipitates occurred, loss of insoluble boron took place during the filtering process. This loss was more marked where other inclusions and precipitates were absent. Both electrolysis and the iodine-methanol procedure were satisfactory for determining boron in small amounts of fine precipitates. In addition, the iodine-methanol dissolution decomposed cementite which is present in some steels, yielding fine carbon particles which were effective in collecting other fine precipitates. The conventional dissolution method with sulphuric acid which has been commonly employed was found to yield erroneously

low values.

Methods for determining total boron by phosphoric acid dissolution, soluble and insoluble boron by electrolytic separation and insoluble boron on the residue from an iodine-methanol extraction have been investigated and modified for ICP measurement.

CHEMICAL TREATMENT

Total Boron

Phosphoric-sulphuric acid dissolution. A sample of 1 g was transferred to a platinum dish and 20 ml of 9:1 $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ solution added. The mixture was heated on a hotplate gently at first until any violent reaction ceased, and then more strongly until dense white fumes occurred (280–300°C). Fuming was continued until the sample dissolved completely (5–10 minutes). The solution was then cooled and diluted to ± 40 ml with distilled water. Gentle heating and agitation ensured complete mixing. The solution was then transferred to a 100 ml polythene volumetric flask and made up to volume with distilled water. Calibration standards were prepared by adding varying amounts of B (0, 1, 2 and 5 ppm) to equal aliquots of a solution of pure iron which had been carried through the above procedure, ensuring similar Fe and acid concentrations.

Soluble Boron

Electrolytic dissolution. The sample in the form of a 10 mm diameter rod was used as anode in a 25% hydrochloric acid electrolyte, a pure graphite rod being used as cathode. At a regulated current of 2 A approximately 1 g of steel was dissolved in 30 min. The sample rods were carefully weighed before and after treatment to determine the total weight loss accurately. The solutions were filtered through a Whatman No. 42 paper and made up to 100 ml volume as before. For preparing a blank and standards an En18 steel rod containing no measurable boron was used.

Insoluble Boron

Electrolytic separation. Boron was determined on the insoluble residue filtered off after electrolysis. After thorough washing the filter paper and residue were ashed at 1000°C in a platinum dish. The ash was treated with 10 ml 9:1 $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ solution and dissolution and preparation of standards carried out according to the method outlined for the determination of total boron using the En18 steel as a blank.

Iodine-methanol extraction. A sample weighing 1 g was transferred to a plastic bottle, and leached for 48 hours with 100 ml of a 14% $\text{I}_2/\text{CH}_3\text{OH}$ solution. The solution was then filtered through a Whatman No. 42 filter paper and the insoluble residue washed with methanol to remove the iodine. The filter paper plus residue were transferred to a platinum dish and ignited at 1000°C. After cooling, 10 ml of 9:1 $\text{H}_3\text{PO}_4/\text{H}_2\text{SO}_4$ solution were added and fuming and dilution effected as for total boron, the final solution being transferred to a 100 ml polythene volumetric flask. Standards were prepared in a similar manner to those for total boron.

Problems Encountered

Some problems were encountered in the experimental stages of these methods,

and therefore special procedures were needed to obtain reliable results. These were that

- a) No pyrex or glassware could be used because of the risk of boron contamination. Thus the fuming step was originally carried out in quartz beakers. On prolonged heating, silica was eroded from the beakers and had to be filtered off. The silica appeared to retain some of the boron. Platinum dishes presented no problem and could be used for ignitions and dissolution.
- b) In the determination of insoluble boron, omission of the ashing step was attempted by the addition of 1 g of $K_2Cr_2O_7$ with the H_3PO_4/H_2SO_4 mixture to dissolve the filter paper. This resulted in a black mush which had to be filtered off. Low boron resulted owing to difficulty in washing.

EMISSION SPECTROMETRIC MEASUREMENTS

An inductively coupled argon plasma (Plasmatherm 5 kW unit) was used as radiation source for the emission spectrometric determination of boron. Optimum conditions were found to be 2 kW power, 20 mm observation height above the coil, 16 l/min coolant argon flow and 350 kPa pressure applied to the concentric glass nebulizer.

A computer-controlled scanning monochromator was used for isolation and measurement of the boron spectral line. The 1 m focal length Czerny-Turner monochromator employed a 3600 lines/mm holographic grating. With 20 μ m and 25 μ m entrance and exit slits respectively, a reciprocal linear dispersion of ca. 0.3 nm/mm and a spectral slit width of 0.0085 nm was obtained.

Measurements of line intensities are made by incremental scanning over the spectral line, allowing a variable measurement time after each movement (1 s used in this work). Twelve measurements were found to be sufficient for reliable measurement of the control portion of the spectral line.

Figure 1 shows a wavelength scan of the spectrum in the region of the B 249.678 nm line, for a solution containing 2 μ g/ml B and 1% Fe. The excellent resolution of the system is also evident from this figure and this high resolution of the monochromator results in the line being separated sufficiently from the Fe 249.653 and Fe 249.699 lines to be used as an analytical line.

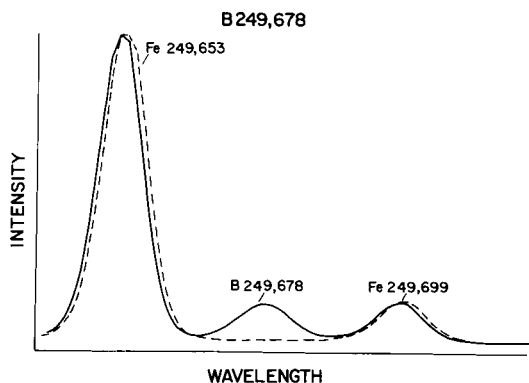


Fig. 1. Wavelength scan in region of B 249.678 nm line.

Figure 2 shows the spectra obtained in this region when spraying 1000 $\mu\text{g/ml}$ solutions of W and Co, these elements being possible spectral line interferences (Boumans' Tables, 1980). Interferent equivalent concentrations of 3200 $\mu\text{g/ml}$ and 1600 $\mu\text{g/ml}$ were indicated for W and Co respectively at the B line peak (meaning that e.g. 3200 $\mu\text{g/ml}$ W will produce the same signal as 1 $\mu\text{g/ml}$ B). Another possible interferent, Ta, also showed a small interfering peak but of less significance than W.

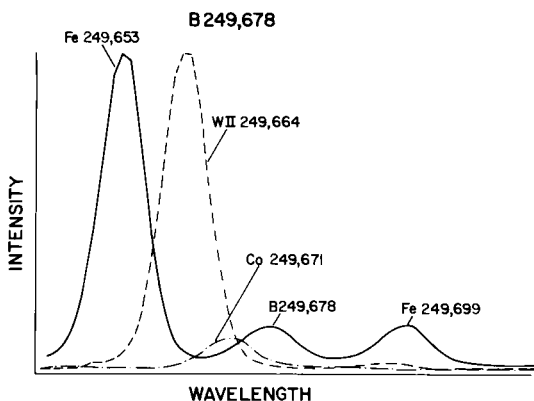


Fig. 2. The effect of W and Co on the B 249.678 nm line.

Figure 3 shows the spectrum of 1% Fe in the region of the more sensitive B 249.773 nm spectral line. Due to the proximity of the Fe II 249.782 nm line this boron line can not be used for analytical purposes. In addition, Al and Ta lines may interfere with this boron line.

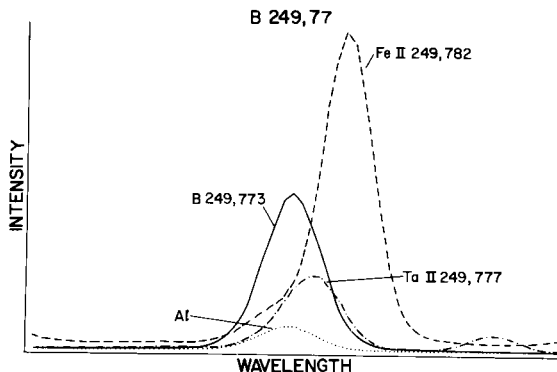


Fig. 3. The effect of Fe, Al and Ta on the B 249.773 nm line.

With aqueous solutions the background at the 249.68 nm line was relatively low with a 0.9% relative standard deviation and a detection limit of 3 ng/ml was obtained (concentration producing a signal equal to 3x the standard deviation of the background). With 1% Fe solutions the continuum produced by the iron results in a 3-4 times increased background and an accompanying

reduction of a factor 2-3 in signal, resulting in a detection limit of approximately 20 ng/ml in the solutions, or 2 µg/g boron in the steel.

Referring to the possible interferents Co and W, it is evident that concentrations of 0.32% Co and 0.64% W in the steel will produce signals equal to the detection limit of 2 µg/g boron. It should therefore be ascertained before analysis that these elements do not exceed these limits.

RESULTS AND CONCLUSION

Ten samples containing different amounts of total boron were analysed independently for total boron, soluble boron and insoluble boron by the methods outlined above. Table 1 shows the results. The relative standard deviation for total boron was 6.7% at the 30 ppm B level. The % RSD of ten concentration readings on the same sample in solution was 8.4%.

TABLE 1 Results for Boron in Steel

Sample	µg/g B					
	Total B H ₃ PO ₄ / H ₂ SO ₄ (a)	Insoluble B I ₂ /CH ₃ OH residue (b)	Soluble B Dif- ference (a) - (b)	Soluble B Electro- lytic (c)	Insoluble B Electro- lytic residue (d)	Total B Addition (c) + (d)
En18	<2	<2	0	-	-	-
Bor 3	35	0	35	-	-	-
Bor 4	28	2	26	-	-	-
Bor 6	61	0	61	-	-	-
Bor 11	10	0	10	8	2	10
Bor 12	10	0	10	10	2	12
Bor 13	24	0	24	24	<2	24
Bor 14	29	0	29	31	0	31
Bor 15	34	0	34	37	0	37
Bor 16	33	0	33	35	0	35

Thus, these methods seem promising for rapid and good correlation of boron values with effectiveness. ICP spectrometric measurement probably has an advantage in speed and manipulation over the conventional spectrophotometric methods, although at this stage their sensitivity and accuracy cannot be matched (Vernon and Williams, 1970; Bhargava and Hines, 1970).

Further investigation of the separation techniques and ICP measurement is necessary, especially as suitable analysed reference materials are not available. Private communication with Flinchbaugh and Fernandez (1982) who have also attempted boron separations followed by dc plasma spectrometric measurement, reported similar difficulties. However, since perfection of these methods would be advantageous to the steel industry, this project seems worth pursuing.

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Copper-containing Steels for Severe Service Rails

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ABSTRACT:

C-Mn railroad rails no longer suffice for the current heavily loaded ore and coal carriers. A departure from the C-Mn-Cr rail has been based on a medium carbon, Cr-V-Ni-Cu composition which combines hardness and yield strength with excellent toughness and weldability. Service tests are described using this composition for rails and switch points in the Belgian National Railroad System.

KEYWORDS:

Rails, switchpoints, copper, chromium, vanadium, wear, alloy steels, heat treatment.

INTRODUCTION:

Modern rail transportation systems are being called upon to handle axle loading well in excess of 25t; much of the recent increase being due to the demands for increased shipments of ore and coal. The result has meant a growing need for rails which resist degradation from wear, fatigue and plastic flow. Damage is particularly severe on curves, and in high traffic areas in tunnels and marshalling yards.

Standard carbon-manganese rail compositions have served admirably for many years, and on less heavily loaded passenger lines they continue to serve quite adequately. However, as service requirements increase, the necessary higher yield strength, tensile strength, fatigue resistance and low crack growth rate requirements may be achieved by using several alternatives, viz., full heat treated rails; surface hardening of the running surface of a suitable steel composition; or by alloying to produce the required structure and properties on cooling

from the hot rolling temperature.

DEVELOPMENT OF THE NEW STEEL

In a program to develop a better understanding of copper additions in HSLA steels carried out at the University of Ghent (De Sy and co-workers, 1974), a composition was developed which seemed well suited to very heavily loaded crane rails. Trials in a shipyard confirmed the ability of this composition to sustain large stresses without plastic flow. This steel, a low carbon, Ni, Cr, Cu, V alloy, has a hardenability unsuited to the cross-section of the typical railroad steel, and a modified alloy was developed using this composition as a point of departure. Since the good performance of Cr-V rail steels was well documented, the decision was made to employ these two elements in a lower carbon steel, seeking additional strengthening through the addition of copper, which would also impart added corrosion resistance of benefit in trackage on over-water bridges, tunnels and in high humidity locations. The use of lower carbon levels would also lead to improved weldability.

The synergistic effect of vanadium and chromium was first examined at a carbon level of 0.4%, which is lower than the typical 0.7% level used in commercial Cr-V rail compositions. Yield strength as a function of Cr and V is shown in Fig. 1, with values for the Cr-V-Ni-Cu alloy also indicated.

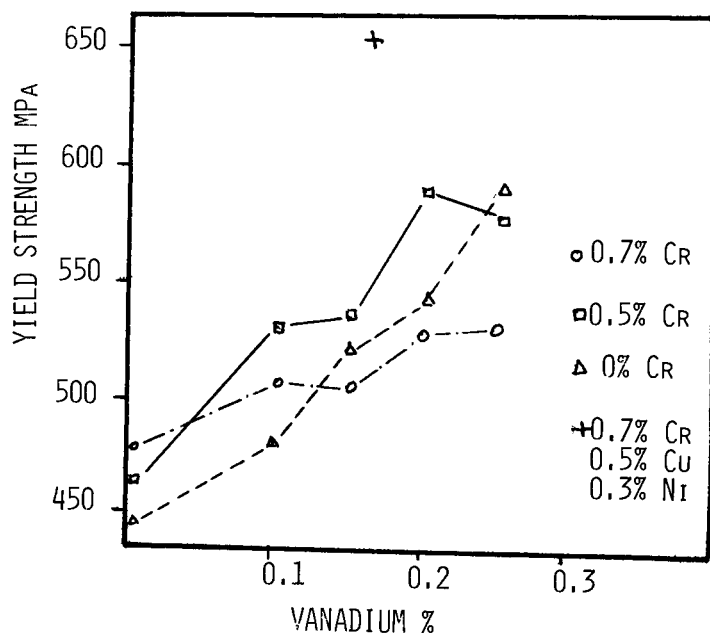


Fig. 1 - Yield strength vs. V content for Cr and Cr-V-Ni-Cu steels

Additions of vanadium to a 0.4% C, 1.1% Mn steel progressively raise the yield strength from 440 MPa to 586 MPa for vanadium content up to 0.26%. The addition of 0.5% chromium increased the yield strength by 33 MPa with little additive effect beyond 0.2% V. When chromium content was increased to 1.0% it had a negative effect on yield strength, apparently due to the refinement of carbide precipitates to a degree at which they were ineffective in strengthening. By raising the vanadium content to 0.2% the yield strength was raised apparently due to return of the carbide particle size to the level observed in the 0.1% V 0.5% Cr composition. Copper additions at the 0.5% level, with the 0.3% Ni to inhibit any hot shortness, increased the yield strength by 80 MPa (Dilewijns, Schetky and Sage, 1979).

METALLOGRAPHIC STUDIES

Metallographic studies of the C-Mn, C-Cr-V and Cr-V-Ni-Cu alloys reveal the change in ferrite/pearlite ratio and decrease in pearlite lamellar spacing with increasing alloy additions. Figure 2 shows a 0.5% Cr, 0.1% V structure which may be compared with the 1% Cr, 0.2% V structure shown in Fig. 3, illustrating the marked decrease in ferrite, which is reduced to low levels in the Cu-containing composition as illustrated in Fig. 4.

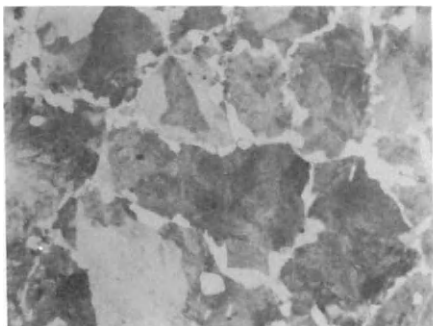


Fig. 2 Ferrite-pearlite in
0.43C-0.55Cr-0.09V
500x

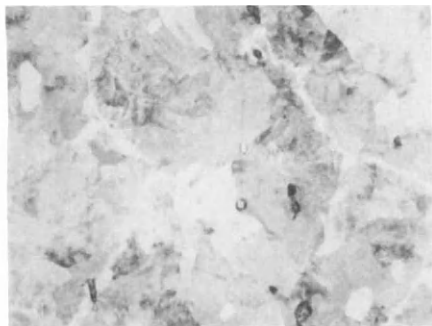


Fig. 3 Ferrite in pearlite in
0.41C-1.00Cr-0.2V
500x

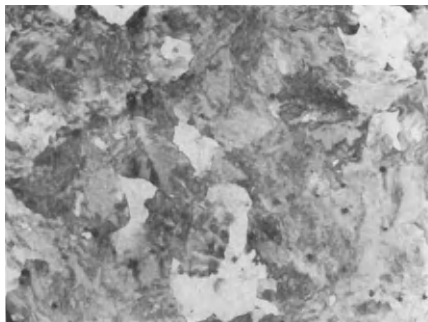


Fig. 4 Ferrite-
Pearlite in 0.4C-
0.8Cr-0.17V-0.4Cu
500x

Electron microscopy reveals more graphically the change in pearlite lamellae spacing and the reduction in the size of carbide precipitates as seen by comparing the Cr-V alloy in Fig. 5 with Cr-V-Cu-Ni structure in Fig. 6. There is apparently an interaction between chromium and vanadium with regard to carbide precipitation and growth kinetics.

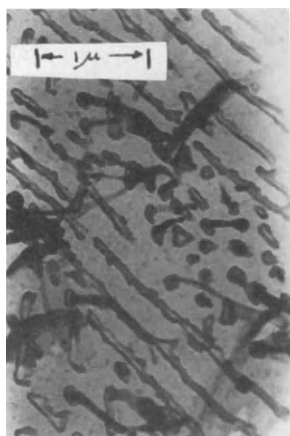


Fig. 5 0.43C-0.55Cr-0.09V
showing carbides
in pearlite



Fig. 6 Cr-V-Ni-Cu showing
pearlite refinement
and fine interlath
carbides

IN-SERVICE OBSERVATIONS

After trial melts of the Cr-V-Cu-Ni composition were rolled into 50 kg/m and 60 kg/m rails, it was found that a slight upward adjustment in vanadium and chromium level was necessary in order to give an adequate margin of safety for the U.I.C. specification for naturally hard grade A rails, i.e. 833 MPa tensile strength. The compositions for the C-Mn, Cr-V and the Cr-V-Ni-Cu rail steels tested are given in Table I. Mechanical properties for these steels are given in Table II where it can be seen that the low carbon content copper containing steel exhibits not only excellent yield strength and hardness, but much higher impact strength than the conventional high carbon rail steels.

TABLE I

	Composition								
	C	Mn	Si	S	P	Cu	V	Cr	Ni
Type II Cr-V Naturally	0.65	1.05	0.6	0.02	0.02	---	0.2	1.15	---
Hard U.I.C.	0.75	1.26	0.3	0.02	0.019				
Cr-V-Ni-Cu	0.42	1.49	0.54	0.026	0.012	0.37	0.18	0.75	0.20

TABLE II

	Properties		
	C-Mn	Cr-V	Cr-V-Ni-Cu
Yield Strength, MPa	467	680	701
Tensile Strength, MPa	938	1130	1056
Elongation	13	12	13
Reduction in %	17	20	30
Impact Test J	16	----	45
Hardness, HB - Surface	283	320	322
Head Interior	280		345

The field testing of the Cr-V-Ni-Cu rail steels has been in progress for four years throughout the Belgian Railway System. Since the economic incentive to use high strength rails relates to service conditions which would cause premature failure of conventional C-Mn rails, the test sites were chosen to yield data on wear, plastic flow and fracture under high axle loading and heavy traffic. The copper containing rails were compared on each site with a naturally hard Grade A rail of nominal composition 0.60-0.75% C, 0.50% Si, 0.8-1.2% Mn (Dilewijn, 1981).

On straight track after four years the copper containing steel shows significantly lower wear, although in four years this is not large. In marshalling yards at Ronet there is a significantly lower plastic flow and the profiles exhibit less bulging of the railhead shoulder. In the Brussels North-South Junction which experiences very heavy passenger traffic the wear to date on the copper containing steel is lower, but of greater importance there is no evidence of shelling which has started on the Grade A rails. Shelling is a fatigue type failure involving the spalling of pieces from the railhead as a result of cracks which initiate below the head surface.

Railroad switch points represent a special case since these cannot be fabricated of naturally hard steel because of a tendency for cracking under the impact loads imposed on these units. Five groups of "arm and side" points in the Cr-V-Ni-Cu steel shown in Fig. 7, have been under test in the Brussels North and South station yards. Negligible wear and no cracking has been observed in four years of very dense traffic, and no failure in winter. A normal steel set of points lasts only 1.5 years. Starting in 1982, 100-point systems of approximately 3 tons each will be placed in service by the Belgian Railroad Company

for a three year test. (J. Dilewijns, 1981).



Figure 7

CONCLUSION:

A new rail composition has been developed featuring lower carbon levels than conventional rail steels and strengthening by Cr-V-Cu additions. Welding properties are superior to steels used for severe service and the wear properties, resistance to plastic flow and fatigue as well as impact properties show definite superiority to Grade A compositions. The superior properties are related to a carbide precipitation hardening in a very fine pearlite matrix which exhibits very little free ferrite.

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On the Fracture and Wear Characteristics of Chromium-Molybdenum Bainitic Steel

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ABSTRACT

This paper summarizes the fracture and wear characteristics of the first bainitic rail steel produced in North America.

KEYWORDS

bainitic; pearlite; fracture toughness; microstructure inhomogeneity; compact tension; wear rate.

INTRODUCTION

In the work of Kalousek and Beynon (1975) it was concluded that rail life, all variables being constant, could be increased by refining both grain size and spacings between pearlite lamellae. Several methods will achieve this - one of which is the alloying method. Out of available alloyed rail composition the chromium-molybdenum rail appeared to be the most desirable for future premium rail.

In order to obtain an optimum pearlitic structure of such rail a three phase gradual structure refinement was suggested, see the work of Ghonem and Kalousek (1978): first, to obtain a rail with a subsurface structure having a hardness level of 340-360 BHN; second, to reach 360-380 BHN; and third, to aim for 380-450 BHN. To carry out the first phase, a 100 ton Cr-Mo heat (identified as C5599) was ingot cast, aluminium-deoxidized and rolled to develop a microstructure of the fine pearlite. During rolling of the ingot, streaks appeared in the webs in localized areas affected by microsegregation of Mn, Mo and Cr. Furthermore some of the rolled rails developed excessive curvature during cooling on the hot bed. To rectify these problems, a second strand cast heat was produced. This heat was also intended to fall into the phase I category, however, the average hardness exceeded 400 BHN with an upper-bainitic microstructure. This is considered the first bainitic rail steel to be produced in North America and this paper summarizes its fracture and wear characteristics.

MICROSTRUCTURE PROPERTIES

The hundred tons of silicon-deoxidized Cr-Mo II* (BOF) heat was produced in billets of cross section 27x32 cm and rolled into 66 kg/m RE rails. Ladle and spectroscopic analysis of head sections of these rails showed the steel composition to have an excess of 0.15-0.20% Mo compared to Cr-Mo I. The microstructure of the rail cross section was found to consist of 70% upper bainite and 30% traditional pearlite with interlamellar spacings of 50-80 nm.

A scanning electron microscope examination of the web region of the bainitic rails revealed that, while the microsegregation was reduced 50% more than in Cr-Mo I, web streaks were equally numerous, arranged in platelet form and oriented parallel to the vertical plane as shown in Figure 1. They consist of lower bainite and traces of tempered martensite and have a hardness of RC55. The microstructure and hardness were unchanged by subzero quenching

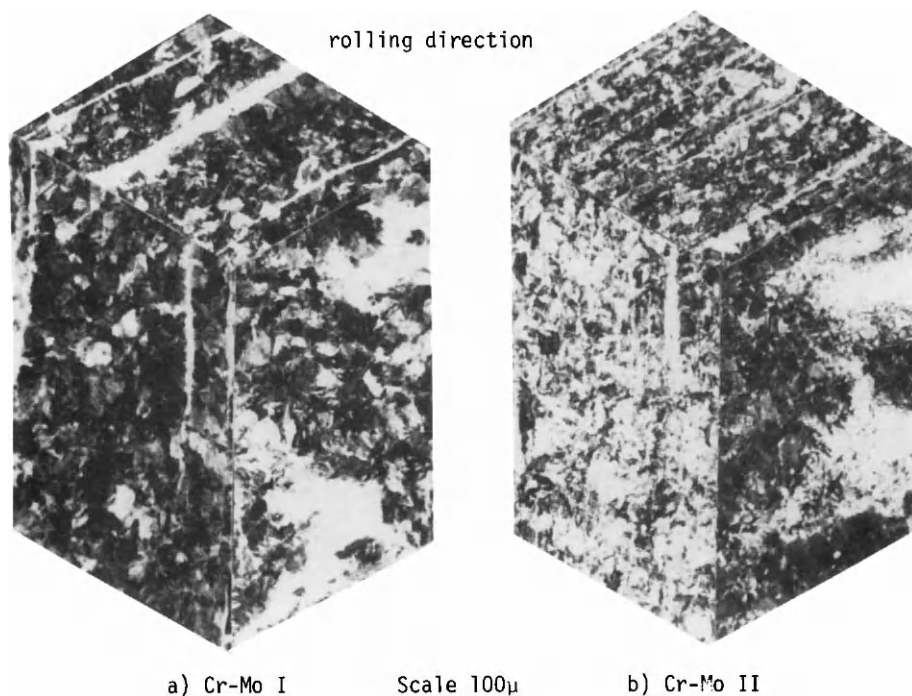


Fig. 1 Microstructure of the Web Region, on the Three Processing Planes Depicting the Shape of Streaks.

or by stress-relief treatment, which suggests that the lower bainite is relatively stable after manufacture.

Tests reported here measured and compared fracture toughness of bainitic and pearlitic steel structures as well as the effect of the lower bainite streaks on the fracture toughness of the bainitic rail web.

*Cr-Mo II will be used to identify the bainitic Cr-Mo steel (heat 9273B) while Cr-Mo I will identify the pearlitic one (heat C5599)

FRACTURE TOUGHNESS AND IMPACT PROPERTIES

Effect of Bainitic Structure

Two different pearlitic rail types were compared with the bainitic Cr-Mo II and the pearlitic Cr-Mo I; namely, heat treated carbon rail steel and plain carbon steel. Out of each rail type 16 compact tension (CT) specimens 32x30x13 mm were machined from web & base sections, as shown in Fig. 2, with transverse starter notches cut in a direction normal to the rail surface. An electric discharge notch (0.23 mm width x 0.76 mm depth) was used to locate the initial fatigue crack.

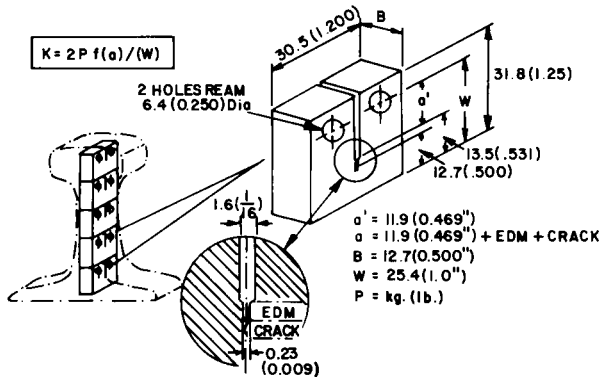


Fig. 2 Standard Compact Tension Test Specimen. (mm(inch))

A similar number of WOL specimens (19x19x29 mm) from the head and base sections of the same rail steels were machined with saw cut notches and similar electric discharge notches (see Figure 3). Fatigue precracking was done using tension-tension loading for CT specimens and full cycle tension-compression loading for WOL specimens.

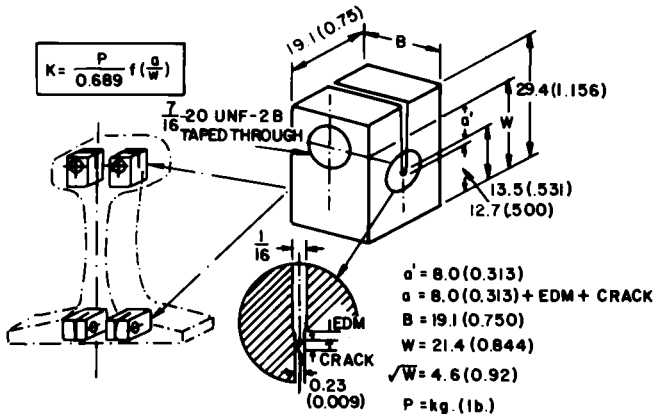


Fig. 3. WOL Test Specimen. (mm(inch))

Keeping in mind that rail steel is known to violate the ASTM E399 condition of $K_{max}/K_Q \leq 1.10$ because of short cleavage bursts which occurs well below the breaking load, test results at 24°C are shown in Table 1. They indicate that i) $K_{IC}(K_Q)$ values for pearlitic steel are 1.6 times higher than those of bainitic steel, ii) the permissible defect size (d_c) of pearlitic steel calculated for $\sigma = 196$ MPa is twice that of the bainitic and plain carbon steel.

TABLE 1 K_{IC} and d_c Values of Bainitic and Pearlitic Cr-Mo Steels

Steel Type	Test °C Temperature	Av. K_{IC} MPa $\sqrt{m}$	d_c (mm)
Cr-Mo I	24	43.4	31
Cr-Mo II	24	32.0	17
Fully Heat Treated	24	39.9	26
Plain Carbon	24	33.5	18

Notched and unnotched Charpy impact tests were also performed on the same rail types in the transition temperature range. Figure 4 indicates that the "energy to fracture" values of Cr-Mo I is comparable to the fully heat treated rail steel while, again, the values of Cr-Mo II are the same level as the plain carbon steel.

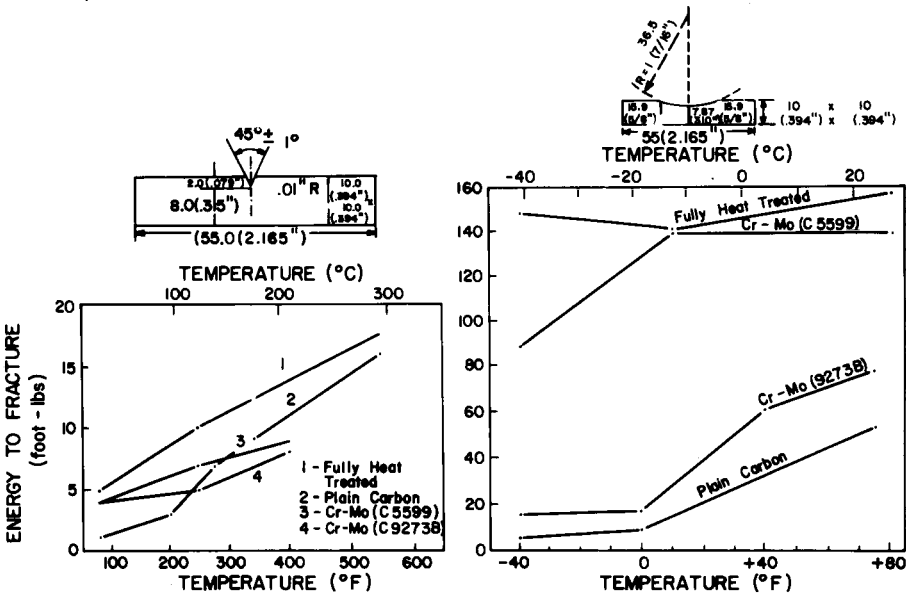


Fig. 4 Charpy Impact Energy vs Temperature.

Effects of "Streaks"

Eight miniature compact tension specimens ($W = 13.5$ mm) were prepared, one pair from each of four web center regions in Cr-Mo I and Cr-Mo II rails, respectively, as shown in Fig. 5. In addition, eight similar specimens were obtained from similar regions of plain carbon and 1% Cr steel rails.

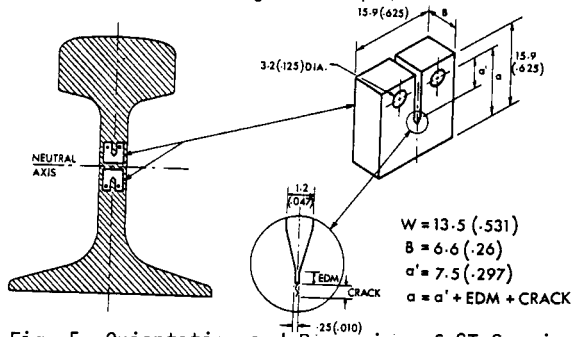


Fig. 5 Orientation and Dimension of CT Specimens Taken From the Center of the Rail Web (mm (inch)).

In each test specimen, the initial machined notch was oriented towards the vertical plane of the rail web while its tip was to be located in a streak region. Preparation of the electric discharge notch, the fatigue precrack and the test procedure was similar to the CT specimens described in the previous section. Crack length traces were observed with an accuracy of 0.05 mm. Tests results, detailed in the work of Kalousek, Parsons and Ghonem (1978), are shown in Table 2. When the values in this table are compared with those in Table 1, it was apparent that the existence of streaks in Cr-Mo rail did not reduce its fracture toughness.

TABLE 2 Fracture Characteristics of Bainitic Steel Containing Streaks

Steel Type	Temp °C	Av. K_Q MPa $\sqrt{m}$	Av. K_{max} MPa $\sqrt{m}$
Cr-Mo I	24	45.8	45.6
	-50	32.5	32.5
Cr-Mo II	24	38.4	37.7
	-50	26.2	27.5
Carbon	24	40.3	40.3
	-50	23.3	
1% Cr	24	26.7	28.1
	-50	27.3	28.5

Fracture surfaces of test specimens were studied using a SEM in order to determine the features of the crack front and the induced effects on its propagation stage due to the presence of streaks. As all test specimens were fractured under a plane strain condition, their features were predominantly transgranular cleavages, with some of the cleavage facets containing

small steps similar to those reported by Park and Bernstein (1978). In the case of carbon and 1% Cr steel, distortion of cleavage facets was observed and related to an extension ductile tearing.

WEAR PERFORMANCE

Twenty lengths of Cr-Mo II were placed in section 3 of F.A.S.T. loop which has a 5° curvature, a 2% grade and a 1/40 cant. Seven other different rail types, in addition to Cr-Mo II, were to be tested in this section; all of these were 66 kg/m. In this experiment, detailed in the work of Steele and Reiff (1982), rails were subjected to programmed regimes of lubricated and dry conditions so that wear and metal flow in both regimes could be studied and compared. The 20 lengths of Cr-Mo II were removed from F.A.S.T. loop after an accumulation of 115 MGT. The main parameter studied during the field tests was high rail curve wear. Wear measurement, included gauge face wear, head height and total head area loss. These measurements were taken at intervals of approximately two months using a "snap gauge" of accuracy ± 0.002 . Profile comparisons obtained from these measurements are shown in Fig. 6. From a complex analysis of this figure an average wear rate was calculated, and results are shown in Table 3.

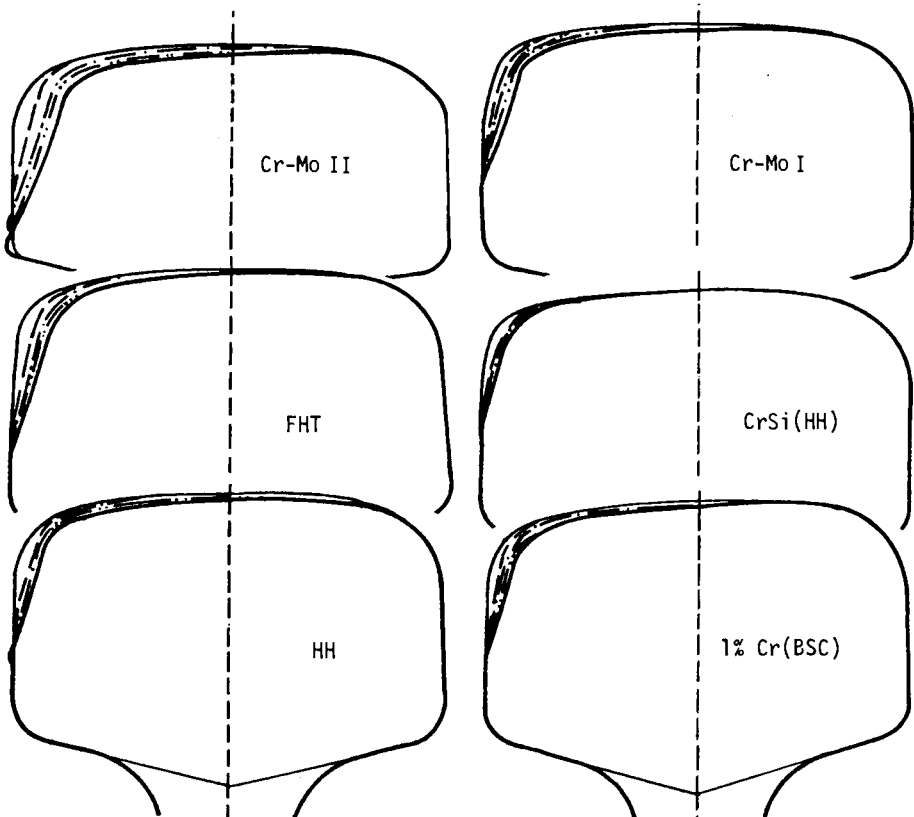


Fig. 6 Comparison of Rails Head Profile which were Tested in F.A.S.T. Loop.

TABLE 3 Wear Rate of Cr-Mo II and Other Pearlitic Steels
Shown in Fig. 6

Steel Type	Av. In./MGT Lubricated	Av. In./MGT Lubricated
Standard	0.0010	0.0066
Head Hardened	0.00075	0.0023
SiCr (HH)	0.00065	0.0017
1% Cr	0.00065	0.0029
Cr-Mo (CF&I)	0.00065	0.0029
Cr-Mo (II)	0.00090	0.0036
FHT	0.0007	0.0031

From Table 3 and Fig. 6 it could be concluded that Cr-Mo II rail performance in the dry regime was similar to most of the premium rails. However, in the lubricated regime, although its surface and gauge hardness were higher than all of the test rails with the exception of SiCr, its wear performance was virtually the same as that of the standard rail. Furthermore, when the wear rate was related to the gauge face hardness in both lubricated and dry conditions, the performance of Cr-Mo II rail was the lowest among all premium rails.

CONCLUSIONS

Data presented in this paper concerning the fracture and wear characteristics of the first production of bainitic chromium-molybdenum rail steel indicates the following

- i - As expected, the fracture toughness of bainitic structure is lower than the fine pearlite structure.
- ii - Existence of lower bainite streaks in an upper bainite matrix does not effect the fracture toughness of the matrix.
- iii - Surface wear characteristics of the bainitic steel in lubricated or dry conditions are not superior to those of pearlitic steel.

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Rolling and Alloying as Influencing Factors on Pipe Steel Properties

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ABSTRACT

Rolling trials on full scale samples have been carried out in a plate mill to optimize the correlation between rolling schedules (finishing temperatures between 750°C and 920°C) and new ideas on alloy design in particular with regard to the niobium content up to 0.18%. The results of investigations on microstructure, texture, precipitation and mechanical properties show, that a niobium content up to 0.04% improves both the strength and toughness of the material. A higher niobium content mainly improves the toughness owing to a higher degree of total deformation in the unrecrystallized austenite region resulting in enhanced grain refinement and a further reduction of mobile nitrogen.

It was found that less severe rolling schedules can be applied for the production of high quality line pipe steels using increased niobium contents. Industrial trials in plate and strip mills using low-carbon manganese steels with the addition of about 0.13% niobium and 0.50% nickel as well as micro-alloying with niobium plus titanium approaching stoichiometric composition confirmed these correlations resulting in pipe steel properties of grade X65 to X75 with excellent low temperature toughness and weldability.

KEYWORDS

Line Pipe Steel, Controlled Rolling, Niobium, Rolling Schedule, Nickel-niobium-steel, Niobium-titanium-steel, Stoichiometry.

INTRODUCTION

In the last 25 years, continuous development in pipeline steel grades has been carried out to fulfil the requirements of high transportation capacity, improved weldability and sufficient safety also in arctic and submarine regions. The most important steel grades for large diameter pipes today are API grades X65/X70, produced via a thermomechanical rolling process of pearlite-reduced microalloyed steel.

To achieve the required tensile properties in pipes longitudinally welded from plate, a certain amount of deformation in the two phase region ($\alpha+\gamma$) is

widely used (Tanaka and co-workers, 1977). Due to this dislocation strengthening process some disadvantages have to be accepted like an impairment of the transition temperatures (Lorenz and co-workers, 1981) and a banded and textured ferrite, which causes texture separations (Engl and Fuchs, 1980). Moreover, plate rolling mill difficulties like mill house cracking and a reduced productivity can be experienced.

Efforts have been made to overcome these problems in plate production by applying accelerated cooling after final deformation (Ouchi, 1979), a process commonly used in strip production. Another possibility is to use alloying elements like molybdenum, boron or chromium, which influence the transformation towards the occurrence of low transformation-temperature products (Masip and Meyer, 1978).

This paper deals with an alternative route to the conventional X65/X70 pipeline steel production and reports about the mechanical properties achieved with such steel grades including weldment properties.

THE FUNCTION OF NIOBIUM IN THE THERMOMECHANICAL ROLLING PROCESS

The thermomechanical rolling process is characterized by a certain amount of deformation in a temperature range, where the austenite does not recrystallize any more. In this context, niobium is the most relevant element owing to its enormous effect on the retardation of recrystallization. Latest results (Akben, Weiss and Jonas, 1981) show that the start of recrystallization is suppressed by niobium in solid solution before it is more intensively retarded owing to stress-induced carbonitride precipitation. Increasing the niobium content raises the temperature of retardation (De Ardo, Grey and Meyer, 1981).

To study the practical aspects of the correlation between the varying niobium contents and appropriate rolling schedules to achieve equivalent properties, a special technique has been applied. Laboratory ingots of 200 kg were embedded in a standard slab for pipe plate production. This technique guarantees essentially the same rolling schedule for the various chemical compositions and realizes full scale plate properties under mill rolling conditions.

Within the base composition of about 0.08% C, 0.30% Si, 1.55% Mn, 0.015% P, 0.015% S, 0.025% Al and 0.0140% N, the niobium content has been varied from 0 to 0.176% Nb. No other alloying or microalloying elements were used in this investigation.

The steels were rolled with a soaking temperature of 1240°C. The rolling schedules are given in Table 1.

TABLE 1 Applied Rolling Schedules

Rolling Schedule	Delay 1		Delay 2		final gauge (mm)	finish rolling temp. (°C)
	thickness (mm)	time (s)	thickness (mm)	time (s)		
A	75	/ 320	50	/ 160	18	800
B	100	/ 240	---	---	20	920
C	100	/ 400	---	---	20	850
D	100	/ 660	---	---	20	750

The microstructural results are shown in Fig. 1. The grain refinement follows the well-known pattern (De Ardo, Grey and Meyer, 1981; Kozasu and co-workers, 1977). Decreasing finishing temperatures and already small niobium additions generate ferrite grain refinement. For rolling schedules B, C and D increasingly finer grains up to the maximum content of 0.176% Nb are achieved.

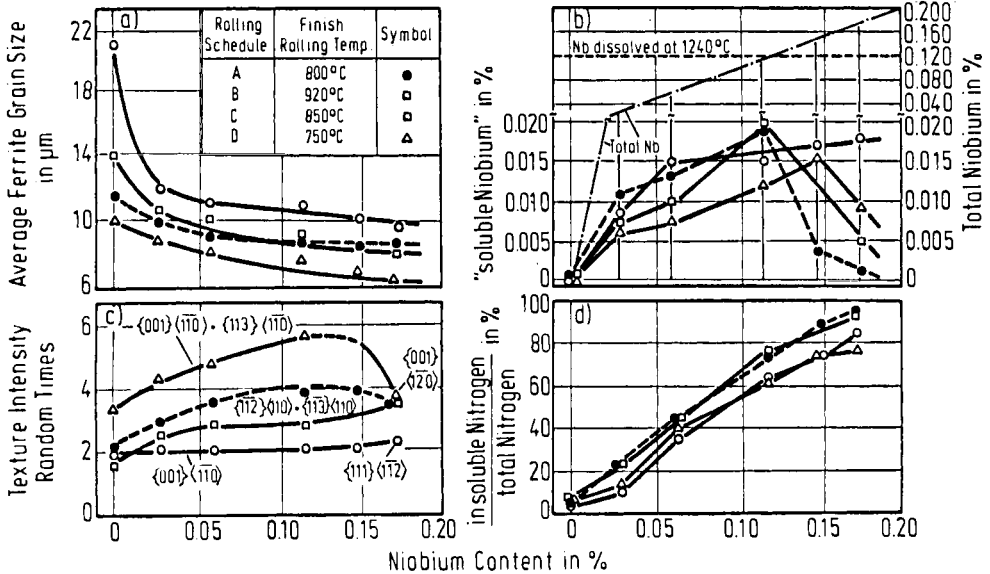


Fig. 1. Results of microstructural and chemical investigations

By means of a chemical extraction technique the amount of "insoluble niobium" and "soluble niobium" can be determined. These two terms stand for:

- Niobium carbonitride precipitation generated in austenite or remaining undissolved during soaking
- Niobium in solid solution and/or very fine and dispersed precipitates in ferrite enhancing precipitation hardening.

Our results showed that 75 to 90% of the niobium precipitates in the early stages of austenite deformation. Taking into account the equilibrium content of dissolved niobium at 1240°C, which is about 0.12% for the given nitrogen (0.0140%) and carbon (0.077%) content, it is evident, that at the most 30% remained undissolved during soaking. For niobium contents in excess of 0.12% it is obvious that the higher the amount of deformation in the temperature range of maximum precipitation rate (800°C and 850°C finishing temperature), the more austenite precipitation occurs. The data also indicate that undissolved niobium carbonitrides enhance precipitation in austenite due to nucleation.

Investigation of the texture show that niobium-free grades are essentially random. This is also true for a finishing temperature of 920°C independent of the niobium content. Rolling schedules A and C show the typical texture

of thermomechanically treated material, formed by γ/α transformation from an unrecrystallized austenite. The texture severity within these two rolling schedules is increased by increasing niobium content and lower finishing temperatures. The highest texture severity appears at the lowest finishing temperature of 750°C.

Fig. 1d shows the nitrogen balance (chemical extraction technique) in the presence of niobium and aluminium. The higher the niobium content, the more nitrogen is "insoluble", i.e. forming compounds with aluminium and/or niobium. High deformation in the 800 - 900°C region (A and C) generate even more precipitates of this type. With the highest niobium content, almost no soluble nitrogen is to be found.

Heating turnings in pure hydrogen at 450° and determining the "mobile" nitrogen as ammonia shows that the analysed amount is only about 20% of the soluble nitrogen. Mobile nitrogen contents of about 15 ppm for microalloyed steels are in general very low and more than acceptable. Further work for the exact determination of free nitrogen in controlled rolled products seems to be necessary.

The mechanical properties of these steels are summarized in Fig. 2. By raising the niobium content e.g. to 0.07/0.08 percent, the strength of the material finished at higher than 850°C reaches 420 MPa. Finishing at 750°C produces 450 MPa. For all schedules, as the niobium content increases the toughness progressively improves, to yield a 50% FATT (FATT = fracture appearance transition temperature) of about -80°C with 0.1 percent niobium and finish rolling at 850°C.

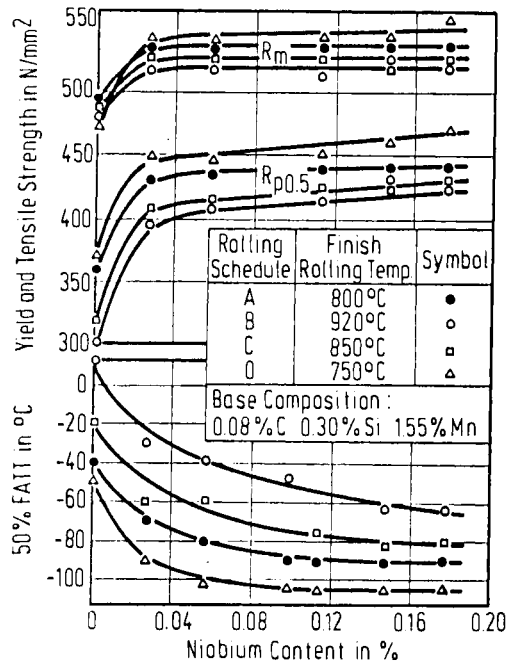


Fig. 2. Mechanical properties of investigated plates

In Fig. 3 the attempt of a Hall-Petch Analysis of all results has been made. The higher yield strength (b) is either a function of the niobium content available for precipitation hardening ("soluble") or of the texture intensity $\{112\} \langle 110 \rangle$. It is well known that this kind of texture increases the strength transverse to the rolling direction (Fukuda, 1968; Lotter, Meyer and Knorr, 1976). A good correlation exists between grain refinement and toughness. However, the deviation from the well-known literature data (Gladman, Dulieu and McIvor, 1977; Morrison, 1966; Speich and Dabkowski, 1979) indicates that besides precipitation hardening the binding of nitrogen by niobium gives an additional improvement according to $FATT(^{\circ}C) = K + 700 \sqrt{N_{(free)}}$ (Gladman, Dulieu and McIvor, 1977). Due to the differences between the various analytical methods, a quantitative evaluation is not yet possible.

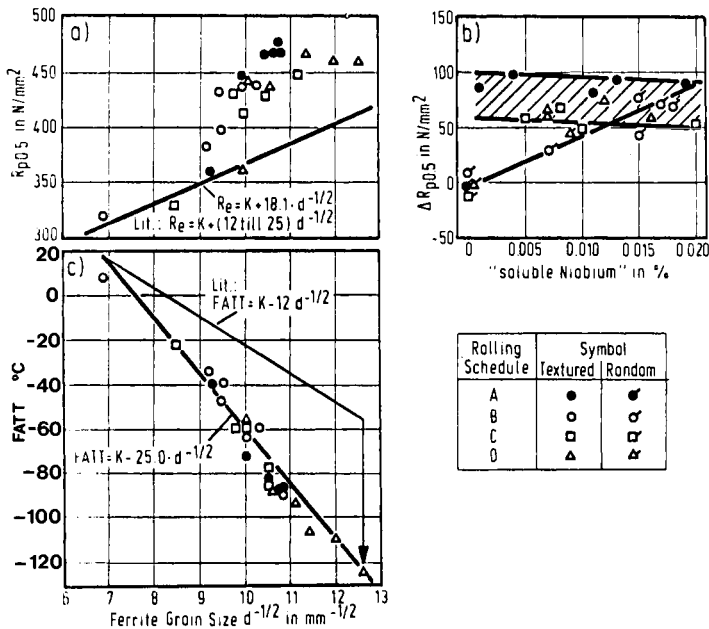


Fig. 3 Correlation between microstructure and mechanical properties

In conclusion one can say that niobium is acting as a strengthening and even more distinctly as a toughening element. The latter is a function of the grain refining effect of niobium and its ability to fix the nitrogen. This is valid for finish rolling conditions in the evaluated temperature range of 920°C to 750°C. To achieve equivalent toughness properties in plate rolling, it is possible to select the correct niobium content for the desired severe or relaxed rolling schedule. Economic considerations will mainly determine which option will be applied. Even though the reduction of texture caused delamination when applying relaxed rolling conditions, technical benefits are still to be gained. The application of such rolling schedules for X70 pipe properties, requires additional alloying elements.

CARBON-MANGANESE-NIOBIUM STEELS WITH 0.5% NICKEL ADDITIONS

In order to increase the strength of low carbon manganese-niobium steels about 0.5% nickel was added. It is known that 1% nickel lowers the transformation temperature by 60°C thus enhancing grain refinement and precipitation hardening during γ/α transformation (Heisterkamp, Gray and Stuart, 1979). Mill trials were carried out with a composition of 0.08% C, 0.40% Si, 1.60% Mn, 0.50% Ni and 0.130% Nb. Various rolling schedules have been applied to produce plate and hot strip.

The investigation (Niobium Products Company, 1983) showed that the steel, even finish rolled at 710°C, was totally in the austenite region. Regarding microstructural observations, the results were similar to those without nickel. The lower the final deformation and the thinner the plates, the finer is the resulting ferrite grain. Accelerated cooling as in strip production gave a further grain refinement. The "soluble" nitrogen content was very low, in the range of 5 to 12 ppm, even for finishing temperatures of 930°C; and the mobile nitrogen was even lower. Again, most of the niobium was precipitated in austenite.

The mechanical properties are shown in Fig. 4. Using only finishing temperatures above 900°C, unsatisfactory strength and toughness properties were achieved. Finish rolling around 820°C gave mechanical properties of X65 under comparable, less severe rolling conditions. With lower finishing temperatures, which implies a rolling break between 900 and 800°C and therefore less precipitation in austenite, much higher tensile properties like for X75 plate properties were obtained with FRT of about 740°C. These properties are caused by very fine homogeneously distributed precipitates formed during final deformation in the metastable austenite region. Toughness for these rolling conditions is sufficient for most of the known requirements including for arctic regions.

Thicker plates up to 50 mm show a reduced yield strength of about 2.5 N/mm² per mm plate thickness and transition temperatures around -60°C.

The best properties have been achieved in strip production, where on top of a sophisticated rolling schedule accelerated cooling was applied.

Some of these plates and the hot strip have been used for pipe production. The mechanical properties, given in Table 2, are adequate for X70 linepipes for arctic application.

The transformation behaviour (Niobium Products Company, 1983) of this steel composition after welding is characterized by a wide zone of bainitic transformation, Fig. 5.

Therefore, even at the high cooling rate (max. 100°C/s between 800 and 700°C) of manual arc welding in arctic regions, no martensite islands appear and the tendency toward cold cracking is negligible. On the other hand, the formation of ferrite is limited to cooling rates of 3.5°C/s (submerged arc welding).

With the right wire/flux combination, a fully acicular ferrite weld metal is easily achievable. The resulting properties are given in Fig. 6 and show that for automatic and manual welding the weldment properties are similar to those of the base plate.

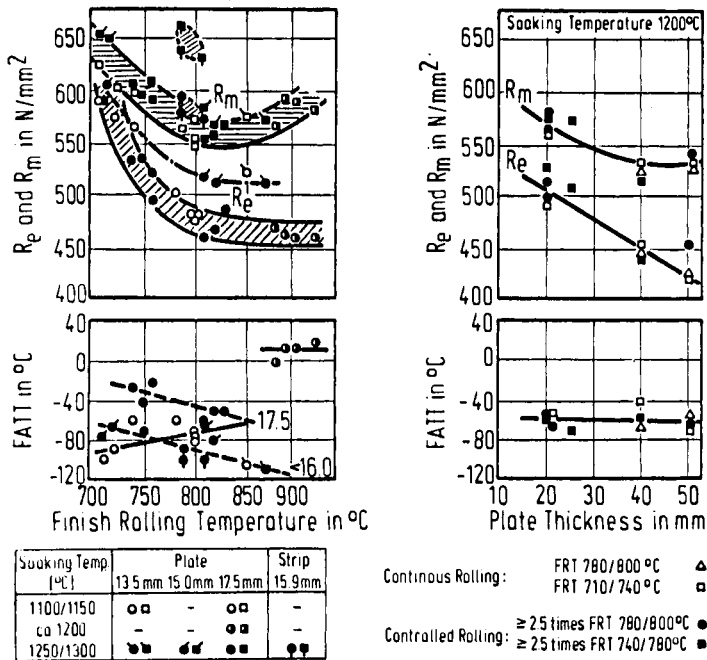


Fig. 4 Mechanical properties of Ni Nb-plate/strip material as a function of rolling schedule and final thickness

TABLE 2 Mechanical Properties of Produced Pipes (0.08% C, 0.40% Si, 1.50% Mn, 0.50% Ni, 0.13% Nb)

Pipe		$R_{p0.5}$ N/mm ²	R_m N/mm ²	A_5 %	$A_V^{+20^\circ C}$ J	50% FATT °C	85% BDWTT °C
Spiral Pipe 56 inch x 15.9mm		540	630	26	200	-90	-60
U-O-Pipe 56 inch x 17.5mm		483	584	26	78	-85	-55
U-O-Pipe 40 inch x 15.0mm	A	491	603	34	90	-80	-45
	B	520	661	28	65	-65	-35
	C	516	641	32	65	-65	-35

The same is true for automatic girth welding - CRC-Crosc Welding - with a heat input of 3 to 11 kJ/cm, which also gave excellent results, for instance, in COD-testing compared to standard X65 / X70 pipeline grade (Kirkwood, 1983).

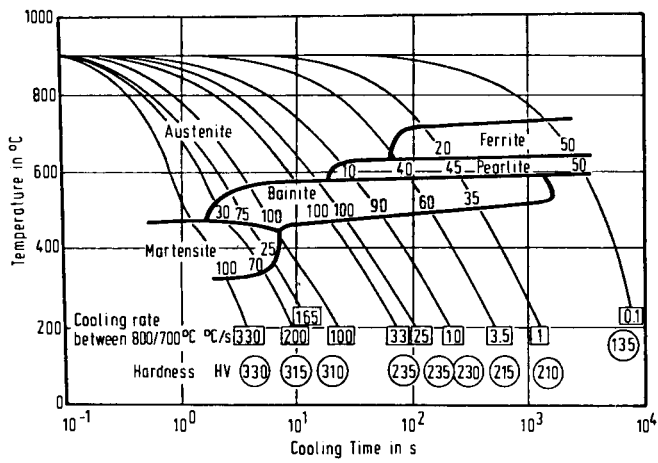


Fig. 5 CCT-Diagram of Ni Nb steel (0.13% Nb) after 1350°C austenitizing

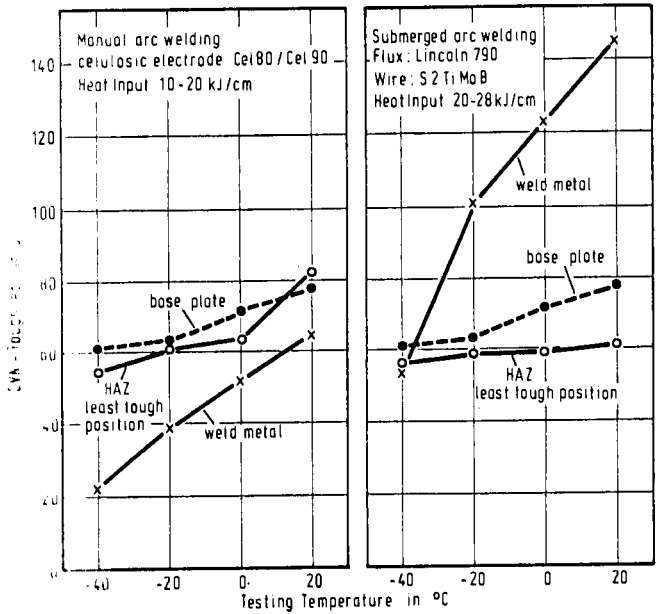


Fig. 6 Weldment toughness of Ni Nb pipe

CARBON-MANGANESE-NIOBIUM STEELS WITH TITANIUM ADDITIONS

For steels with reduced carbon contents, titanium can play an important role as an alloying element. Titanium nitrides will not go into solution during soaking and therefore inhibit austenite grain coarsening (Nakasuji, Matsuda and Tamehiro, 1981; Kaspar, Peichl and Pawelski, 1981). Moreover, the stable titanium nitride formation reduces the mobile nitrogen even further thus improving toughness. The titanium content not combined with nitrogen or sulphur is called effective titanium. Titanium carbides, mainly formed in ferrite, will increase strength by precipitation hardening, which is in the range of 16 to 35 N/mm² per 0.01% effective titanium (Nippon Steel Corporation, 1979), depending on product thickness and rolling conditions.

Results of Nb + Ti microalloyed low-carbon manganese including weldment properties have been reported recently (Heisterkamp and co-workers, 1981). It is well known (Wadworth, Woodhead and Keown, 1976) that steels with a composition close to stoichiometry of carbide and/or nitride formation show further improved properties. Fig. 7 shows that when the stoichiometric ratio of titanium and niobium carbide formation is approached, the amount of both carbides available for precipitation below 900°C increases. By the same token, the yield strength increases except in the presence of excessive niobium and titanium. Similar behaviour has been encountered in interstitial-free steels (Meyer, Heisterkamp and Müschenborn, 1977).

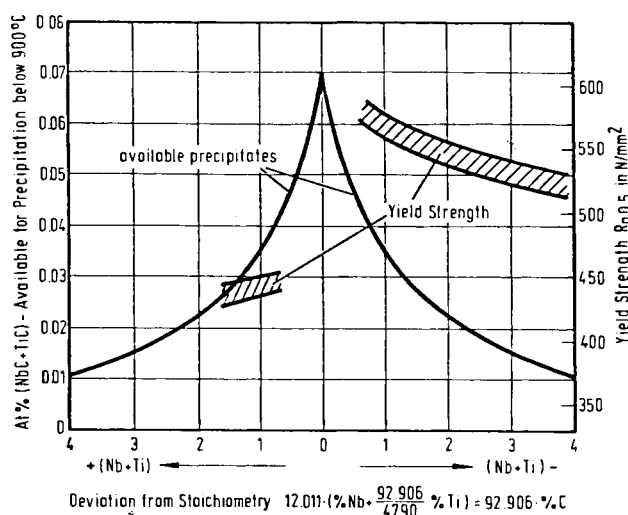


Fig. 7 Correlation between stoichiometry, available precipitates and yield strength

CONCLUSION AND OUTLOOK

Our investigations showed a correlation between niobium content and rolling conditions to achieve equivalent properties.

To reach the tensile properties of X70 pipe, additional measures have to be used. The addition of about 0.50% Ni to low-carbon manganese-niobium steel results in very good pipe properties of X65 to X75 under comparatively

relaxed rolling conditions. Another possibility is to use further precipitation hardening in ferrite; in this case, good properties have been achieved with additional titanium-microalloying.

Weldment properties of microalloyed grades with increased niobium or niobium plus titanium contents showed no impaired toughness properties in the weldment.

Further investigations will be carried out to study the influence of niobium and rolling conditions in ultra low-carbon bainitic steel grades - the transformation hardening type and the precipitation hardening grades when approaching stoichiometric composition.

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The Role of Molybdenum as an Alloy Element in Adhesive Wear Resistance

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ABSTRACT

The beneficial effect of molybdenum as an alloy element on corrosion resistance of nickel-base alloys is well known and understood. Less well known and not well understood is the role of molybdenum as an alloy element on sliding wear resistance. This paper deals with the influence of molybdenum on sliding wear of nickel-base and cobalt-base alloys. The wear behaviour was investigated using a combination of a rotating ring and a flat stationary block. Scanning electron microscopy (SEM) and electron microprobe examination were also used as an aid in understanding the wear mechanism. Cobalt-molybdenum based alloys have superior wear resistance compared to that of the nickel-molybdenum alloys. The superior wear resistance of the cobalt-molybdenum alloys is attributed to hard second phase precipitates (Laves of $\text{Co}_3\text{Mo}_2\text{Si}$ to $\text{Co}_5\text{Mo}_2\text{Si}$ composition) and to the close packed hexagonal (CPH) structure of both matrix and precipitate which limits deformation under the influence of loading. The mechanism of wear of these alloys is consistent with Archard's adhesion theory. Nickel-molybdenum alloys exhibit considerable wear which is attributed to the lower hardness of the second phase precipitate and to the cubic structure of this alloy system which (with twelve slip systems vs three for CPH alloys) promotes deformation and hence wear under loading. The mechanism of wear of the nickel-molybdenum alloys most likely involves formation of subsurface cracks and flake-like wear debris (delamination theory).

KEYWORDS

Adhesive wear; sliding wear; role of molybdenum on wear; cobalt-molybdenum-base alloys; nickel-molybdenum base alloys.

INTRODUCTION

Wear and corrosion are the principal causes of failure in a large percentage of industrial equipment and machines such as valves, pumps, etc., where lubricants cannot be used and a process stream may be the only fluid present. Wear is by far the least understood of the two phenomena, and its importance

cannot be overemphasized. The form of wear which is generally considered to apply in these systems is that due to the relative sliding motion between two metallic surfaces. The prediction of wear rates during sliding metal contacts and the understanding of the mechanism of wear is of great practical importance, and has been the aim of several proposed theories (Archard, 1953; Suh, 1973; Rigney and Glaeser, 1977).

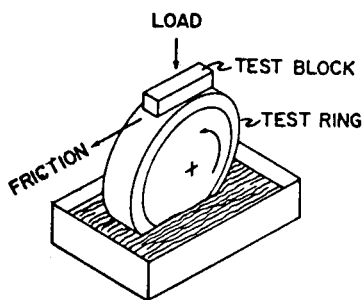
To combat wear in critical equipment, commercially available alloys include cobalt-base alloys which contain a substantial amount by weight of chromium and tungsten carbides, (e.g., Stellite[†] 12) and nickel-base alloys which contain chromium carbides, such as Haynes[†] Alloy No. 40. The carbide phase is considered to be a major contributor to the wear resistance of these alloys. More recently wear resistant alloys which contain molybdenum as a major alloying element (Triballoys[†]) became available. These alloys have a very low carbon content so that formation of carbides does not occur. There is only limited information available concerning the service performance of these alloys. In addition, there is very little known about the mechanism of wear and the role of molybdenum as an alloy element in enhancing wear resistance of these alloys. This paper summarizes the results of a laboratory study of sliding wear of three molybdenum-containing commercial alloys and analyses the data in terms of the available theories. In addition, it presents some insight into the probable role of molybdenum as an alloy element in enhancing wear resistance.

EXPERIMENTAL

The laboratory test programme used a Falex Model #1 wear testing machine which combines a rotating ring and a flat stationary block. Figure 1 shows the experimental set-up. Figure 1a shows the overall view of the wear testing machine on the left and the electronic control and instrumentation system on the right. Figure 1b shows schematically the ring and block assembly.



1a



1b

Fig. 1. Experimental set-up of wear testing machine (left) and ring and block assembly (right).

[†] Registered trade name by Cabot Corp.

This machine uses dead-weight load amplified thirty times by a compound lever system so that normal loads from about 15 to about 285 kg can be applied between the flat stationary block and the rotating ring. During testing the complete set-up, including the ring and block, was enclosed in a reservoir containing distilled water which acted as a coolant. During most of the tests a normal load of 95.3 kg (210 lbs) between the flat block and rotating ring was used which provided an initial Hertzian stress of 361.2 kPa (52 550 lb. in⁻²). Several tests were also carried out using normal loads between the ring and block in the range of 25 to about 120 kg. Rings were rotated at 80 rev min⁻¹ to give a surface velocity of 8.8 m min⁻¹ (28.8 ft. min⁻¹). Tests were run up to a maximum of 50 000 rev. (5.5 x 10⁵ cm sliding distance). The rings and blocks were of standard size as specified in ASTM D-2714 (Annual Book of ASTM Standards).

Test blocks and rings were prepared from AISI 304 stainless steel and hardfaced with the appropriate alloy. For preparation of the test rings a round bar stock of about 2.9 cm diameter was hardfaced using inert gas tungsten arc welding. Uniform alloy deposition throughout the circumference was achieved by rotating the bar during hardfacing. The bar was subsequently cut in several sections and each section was used to machine a test ring. Test rings were about 0.34 cm thick with about 3.5 cm OD and a tapered ID varying from 2.58 to 3.12 cm. Blocks were machined from flat AISI 304 stainless steel stock which was hardfaced on one side of the flat surface. In both blocks and rings a hardfacing alloy layer of about 0.32 cm was obtained after machining. The surface finish of both blocks and rings was 7-10 rms. To evaluate the mechanism of wear the weight loss of block and ring produced as a result of wear was determined to 0.1 mg accuracy prior to and after testing. In addition to block and ring weight loss, the wear scar was also examined by means of a scanning electron microscope (SEM). An electron microprobe was also used to identify the chemical composition of the alloy phases present.

The wear resistant alloys studied in this work included two cobalt-base alloys containing about 28% molybdenum (Tribaloy 400 and 800) and a nickel-base alloy containing about 32% molybdenum (Tribaloy 700). Typical chemical composition of the alloys used in this programme is given in Table 1.

TABLE 1 Analysis of Wear Resistant Alloys

Type of Alloy	Hardness Rc	Chemical Composition, wt%							
		Co	Ni	Mo	Cr	Si	C	W	Fe
Tribaloy 400	51-58	62	-	28	8	2.6	0.06	-	-
Tribaloy 800	54-62	52	-	28	17	3	0.06	-	-
Tribaloy 700	42-48	3.0 (Co+Fe)	46	32	15	3.4	0.06	-	-
Stellite 12	40-47	62	-	-	29	-	1.3	8	-
Haynes No. 40	57	-	72	-	15	-	0.75	-	4.0

RESULTS AND DISCUSSION

Several experiments were carried out to establish the kinetics of the wear process using sliding distances in the range of 0.5 to 4 x 10⁵ cm, and a constant load of 95.3 kg and at 80 rev.min⁻¹. During these tests the ring and block assembly was completely immersed in distilled water which served

as a coolant and maintained the ring and block at 30-35°C. In these studies individual weight loss values of the rotating ring as well as the stationary block were obtained. The data in Table 2 show the block and ring weight losses sustained by Tribaloy 700 as a function of time under a load of 95.3 kg (210 lbs) at 80 rpm. The data show that the weight losses sustained by the blocks were considerably smaller than the weight losses of the rings. Similar behaviour was also observed for the other alloy systems studied.

TABLE 2 Weight Loss of Tribaloy 700 Ring and Block
as a Function of Time Under 95.3 kg (210 lbs)
Load at 80 rpm

Test Time (Hrs)	Block Weight Loss (g)	Ring Weight Loss (g)
0.52	0.0035	0.1660
1.00	0.0177	0.2943
1.56	0.0357	0.4701
2.00	0.0405	0.6854
2.60	0.0523	1.0345
3.60	0.0792	1.3656
4.20	0.0900	1.6783
4.70	0.1058	1.8925
5.70	0.1289	2.2339

The difference between block and ring weight losses is attributed mainly to the much larger ring surface area which is subject to wear. It is therefore considered useful to use the total weight loss of both ring and block as a measure of the weight loss sustained by a given alloy system. The combined ring and block weight losses as a function of sliding distance for the cobalt-molybdenum and nickel-molybdenum alloys are shown in Figure 2.

The data shows that the total weight loss follows a linear relationship with sliding distance. The cobalt-molybdenum alloys (Tribaloys 400 and 800) showed quite a remarkable wear resistance, whereas the nickel-molybdenum alloy was subject to considerable wear. The observed linear relationship between metal weight loss (or volume) due to wear and sliding distance can be expressed by Archard's eq.:

$$V = \frac{kWL}{3P} \quad (1)$$

where: V = volume of wear in mm^3 ; W = load on sliding surfaces in kg; L = sliding distance in mm; P = penetration hardness of the softer of the two contacting surfaces in kg/mm^2 ; and k = coefficient of wear

The wear coefficients for these alloy systems were calculated from the wear data plotted in Figure 2, using equation (1) and the densities and penetration hardness values given in Table 1. The wear coefficients of the three self-mated molybdenum-containing alloys are tabulated in Table 3. For comparison, the wear coefficient for self-mated Stellite 12 and Haynes No. 40 alloys are also included in this table.

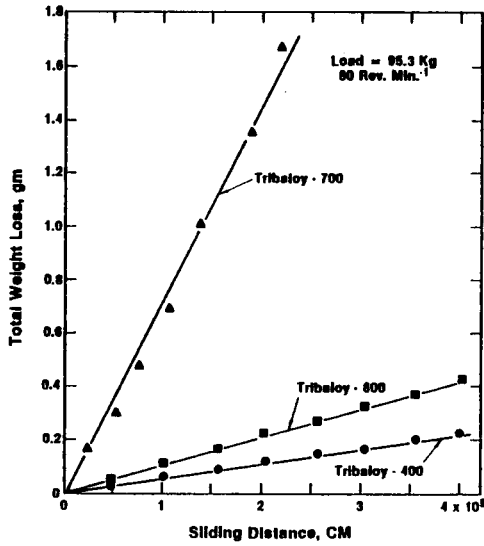


Fig. 2. Combined weight loss of ring and block due to wear as a function of sliding distance.

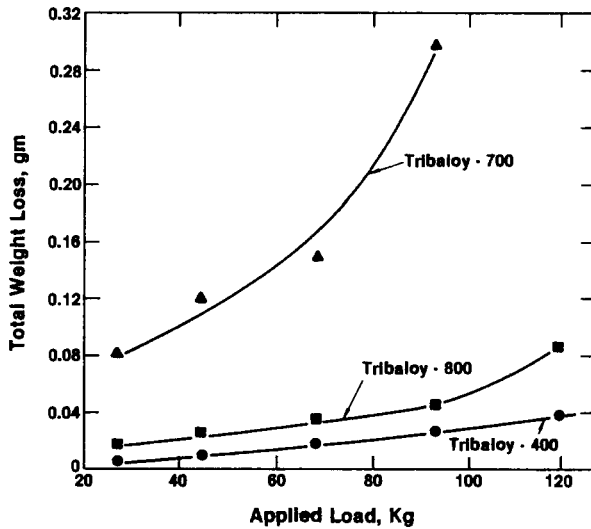


Fig. 3. Combined weight loss of ring and block due to wear as a function of applied load.

TABLE 3 Wear and Friction Coefficients for Several Self-Mated Alloys Calculated from Data Presented in Figure 2, and using eq. (1). Friction Coefficients were calculated using eq. (2).

Type of alloy	Wear Coefficient, k	Friction Coefficient, μ
Tribaloy 400	1.12×10^{-4}	0.42
Tribaloy 800	2.4×10^{-4}	0.45
Tribaloy 700	1.3×10^{-3}	0.42
Haynes No. 40	1.6×10^{-4}	0.54
Stellite 12	4.67×10^{-4}	0.49

The data in Table 3 show that the wear coefficient for cobalt-molybdenum alloys (Tribaloy 400 and 800) are comparable to those of the well-known hardfacing Stellite 12 and Haynes No. 40 alloys. On the other hand, the nickel-molybdenum alloy (Tribaloy 700) exhibited an order of magnitude higher wear coefficient.

Several experiments were also carried out to establish the effect of applied load on wear of these alloys at 80 rev.min^{-1} and at 5000 total revolutions (Figure 3). The cobalt-molybdenum alloys, particularly Tribaloy 400, appear to exhibit only mild wear up to the maximum load of 120 kg investigated. In particular, Tribaloy 400, and to a certain extent, Tribaloy 800, exhibit a linear dependence of wear vs applied load as predicted by Archard's equation. In contrast, Tribaloy 700 (the nickel-molybdenum alloy) was subject to severe wear, particularly at loads higher than about 60 kg.

Friction data obtained for cobalt-molybdenum and nickel-molybdenum alloys sliding on similar alloys while immersed in distilled water are shown in Figures 4 and 5. Figure 4 shows the measured friction force for Tribaloy 700 alloy sliding on Tribaloy 700 at $T_m \sim 35^\circ\text{C}$, as a function of sliding distance, at a load of 68 kg and at 80 rev.min^{-1} . Following an initial period of slightly higher value, the friction force reached a steady-state value of about 28 to 30 kg. Figure 5 shows the measured friction force for Tribaloy 400 alloy sliding on Tribaloy 400 at $T_m \sim 35^\circ\text{C}$ as a function of sliding distance, at a load of 68 kg and at 80 rev.min^{-1} . Figure 4 shows a typical "stick-slip" type of behaviour in which the frictional force fluctuates in a regular manner between two somewhat well-defined positions. This type of behaviour is characteristic of mild frictional behaviour between two sliding surfaces when small particles are transferred from one sample to the other (Rabinowitz, 1965).

Figure 5 shows a more irregular friction force pattern. The initial larger fluctuation in the frictional force is attributed to transfer of larger size particles, probably hard second-phase precipitates (Laves), between the two sliding surfaces during the initial test period. The steady-state friction coefficients of self-mated Triballoys under a load of 95.3 kg is shown in Table 3. The effect of load on the steady-state friction coefficient of self-mated Triballoys is likewise shown in Table 4.

The friction coefficients summarized in Tables 3 and 4 were calculated from steady-state friction force data and applied loads using eq. (2):

$$F = \mu W \quad (2)$$

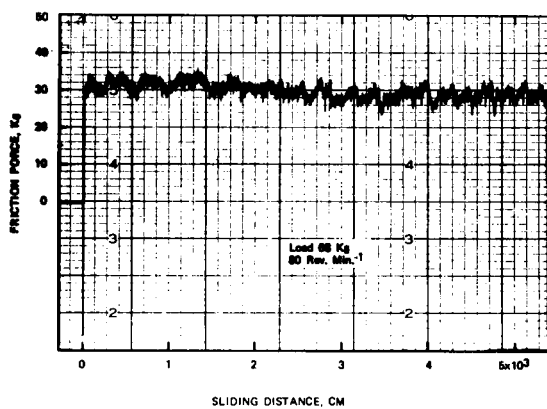


Fig. 4. Typical friction force trace of self-mated Tribaloy 700.

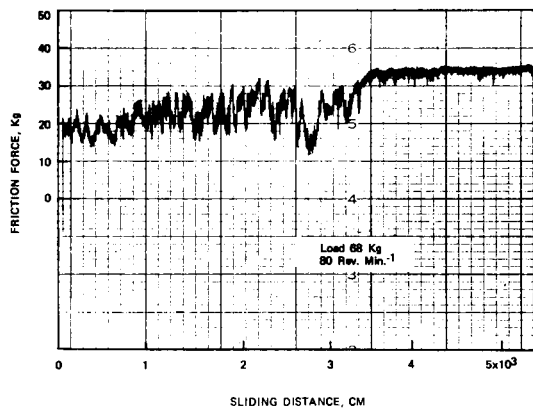


Fig. 5. Typical friction force trace of self-mated Tribaloy 400.

where: F is friction force; W is load on sliding surfaces;
and μ is the friction coefficient

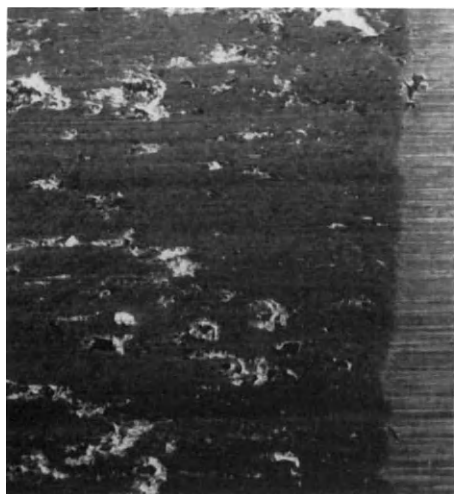
TABLE 4. Effect of Load on Friction Coefficient for
Several Self-Mated Alloys

Load, kg	Friction Coefficient, μ	
	<u>Tribaloy 400</u>	<u>Tribaloy 700</u>
27.2	0.50	0.53
45.4	0.40	0.52
68.1	0.48	0.43
95.4	0.47	0.43
118.1	0.40	0.43

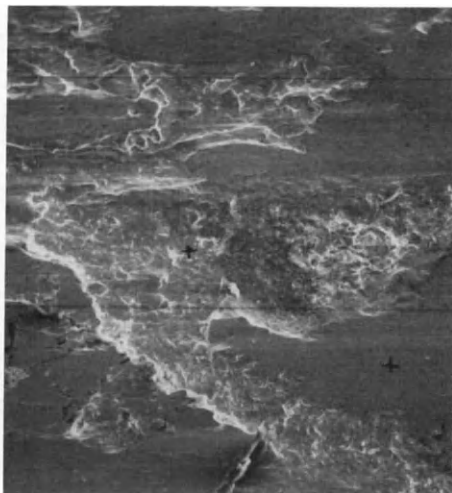
To understand the mechanism of wear, scanning electron microscopic (SEM) examination of the alloy surfaces following the wear tests were carried out. Typical appearance of the wear surface of the alloys investigated is shown in Figure 6. Figures 6a, c, and d show the topography of the surface of blocks and rings of cobalt-molybdenum alloys after 2000 revolutions. The mechanism of wear in this type of alloy appears to involve the transfer of particles from one surface to the other. The mechanism of particle removal during sliding wear of the cobalt-molybdenum alloys is likely to involve asperity contact, where adhesive forces will tend to be strong enough to tear out a wear particle. This mechanism of wear, known in the literature (Archard, 1953) as "adhesion wear theory" first proposed by Archard predicts a linear relationship between wear volume (or mass) and sliding distance at constant load, and also a linear dependence of wear volume (or mass) and applied load at constant sliding distance. The data shown in Figures 2 and 3 confirm that the kinetic wear data for cobalt-molybdenum alloys are consistent with the adhesion wear theory (Archard, 1953).

Figure 6b shows the topography of the wear surface after 2000 revolutions of the nickel-molybdenum alloy (Tribaloy 700). The mechanism of wear in this case appears to be characterized by small cracks parallel to the wear surface (see left bottom side in Figure 6b) which eventually led to the formation of flake-like wear debris. The origin of these subsurface cracks may be the result of void coalescence as proposed (Suh, 1973) in the delamination theory. The delamination wear theory postulates formation of voids (which eventually coalesce into cracks) by the pile-ups of dislocations at a finite distance below the surface, caused by the sliding motion between materials. This mechanism of sliding wear of nickel-molybdenum alloys is consistent with the linear relationship between wear and sliding distance shown in Figure 2 and the accelerated change in wear rate with applied load (Figure 3).

Neither of the two theories (Archard, 1953; Suh, 1973) used to explain the experimental data, takes into consideration the environmental effects and their possible influence on the wear processes. It has been recognized in recent years that the development of relatively thick oxide layers on metal surfaces during sliding often plays an important role in friction and wear (Foley, Peterson and Zapf, 1963; Aronov, 1977; Barries, and co-workers, 1977). However, the role of adsorbed water and/or oxygen molecules or extremely thin oxide films on wear is not understood. The work of Foley and co-workers (Foley, Peterson and Zapf, 1963), which showed small differences in the coefficient of friction of cobalt at ambient temperature in vacuum and in several reactive gaseous atmospheres, suggests that the effect may be small.



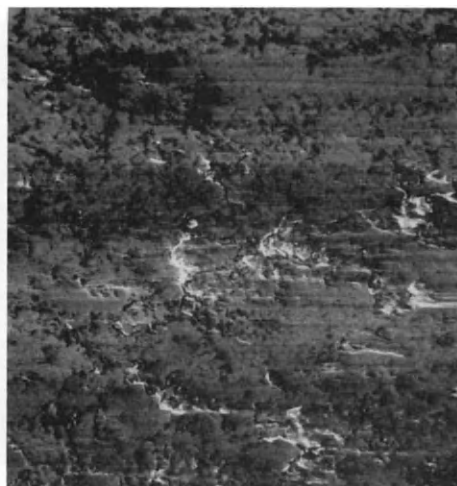
a) Tribaloy 800 block x50



b) Tribaloy 700 block x200



c) Tribaloy 400 block x200



d) Tribaloy 400 ring x200

Fig. 6. Typical wear topography of surface of test rings and blocks under scanning electron microscope (SEM). Wear test at 80 rev.min^{-1} , 2000 total revolutions and load of 95.3 kg.

To understand the role of alloy composition and alloy phases on the wear characteristics of the alloys investigated, an electron microprobe was also used to quantitatively identify the chemical composition of the alloy phases present. A summary of the microprobe data is shown in Table 5. In this table, Knoop microhardness numbers of the different alloy phase are also included.

TABLE 5. Electron Microprobe Analyses and Knoop Hardness Numbers (KHN) of Alloy Phases found in Cobalt-base and Nickel-base Alloys containing Molybdenum

Type of Alloy	Alloy Phase	Major Alloying Elements, wt%						KHN
		Cr	Co	Si	Mo	Ni	Fe	K ₂₅ ^{gr}
Tribaloy 800	Solid solution	28	47	4.6	6.3	0.5	3	-
Tribaloy 800	Laves Phase	15.7	40	13	28	0.4	1.7	-
Tribaloy 800	Laves Phase	26	44	8.3	18.4	0.2	2.0	-
Tribaloy 400	Solid solution	11.4	62.7	4.3	14.9	1.0	5.5	820
Tribaloy 400	Laves Phase	7.4	46.6	12.7	28.9	0.6	3.7	2100
Tribaloy 700	Solid solution	21.8	0.1	3.6	8.7	59.6	6	665
Tribaloy 700	Second Phase Precipitate	15.6	0.1	12.1	26.9	41.8	3.4	1300

A back scattered electron image of the surface of Tribaloy 400 and Tribaloy 700 in cross-section is also shown in Figures 7 and 8, respectively. These alloys are essentially free of carbide phases (because of the low carbon content). The alloys are hyper-eutectic, and structurally contain about 35 to 70 percent by volume of a second phase precipitate. In the case of the cobalt-molybdenum alloys, the second phase is a Laves phase of the MgZn₂-type, with a composition typically between Co₃Mo₂Si and Co₅Mo₂Si. According to the literature, the composition of the Laves phase should be between CoMoSi and Co₃Mo₂Si (Schmidt and Ferriss, 1975; Gladyshevskii and Kuz'man, 1960; Gladyshevskii, 1962; Skolozdra and co-workers, 1966). The solid solution was found to have a typical composition of about Co₉Mo_{1.3}Si; the chromium partitioned itself about 1/3 in the Laves phase and 2/3 in the solid solution.

In the case of the nickel-molybdenum alloy (Tribaloy 700) the second phase precipitate is enriched in nickel and chromium and somewhat depleted in molybdenum and silicon. Again, because of the low carbon content carbide phases are completely absent.

The second phase precipitates in both the cobalt-molybdenum and the nickel-molybdenum alloys have considerably higher hardness than the matrix (Table 5), and in that respect play a similar role in the wear performance of these alloys as the tungsten and chromium carbide phases in the Stellite 12 and Haynes No. 40 alloys respectively.

The superior wear resistance of the cobalt-molybdenum alloys (Tribaloy 400 and 800) in comparison with that of the nickel-molybdenum alloy (Tribaloy 700) is attributed to the differences in hardness and distribution pattern of the second phase precipitate (Figures 7 and 8 and Table 5) and also to the different crystallographic structure of these alloy systems. The cobalt-molybdenum alloys have a close packed hexagonal (CPH) structure (at ambient temperatures) whereas the nickel-molybdenum alloys have a cubic structure.

The superior wear performance of the CPH structure can be attributed to the small number (three) of slip systems in comparison to twelve slip systems possible in cubic alloys. The smaller number of slip systems will tend therefore to limit deformation and hence wear under the influence of loading. The importance of crystallographic structure on friction and wear was demonstrated previously by Buckley and Johnson, 1966.

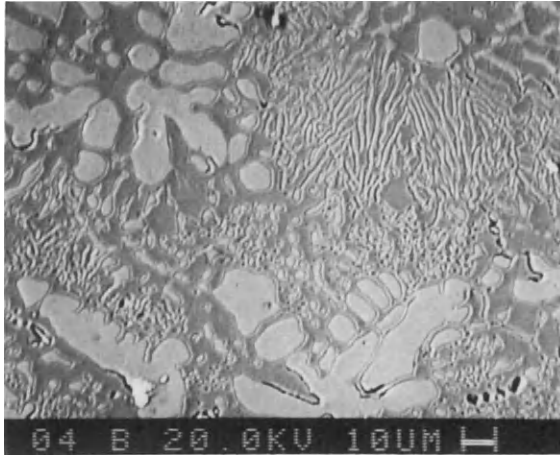


Fig. 7. Microstructure of Tribaloy 400 weld overlay. Light phase is primary Laves phase in eutectic with softer solid solution (dark phase). Back scattered electron image. x500

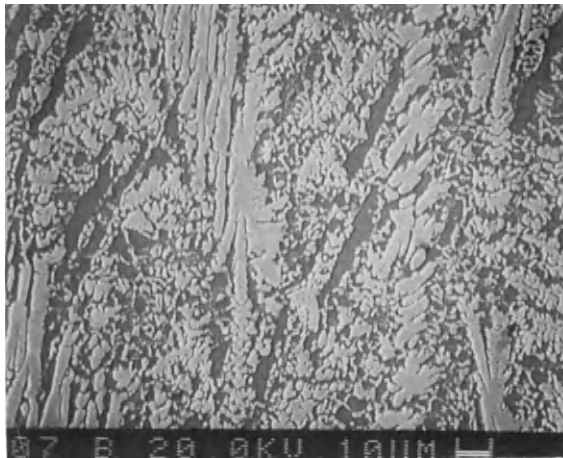


Fig. 8. Microstructure of Tribaloy 700 weld overlay. Light phase is second phase precipitate; dark phase is softer solid solution. Back scattered electron image. x500

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The Development of Wear Resistant Alloys for the South African Gold Mining Industry

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ABSTRACT

The environment in the gold mines is harsh due to the abrasive nature of the ore and the aggressive mine waters and atmospheres in the working areas. Often the wear of materials involves varying contributions of corrosion and abrasion and tests conducted underground have shown that conventional abrasion resistant materials are not adequately resistant to the wear processes prevalent in gold mines. This work has highlighted the need for the development of a general purpose, abrasion and corrosion resistant steel for the gold mining industry. Alloys with potential for this role are discussed.

KEYWORDS

Abrasive wear, corrosive wear, wear resistant alloys, alloy design, materials for mining equipment.

INTRODUCTION

Equipment used in the South African gold mines is exposed to a particularly harsh environment which is a result of the abrasive nature of the rock, the corrosivity of mine waters and the aggressive nature of the atmosphere in certain areas of mines. The individual actions of abrasion and corrosion cause rapid deterioration of materials, but when combined, which is often the case underground, conventional engineering materials wear at unprecedented rates.

In this paper the nature of the wear processes as well as the shortcomings of conventional abrasion resistant alloys are described. The need for one or more general purpose abrasion and corrosion resistant steels is identified and some possible alloys are considered. Finally the means of obtaining suitable alloys are discussed.

THE WEAR PROBLEM

The three types of abrasion which commonly occur in the gold mining industry are impact abrasion, two body abrasion and three body abrasion. In general, these affect the external parts of machines, but with the increasing mechanisation of gold mining, abrasion of internal parts of hydraulically powered machines is also becoming a problem. The abrasion of internal parts occurs because of the unavoidable ingress of fine quartzite particles into the hydraulic systems of machines, either from the environment or as a result of the use of mine service water as a hydraulic fluid.

Certain areas of a mine are very corrosive and materials usually wear by the combined action of corrosion and abrasion. A spectrum of wear processes occurs varying from predominantly dry abrasive wear through simultaneous abrasive-corrosive wear to predominantly corrosive wear.

In our experience, from tests conducted on mining machines, there is a large corrosion contribution to the overall wear process in systems in which two body abrasion occurs, while in systems in which three body abrasion occurs, corrosion makes a lesser contribution to the overall wear process. This variation in the contribution of corrosion with the different types of abrasion is highlighted by the results in Table 1. The compositions of the various alloys are given in Table 2. In a three body abrasion system, the proprietary abrasion resistant steels perform about twice as well as the austenitic and ferritic stainless steels whereas the opposite is true in a two body abrasion system.

TABLE 1 The performance of various steels under two body and three body abrasion conditions.

Three body abrasion conditions		Two body abrasion conditions	
Material	RWR*	Material	RWR*
AR Steel 1	3.9	AISI 316 L	3.6
AR Steel 2	3.8	ALLOY B (800°C)	3.6 ± 0.6
AR Steel 3	3.2 ± 0.4	AISI 304 L	2.8 ± 0.7
AR Steel 4	3.1	ALLOY A (800°C)	2.0
AR Steel 5	3.1 ± 0.4	AR Steel 8	1.5
Hadfields Steel	2.7	AR Steel 5	1.45 ± 0.05
AR Steel 6	2.1	AR Steel 7	1.35 ± 0.25
AISI 304	1.5 ± 0.2	AR Steel 2	1.3
AISI 316	1.3	AR Steel 4	1.2
ALLOY A (800°C)	1.1	AR Steel 3	1.2
Mild Steel	1.0	AR Steel 6	1.1
ALLOY B (800°C)	0.7	AR Steel 1	1.0
		Mild Steel	1.0

* RWR = Relative Wear Resistance
 = $\frac{\text{Volume loss of mild steel}}{\text{Volume loss of material x}}$

AR Steel = Proprietary Abrasion Resistant Steel.

(°C) = Annealing Temperature.

TABLE 2 Typical compositions of steel alloys evaluated
in underground tests

Material	C	Mn	Si	Cr	Ni	Mo	Cu	Ti	Others
AR Steel 1	0.28- 0.32	1.65 max	0.20- 0.50	1.20 max	-	0.35 max	0.20 max	-	B 0.0025 max
AR Steel 2	0.25- 0.32	0.40- 0.65	0.20- 0.35	0.80- 1.15	-	0.15- 0.25	-	-	-
AR Steel 3	0.4	1.0	0.3	0.6	0.7	0.25	-	-	-
AR Steel 4	0.3 max	1.75 max	0.20- 0.50	1.30 max	-	0.25 max	-	-	B 0.002 max
AR Steel 5	0.25- 0.32	0.40- 0.65	0.20- 0.35	0.80- 1.15	-	0.15- 0.25	-	-	-
AR Steel 6	0.41- 0.55	0.6- 1.0	0.10- 0.30	-	-	-	-	-	-
AR Steel 7	0.17 max	1.60 max	0.50 max	0.65- 0.95	-	0.30- 0.50	-	-	-
AR Steel 8 ^a	0.24	0.53	0.29	1.54	1.30	0.56	-	0.03	V 0.09 B 0.002
Hadfields ^a	0.81	14.46	0.79	0.14	0.08	-	-	-	-
AISI 304 ^b	0.08 max	2.0 max	1.0 max	18.0- 20.0	8.0- 10.5	-	-	-	-
AISI 316 ^b	0.08 max	2.0 max	1.0 max	16.0- 18.0	10.0- 14.0	2.0- 3.0	-	-	-
Alloy A ^c	0.01- 0.05	0.84- 0.90	0.39- 0.58	11.04- 12.60	1.37- 1.79	0.19- 0.22	-	0.29	-
Alloy B	0.03 max	1.5 max	1.0 max	11.0- 12.0	1.5 ^d - max	-	-	4(C+N) min	-

a Actual chemical compositions.

b AISI 304L and AISI 316L differ from AISI 304 and AISI 316 only in carbon content. The specified carbon content of L grades is 0.03 max.

c ALLOY A is an experimental alloy and the composition given covers the range of compositions of the samples tested.

d 1.5 per cent max. nickel is the manufacturer's specification. However, the nickel content is usually less than 0.6 per cent which makes ALLOY B distinct from ALLOY A.

AR Steel = Proprietary Abrasion Resistant Steel.

In general, we have found that proprietary abrasion resistant steels perform poorly in the environment of the gold mines. Corrosion resistant steels, such as the 12 per cent chromium containing steels, ALLOYS A and B (see Table 2), on the other hand, perform well in a two body abrasion situation and they are cost effective as well (Allen, Protheroe and Ball, 1981). But, in a three body abrasion situation, they perform about the same as, or worse than mild steel. Also the other more corrosion resistant stainless steels, such as AISI 304 and 316, do not perform much better than ALLOYS A and B in two body abrasion nor much better than mild steel in a three body abrasion situation. This indicates that a chromium content of 12 per cent in a steel provides sufficient resistance to corrosion in the underground environment.

Other materials, more wear resistant than the proprietary abrasion resistant alloys, such as the high chromium cast irons, hard faced plates and ceramics, are generally not suitable for use in mining machines underground. This is because of their poor mechanical properties, particularly toughness, or, in some cases, because of their high cost. In addition, coatings, such as hard chromium plating and electroless nickel, in our experience, do not always provide adequate protection against corrosion and abrasion. On the other hand, the spray-and-fuse, nickel-chromium coatings have proved successful but have limited application and are very expensive.

These findings indicate the need for one or more low cost, general engineering steels which are resistant to both general corrosion and abrasion by quartzite irrespective of the type of abrasion. These steels would find application throughout the gold mining industry and could be used for both internal and external parts of machines subject to abrasion and/or corrosion.

THE PRACTICAL REQUIREMENTS AND CHARACTERISTICS OF A GENERAL PURPOSE, WEAR RESISTANT STEEL

Existing knowledge on the corrosive and abrasive wear of steel alloys (Noel, 1981) and the welding, forming and mechanical property requirements of the proposed steels, dictate, to some degree, the compositional and mechanical characteristics of any general purpose, wear resistant steels. These are as follows:-

- (i) The steels must be resistant to general corrosion in the underground environment.
- (ii) The steels must have a high resistance to abrasion by quartzite.
- (iii) The steels must be tough and this can be represented by a minimum Charpy impact energy of about 35 joules at room temperature. This is the minimum impact value required for general structural engineering applications.
- (iv) Ideally, it should be possible to alter the hardnesses and therefore toughnesses, of the steels by simple heat treatments.
- (v) The steels must be reasonably formable and therefore the steels should have a strain-to-fracture value of at least 10 per cent at room temperature.

- (vi) The steels should be weldable in sections up to about 50 mm. The influence of this requirement on the alloy composition will vary depending on the alloy type.
- (vii) The cost of the steels should be kept as low as possible, and for this reason the chromium contents of the alloys should be kept to less than about 13 per cent. For the same reason high concentrations of alloying elements such as nickel, molybdenum and cobalt should be avoided.

As regards the corrosion resistance requirement, this is normally achieved by adding at least 10 per cent chromium to steels which results in the formation of the passive oxide layer. However, a high chromium content steel can only be flame cut with a plasma arc system. This is obviously a disadvantage for a general purpose engineering steel. Therefore, the possibility of achieving the necessary corrosion resistance by other means, which will allow flame cutting by an oxy-acetylene system, should be examined.

Having defined the characteristics of general purpose wear resistant steels for the gold mining industry, the design and production of suitable steels will now be considered.

ALLOY DESIGN CONSIDERATIONS

Material is lost from a metal surface by abrasive wear when a critical fracture strain condition is experienced. This strain may be achieved locally after a single abrasion event or as a cumulative effect of many events. In addition, the strain is imparted at a very high rate. The deformation is dynamic in the sense that as surface material is lost at the attainment of the critical strain, material well below the surface is at the point of plastically yielding.

In order to design an alloy to resist abrasive wear, attention must be given to developing a microstructure which ideally never accumulates the critical fracture strain under abrasive wear conditions or which at least has a large value of critical strain. This can be achieved in an alloy by having a microstructure which has a high resistance to particle indentation (high surface hardness) and a high resistance to fracture (good toughness). Note that it is the final surface hardness attained prior to removal of material which is important and not necessarily the bulk hardness of the material.

As regards the hardness of the alloy, it has been reported (Richardson, 1968) that a material should be at least half as hard as the abrasive material if any resistance to abrasive wear is to be achieved. Since quartzite has a hardness of about 1000 HV, a general purpose wear resistant alloy should be capable of developing a surface hardness of at least 500 HV.

There are a number of existing corrosion resistant steels which can develop a high hardness while maintaining good toughness, for example the high nickel maraging steels and the highly alloyed controlled transformation stainless steels. But these steels are not considered to be economically viable as general purpose, abrasion and corrosion resistant steels.

TABLE 3 Typical compositions and mechanical properties
of TRIP and dual phase alloys.

Steel grade or name	Composition %						0.2% proof stress (MPa)	UTS (MPa)	Elongation (percent)	Charpy Impact Energy (joules)	max. work hardened hardness (HV)
	C	Cr	Mn	Ni	Si	Mo					
301(hardened)	0.08	17	1.5	8	-	-	1200	1500	20	50	450
TRIP Steel 1	0.3	9	2	8.5	2	4	1530	1750	30	40	500
TRIP Steel 2	0.3	8	13.5	-	-	-	1490	1690	7.6	-	500
12% Cr Steel Alloy B	0.03 max	11.0 12.0	1.5 max	1.5 max	1.0 max	- 4(c+N) min	360	510	28	75	150
Quatough	0.3	4.0	2.0	-	-	-	1400	1660	17	35	500

There are certain alloy types, however, from which suitable steels could be derived, namely the dual phase steels and the TRIP steels (transformation induced plasticity steels). Alloys from these groups have, with some modification, the potential to satisfy the four main requirements of general purpose wear resistant steels, that is high hardness coupled with good toughness, corrosion resistance and low cost. Table 3 lists some representative alloys together with their pertinent mechanical properties while Table 4 is an analysis of the alloys in terms of their suitability as general purpose, abrasion and corrosion resistant steels.

TABLE 4 An analysis of the properties and characteristics of the alloys in TABLE 3

GRADE OR NAME	301	Trip Steel 1	Trip Steel 2	Alloy B	Quatough
Corrosion resistance	A	A (probably)	I (probably)	A	I
Surface hardness	I	A	A	I	A
Toughness	A	A	I	A	A
Weldability	A	U	U	A	I
Formability	A	A	A	A	A
Cost	H	H	Ac	Ac	Ac
Ease of production	A	D	D	A	A

- A - Adequate
- Ac - Probably acceptable
- I - Inadequate
- U - Unknown to authors or no detailed information available
- H - High cost (relatively)
- D - Difficult

The steel designated ALLOY B is a ferritic-martensitic steel recently developed in South Africa (Ball and Hoffman, 1981; Thomas, 1981) while Quatough is a high strength, tough, non-corrosion resistant, martensitic-austenitic steel developed in the U.S.A., chiefly by Thomas and co-workers (Salesky and Thomas, (1982); Rao and Thomas (1980)). In both these types of steel the martensite is in the form of parallel laths (approximately $0.5\mu\text{m}$ in width and $5\text{--}10\mu\text{m}$ in length) with a very high dislocation density.

Economically and practically ALLOY B has the most potential for modification to a general purpose wear resistant steel. The main deficiency of ALLOY B is in its low hardness and hence abrasion resistance. The hardness of this alloy may be improved by an increase in the carbon content of the lath martensite, but it is important that any adjustment to the composition does not change the "ferrite factor" (Ball and Hoffman, 1981). An increase in the ferrite factor would lead to a fully ferritic structure while a decrease would result in a fully martensitic steel. The required fine grained, tough alloy with good work hardening characteristics is achieved in a dual phase structure obtained within a small range of the ferrite factor. The hardness of the lath martensite could be increased to some extent by the omission of the stabilising element titanium which would release small amounts of carbon and nitrogen. If the omission of titanium does not provide sufficient abrasion resistance further carbon or nitrogen could be added together with chromium. These changes will probably create difficulties with weldability and a compromise would have to be made.

The main deficiency of Quatough is in its lack of corrosion resistance. The easiest method of improving corrosion resistance is to increase the chromium content. However, it is possible that addition of other elements, such as copper or aluminium in combination with chromium, could also provide the necessary corrosion resistance. This route will be investigated. The consequences of an increase in chromium on the strength and toughness of the Quatough type alloy have been investigated by McMahon and Thomas (1973). Steels with carbon contents of about 0.17 and 0.35 per cent and chromium contents ranging from 4.0 to 12.2 per cent were examined. The strengths of the as-quenched alloys containing 0.17 per cent carbon were virtually unaffected by an increase in chromium content. Also they showed only a 15 per cent decrease in toughness at chromium contents above about 8 per cent. On the other hand, the 0.35 per cent carbon alloys, in the as-quenched state, showed a significant increase in strength and a large decrease in toughness with increasing chromium content. The strength of the 0.17 per cent carbon alloys and the toughness of the 0.35 per cent carbon, high chromium alloys do not satisfy the requirements of a general purpose, corrosion and abrasion resistant alloy. However, an alloy of intermediate composition (about 0.25 per cent carbon and 10 per cent chromium) could have a suitable combination of properties and such an alloy is under investigation at present.

General purpose abrasion and corrosion resistant steels might also be derived from the group of TRIP steels. These fully austenitic steels which transform to martensite during plastic deformation have very large work hardening capacities which result in high strength and toughness. The steel designated 301, although not designed as a TRIP steel, does undergo a martensitic transformation during plastic strain. The 0.2 per cent proof stress is higher than that for a 304 type steel and the considerable work hardening results in an ultimate tensile strength of about 1500 MPa. This high degree of work hardening gives this steel an

optimum dry abrasion resistance within the group of commercially available stainless steels previously tested (Allen, Ball and Protheroe, 1981 and 1982). Improved abrasion resistance may be obtained from a 301 type steel by modifying the work hardening characteristics. A reduction in the nickel content provides a higher work hardening rate (Pickering, 1976) and a decrease in cost. These adjustments would have to be made while maintaining the M_d temperature above ambient and the M_s temperature below ambient.

A range of high strength TRIP steels has been developed by various research and industrial laboratories during the past few years (Zackay and coworkers, 1967) and two typical TRIP steels are included in Table 3. The one is a relatively highly alloyed steel with good toughness while the other is less highly alloyed and therefore cheaper but it has poor ductility and toughness. The optimum TRIP steel for gold mining applications will probably have a composition between these two alloys. It is anticipated that the abrasion resistance of this type of steel will be excellent because of the high work hardening capacity which provides the required high strength and good toughness.

SUMMARY AND CONCLUSIONS

Research into wear processes in gold mines and into the requirements of alloys capable of resisting these processes has identified a need for general purpose, corrosion and abrasion resistant steels for the industry. An alloy development programme has been initiated to design and produce suitable steels.

The main conclusions drawn from the work to date are as follows:

- (i) A spectrum of wear processes occurs in mining machinery ranging from corrosion dominated processes to abrasion dominated processes which affect both the external and internal components of machines.
- (ii) There is no existing low cost alloy which can withstand the range of wear processes in the mines and hence there is a need for one or more general purpose, corrosion and abrasion resistant steels for the gold mining industry.
- (iii) A general purpose corrosion and abrasion resistant steel must have a hardness greater than 500 HV and a Charpy impact energy of about 35 joules at room temperature. It must also be resistant to general corrosion underground.
- (iv) The only two economically viable steel types which could possibly meet the specified requirements are (a) a corrosion resistant dual phase steel and (b) a corrosion resistant, TRIP steel.

ACKNOWLEDGEMENTS

The work described in this paper forms part of the research programme of the Materials Engineering Division of the Mining Technology Laboratory, Research Organization, Chamber of Mines of South Africa. Part of the work was carried out in collaboration with the Department of Metallurgy, University of Cape Town.

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Metallurgy of a 12% Chromium Steel

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ABSTRACT

The weldability of a 12% chromium duplex ferritic-martensitic steel, as well as the effects on mechanical properties of changes in composition and annealing treatment are briefly reviewed.

KEYWORDS

Duplex stainless steel, martensitic/ferritic structure, grain growth, austenitic stainless steel, filler materials, heat-affected zone embrittlement.

INTRODUCTION

Previous publications have considered the development of a 12% chromium corrosion resisting steel in South Africa (Melvill and co-workers, 1980; Ball and Hoffman, 1981). Parallel research elsewhere in the world has concentrated on steels for the ocean freight container market (Lefevre, Tricot and Castro, 1973; Abo and others 1978; Yoshioka and co-workers, 1981), catalytic convertors (Hartley, 1978) and bus and coach construction (Ekenrod and Kovach, 1980). Present research concentrates on optimising the ductility, toughness and corrosion resistance of duplex ferritic-martensitic stainless steels. The phase balance between ferrite and martensite, as well as the use of stabilising elements such as titanium are crucial to the development of optimum properties (Castro and de Cadenet, 1975; Wright and Wood, 1977).

TABLE 1 Composition and Properties of Duplex Ferritic - Martensitic 12% Cr Steel - 3CR12

C	N	Cr	Ni	Ti	Si	Mn
0.020	0.015	11.5	0.6	0.25	0.4	0.9
0.2% Proof Strength				(MPa)	310	
Ultimate Tensile Strength				(MPa)	530	
Elongation				(%)	24	
Hardness				(BHN)	185	
Impact Strength (20 °C, CVN, J/cm ²)					80	

COMPOSITION AND STRUCTURE

The critical balance between ferrite and austenite in the hot rolled structure of 3CR12 can be controlled using certain relationships (Kaltenhauser, 1971; Lefevre, Tricot and Castro, 1973) based on the ferrite or austenite forming tendencies of alloying elements. A high austenite content (low ferrite factor) in the steel ensures that a high martensite content is obtained in the final product. The M_s temperature for 3CR12 is of the order of 550 °C ensuring that no retained austenite occurs in the steel.

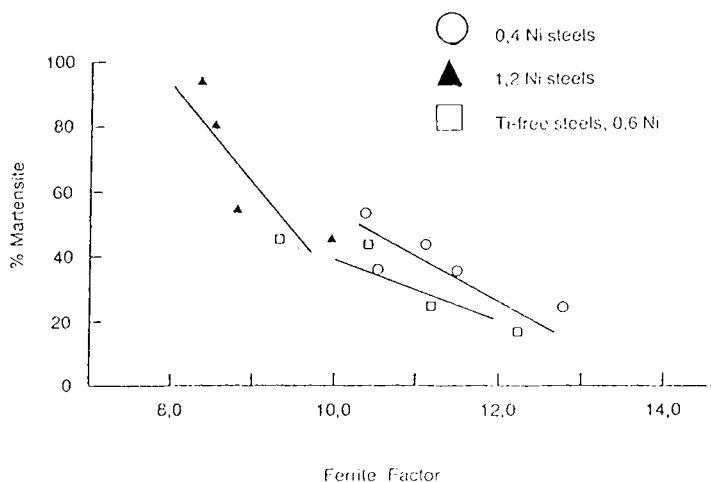


Fig. 1 Effect of ferrite factor on volume fraction of martensite in steels quenched from 1 000 °C.

The results of limited work on the effect of nickel on the phase diagram of 12% chromium steels containing up to 3.5% nickel are shown in Fig. 2.

The ferrite factor also establishes the temperature region at which duplex austenite-plus-ferrite occurs and as this affects the hot rolling characteristics of the steel, it is controlled to maintain a minimum of about 30% austenite at the finish rolling temperature. Low carbon martensite (high dislocation density) is the preferred structure, but since the partitioning of carbon to the austenite at high temperature occurs very rapidly, it is essential to use titanium to lower the soluble carbon content. (Ball and Hoffman, 1981).

The actual amount of titanium required has to be carefully controlled. Excess titanium in the steel leads to embrittlement by Fe_2Ti and other complex intermetallics. (Semchyshen, Bond and Dundas, 1971; Wright, 1971). On the other hand, insufficient titanium will not ensure the formation of low carbon martensite. During solidification and hot rolling, titanium-rich inclusions tend to segregate and problems known as blisters or stringers can occur in steels of high titanium content.

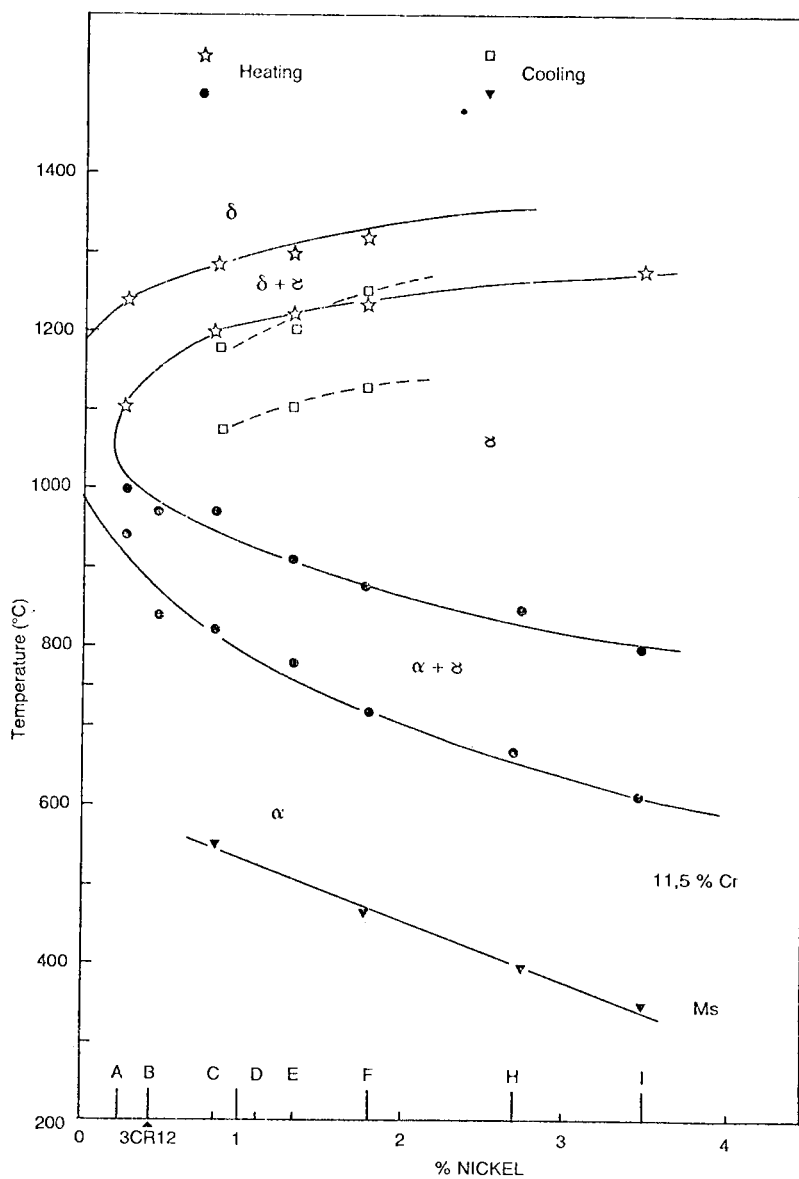


Fig. 2 Effect of Nickel on duplex ferrite/martensite 12% Cr Steel. Results for eight melts designated A-I are shown.

The role of sulphur in the steel is also important. Complex titanium sulphides and carbo-sulphides ($Ti_4C_2S_2$ and TiS_2) may form in the steel and reduce toughness drastically. A high manganese to sulphur ratio (as high as $Mn/S=200$) changes the morphology and type of sulphides and reduces their detrimental effect on mechanical properties. It is believed that rare earths would have a similar effect.

The banded hot rolled structure of ferrite and martensite necessitates annealing to achieve optimum and isotropic strength, ductility and toughness. Subcritical annealing (a high temperature tempering procedure) is used to achieve this softening. Titanium affects the response of the steel to annealing. High titanium contents cause grain growth at high annealing temperatures, while low titanium contents restrict the sub-critical annealing temperature by lowering the A_1 . Nickel retards tempering of the martensite and the time required for significant tempering can be excessive. The finishing temperature also affects mechanical properties as hot rolling in the duplex region with considerable work on the ferrite (soft) phase leads to good toughness as fine grained martensite-plus-ferrite forms on cooling (Ball and Protopapas, 1981).

Work on an unstabilised 3CR12-type steel in the United States has shown that cold work reduces toughness quite drastically (Vigor, 1980). The problem does not occur with 3CR12, as the low work-hardening rate (work-hardening exponent 0.15) and the very low total dissolved carbon content of 3CR12 prevent any significant embrittlement. Mechanical tests on 3CR12 often reveal tears or splits. These have been described previously (Mintz, 1980) and are due to intergranular decohesion, common to hot rolled duplex steels.

The hot strength of 3CR12 is acceptable for many applications at temperatures where mild and low alloy steels are subject to scaling, or have inadequate strength. Creep tests are incomplete but preliminary results show that designs using 3CR12 above 500 °C, must take creep properties into consideration. The embrittlement common to all ferritic stainless steels at 475 °C does not occur with 3CR12 (Nichol, Datta and Aggen, 1980).

CORROSION RESISTANCE

The corrosion resistance of 3CR12 has been tested in numerous applications involving dilute acid, base and salt solutions. The corrosion rate in many of these applications is low enough to consider use of the material as an alternative to coated mild steels.

The low chromium content of 3CR12 causes a protective film to form rather slowly on the surface. This can lead to rather high corrosion rates in very aggressive media. It is essential to passivate 3CR12 using dilute nitric acid solutions before service in all corrosive environments.

3CR12 is not subject to stress-corrosion cracking in chloride, nitrate or hydroxide solutions (Sandenbergh, 1980). Nevertheless in highly stressed situations in H_2S environments, stress-accelerated corrosion cracking does occur. While 3CR12 is welded with austenitic stainless steel electrodes, there is little likelihood of stress-corrosion cracking in the weld metal, as it usually contains about 5% ferrite (Gooch and Honeycomb, 1979).

WELDABILITY

The duplex nature of 3CR12 at high temperatures causes a considerable portion of the HAZ to transform to martensite during subsequent rapid cooling.

The formation of the second phase in the HAZ causes an effective reduction in the grain size. The volume fraction of martensite is directly responsible for changes in the DBTT. The martensite that forms is of low carbon content and is relatively tough (Decroix, 1979; Grobner, 1980).

Dissolution of titanium carbonitrides at high temperatures results in the entry of carbon and nitrogen into the austenite (very close to the fusion boundary) and in this region the martensite which forms is somewhat harder than elsewhere. The strength of the HAZ is considerably greater than that of the base material. A micro-hardness traverse across the HAZ does give a misleading picture and it is better to measure the hardness of individual phases for comparison purposes. Some grain coarsening does occur in the HAZ, particularly if the volume fraction of martensite remains small. The gamma loop shows some hysteresis on heating, and coarse grain austenite transforms to martensite on cooling. The overriding effect on mechanical properties due to the weld thermal cycle is the formation of martensite (Thomas and Apps, 1980). The morphology of martensite is both inter- and intragranular. It is likely that the intragranular martensite is of relatively high carbon content, because of high austenitising temperature. Intergranular martensite does show greater toughness and a tough grain boundary second phase has a beneficial effect on mechanical properties (Castro and de Cadenet, 1975).

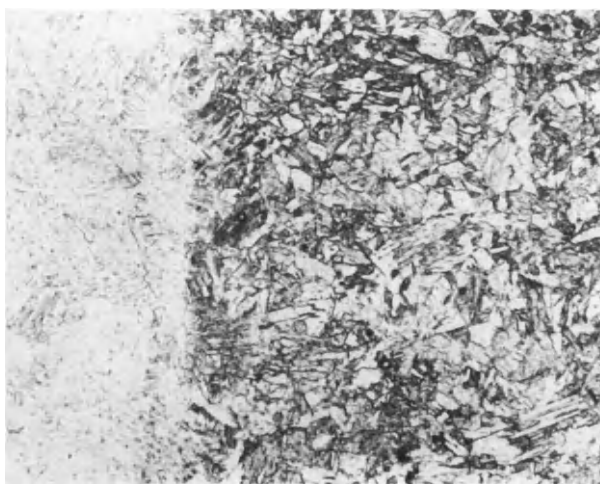


Fig. 3 Heat-affected zone in 3CR12, showing fine-grained duplex ferrite-plus-martensite. (Vilella's Reagent) (x350)

In the high temperature HAZ, carbonitride dissolution is followed by reprecipitation of much finer titanium carbonitrides with the austenite and subsequent martensite. This may contribute to increased martensite hardness, but the overriding effect is due to solid solution hardening by nickel.

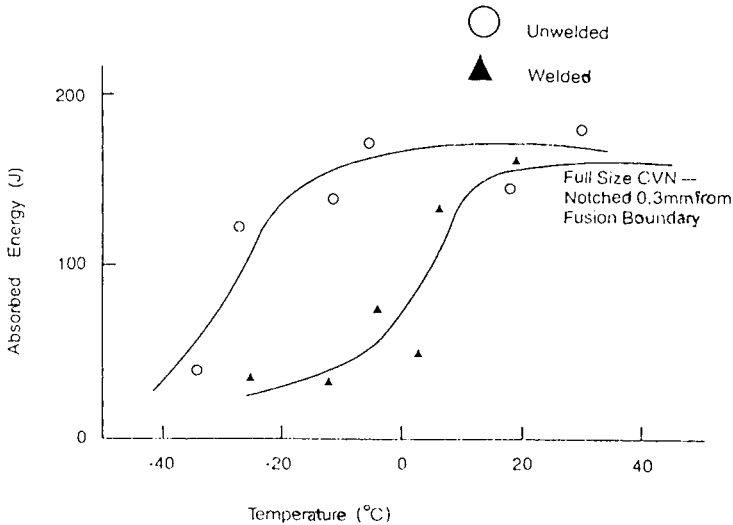


Fig. 4 DBTT of 3CR12 tested after welding.

The loss in toughness in the high temperature HAZ is limited to an increase in the DBTT of about 15 - 40 °C. The actual increase is determined by the heat input and the cooling rate during welding, which are affected by welding process and procedure. The corrosion resistance of the HAZ is reduced, as galvanic action on a two phase structure causes accelerated attack on the less noble martensite. This loss of corrosion resistance is serious in highly oxidising conditions (Thomas and Apps, 1980) but it is of little consequence in most practical applications.

A number of previous publications have discussed welding consumables for 3CR12 in some detail (Martin and Hoffman, 1981; Davey, 1981). The manufacturer's recommendation is that 3CR12 be welded with AWS E309 electrodes. Other austenitic weld materials may also be used to weld 3CR12. The effect of filler metal composition and dilution can be gauged by studying the Schaeffler-Delong diagram. Research is continuing on the development of a matching martensitic-ferritic filler material (Pagani, 1982).

3CR12 can be welded to mild steel and low alloy steels, using austenitic stainless steels filler materials. Table 2 gives the results of the mechanical tests on a mild steel/3CR12 weldment.

TABLE 2 Mechanical Properties of Weld Joint* 3CR12/BS 4360:43A

0.2% Proof Strength	(MPa)	247
Ultimate Tensile Strength	(MPa)	491
Elongation	(%)	25
Maximum HAZ Hardness	(BHN)	208
Location of Failure		Mild steel, Parent Metal

*6mm plate, MMA welded with AWS E309MoL-16 electrode.

CONCLUSIONS

A low-cost corrosion resisting steel 3CR12 has been developed for use in applications where mild and constructional steels are inappropriate. The chemical, structural and mechanical properties of this steel have allowed its widespread substitution for mild steel in corrosive and wet abrasive environments (Thomas, 1981). The metallurgy of this low chromium steel presents users with the opportunity of matching end uses to structure and properties without complex heat treatment.

ACKNOWLEDGEMENT

The authors wish to thank the board of Middelburg Steel and Alloys for permission to publish this paper.

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Alloying Effects of Reactive Elements in Ferritic Stainless Steels

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ABSTRACT

Niobium and tantalum additions through what appears to be precipitation hardening by Laves phases can improve creep life in ferritic stainless steels. Amounts over and above of those required for stabilization are necessary to obtain this effect. The stabilization, however, can be totally or partially accomplished with a more reactive element such as titanium, leaving the entire niobium or tantalum content available for precipitation hardening. Higher than normal annealing temperatures are required to dissolve the Laves phase for precipitation hardening. Other reactive elements investigated produced no strong precipitation hardening effect.

Titanium stabilization in ferritic stainless steels has been found to adversely affect wettability when copper brazing. Niobium stabilization has little effect on braze wetting and thus niobium-stabilized stainless steels with restricted titanium content can be easily brazed.

A special heat treatment has been developed to cause Al_2O_3 whisker-like filaments to form perpendicular to the metal surface of FeCrAlloy for use as catalyst substrates. Use of mischmetal additions to replace yttrium also provides scale adherence and is amenable to the whisker growing treatment.

KEYWORDS

Ferritic stainless steels; Laves phase; titanium; niobium; tantalum; zirconium; brazing; catalyst substrates; rare earths; yttrium.

INTRODUCTION

Implementation within the past decade of melting technologies such as Argon Oxygen Decarburization and Vacuum Oxygen Decarburization have made common a previously unavailable low level of interstitial elements in steel compositions. Among the chief beneficiaries of this technology have been the ferritic stainless steels where control of interstitial elements has provided an

ability to increase chromium content while retaining acceptable toughness at ambient temperatures. These high chromium ferritic stainless steels now represent some of the most corrosion resistant materials available and are particularly suited for service in oxidizing corrosion media.

EXTENDED CREEP LIFE

Ferritic stainless steels, because they have a lower coefficient of thermal expansion than austenitic stainless steels, are also candidate materials for high temperature low stress applications such as heat exchangers and automotive exhaust parts including catalytic converters. In many of these applications the elevated temperature strength required is little more than that necessary for the material to support its own weight or to withstand stresses imposed by thermal expansion acting upon the component design.

The sensitization of ferritic stainless steels by precipitation of grain boundary chromium carbides causing a chromium depletion in the adjacent areas has long been recognized and the use of elements highly reactive with carbon to remove carbon from the alloy matrix as stable carbides is well known. Those elements with a great affinity for carbon, however, also tend to be strongly attracted to other interstitial elements such as nitrogen and therefore many specifications for stabilization elements require a minimum content of the stabilizing element which is some multiple of the combined carbon and nitrogen contents. Decreasing the total interstitial element content thus lowers the requirement for reactive stabilizing element content to be withdrawn from the alloy matrix by combination and provides an opportunity to use small amounts of these stabilizing, reactive elements as matrix alloy additions.

Titanium and niobium, for a number of reasons including cost and carbon affinity, are the principal elements utilized for stabilization. A number of other reactive elements, however, which have a stabilization effect to a greater or lesser degree can also be considered for alloy additions when interstitial contents are lowered. Among these are tantalum, zirconium, hafnium, and vanadium.

As a method of evaluating the effects of stabilizing elements in alloying the ferritic stainless steels, creep tests at 871°C were loaded to 8.274 MPa until elongation greater than 2% was obtained. Figure 1 shows the curve form obtained. In the usual case, the three stages of creep were almost indiscernible. First stage creep is essentially absent while the second and third stages appear to blend together in a smooth transition as the curve changes from horizontal to near vertical. For convenience in comparing a large number of alloys and treatments, the time in hours to 1% and 2% creep elongation provide convenient criteria.

Experimental alloys were melted as 23 kg vacuum induction furnace heats tapped into three 7.7 kg ingots with an addition of the element under investigation made between ingot tappings. Ingots were hot rolled from 1121°C to 2.5 cm x 10 cm sheet bar, conditioned and hot rolled from 1232°C to 0.25 cm x 10 cm band and water quenched. This hot rolled band was conditioned and cold rolled to 0.102 cm x 10 cm strip without annealing.

To simulate continuous mill annealing of the cold rolled strip, tensile and creep sample blanks were sheared and then drilled to accommodate hanging by wire from an austenitic stainless steel bar. This bar was placed atop a U-shaped piece of austenitic stainless plate in the annealing furnace allow-

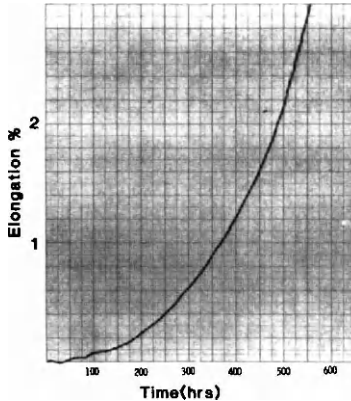


Fig. 1. Curve form generated in creep testing of ferritic stainless steels at low stress levels (6.89-8.29 MPa) and higher temperatures (732-871°C).

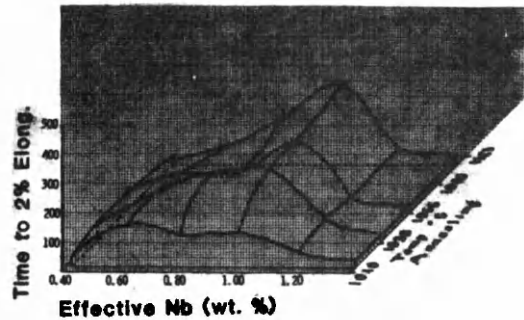


Fig. 2. Response surface of creep life to 2% elongation at 871°C-8.274 MPa in 16% chromium stainless steels as a function of effective niobium content and annealing temperature.

ing the separated specimens to be suspended between the arms of the U. One dummy sample in each lot was fitted with a thermocouple attached to a high speed recorder, allowing monitoring of the temperature profile of the specimens. A constant furnace time of 3 minutes was used for each specimen lot and generally the specimens reached furnace temperature for a period of 45 seconds to one minute.

As a frame of reference Table 1 shows creep life in hours to 1% and 2% elongation obtained with material from two commercial heats of 11.5% chromium stainless steels with titanium overstabilization (i.e., titanium content greater than that theoretically necessary to consume all of the carbon and nitrogen as simple carbides or nitrides). Because these stainless steels are essentially alloys of chromium and iron, elements which have similar atomic weights, there will be little variation in average atomic weight of the alloys over the range of chromium contents studied. It therefore is

TABLE 1 12% Chromium Alloys With Titanium Overstabilization

			Hours to Creep at 871°C-8.274 MPa							
Alloy	Effective	Effective	Annealing Temperature (°C)							
	Ti Content	Atom Fraction	1010		1038		1066		1093	
	Wt. (%)	Ti	1%	2%	1%	2%	1%	2%	1%	2%
A	0.19	0.40	3	5	2	5	3	5	5	12
B	0.52	1.08	25	41	18	30	20	34	10	20

Compositions

Alloy	C	N	Mn	P	S	Si	Cr	Ni	Al	Mo	Cu	Ti	Nb	Ta
A	0.026	0.016	0.37	0.027	0.011	0.42	11.54	0.21	0.020	0.073	0.14	0.35	0.01	NA
B	0.015	0.012	0.39	0.015	0.004	0.43	11.62	0.15	0.026	0.024	0.096	0.62	0.01	NA

convenient to compare the effects of different stabilizing elements by expressing the degree of overstabilization as an atom fraction by dividing the weight percent of the element over and above that required for theoretical stabilization by one hundredth of the atomic weight. Table I shows a small increase in creep life with increased titanium overstabilization but no identifiable effect of annealing temperature.

Table 2 shows creep life to 1% and 2% elongation obtained with 11% chromium alloys having varying degrees of tantalum overstabilization. Here a marked effect of tantalum on creep life can be seen with an indication of an optimum in the vicinity of 0.75 effective atom fraction. An effect of annealing temperature can also be seen but is less well defined. Several samples fractured at relatively long times before reaching 1% or 2% elongation. It should be noted that essentially all of the stabilization in these alloys was provided by the tantalum thus increasing the alloy cost.

TABLE 2 11% Chromium Alloys With Tantalum Stabilization and Low Titanium Content

Alloy	Effective Ta Content (Wt %)	Effective Atom Fraction Ta+Nb	Hours to Creep at 871°C-8.274 MPa							
			Annealing Temperature (°C)							
			1010		1038		1066		1093	
			1%	2%	1%	2%	1%	2%	1%	2%
C	0.010	0.0055	5	8	5	8	5	8	5	8
D	0.255	0.14	245	260	†237		245	270	590	660
E	1.364	0.748	1495	†1542	†5050		†984		1170	1425
F	1.366	0.755	423	455	1400	1690	--	2020*	2150	2275
G	2.24	1.17	368	501	315	530	412	546	702	950
H	3.35	1.85	640(?)	920(?)	92	161	325	467	515	657

† = Prior Fracture Hours; * Extrapolated Value--Transducer Sticking.

Compositions														
Al- loy	C	N	Mn	P	S	Si	Cr	Ni	Al	Mo	Cu	Ti	Nb	Ta
C	0.016	0.0175	0.37	0.042	0.003	0.38	10.98	0.05	0.017	0.047	0.066	0.004	<0.01	0.46
D	0.0165	0.0165	0.37	0.040	0.003	0.39	10.98	0.05	0.011	0.045	0.067	0.004	<0.01	0.70
E	0.017	0.016	0.34	0.037	0.002	0.40	10.98	0.05	0.008	0.045	0.067	0.004	<0.01	1.80
F	0.0205	0.016	0.34	0.031	0.005	0.38	10.94	0.21	0.001	0.043	0.038	0.001	0.006	1.87
G	0.0195	0.015	0.32	0.032	0.005	0.39	10.83	0.22	0.001	0.043	0.054	0.001	0.007	2.60
H	0.020	0.0135	0.31	0.032	0.004	0.40	10.70	0.22	0.001	0.043	0.073	0.001	0.008	3.81

Table 3 presents creep life to 1% and 2% elongation values for a series of 16% chromium steels with titanium content high enough to provide theoretical stabilization and with tantalum additions ranging from about 0.1 to 1.4 effective atom fraction. Once again a similar strong maximum in the effect of tantalum content on creep life can be seen and a superimposed effect of annealing temperature is evident.

Unfortunately, tantalum is a costly alloying element, and although rather large increases in creep life are produced by tantalum additions the cost effective applications available to utilize such properties are severely limited.

TABLE 3 16% Chromium Alloys With Tantalum Additions and Titanium Stabilization

			Hours to Creep at 871°C - 8.274 MPa							
Alloy	Effective Ta Content (Wt %)	Effective Atom Fraction Ta+Nb	Annealing Temperature (°C)							
			1010		1038		1066		1093	
			1%	2%	1%	2%	1%	2%	1%	2%
I	0.16	0.099	22	39	55	94	26	37	52	73
J	0.34	0.199	93	129	100	138	145	263	20	36
K	0.57	0.327	258	333	174	265	135	277	95	151
L	0.90	0.508	468	1050	247	333	575	1110	1465	2450
M	1.68	0.939	485	585	697	997	790	1105	1757	2585
N	2.56	1.425	258	333	174	265	135	277	95	151

Compositions

Alloy	C	N	Mn	P	S	Si	Cr	Ni	Al	Mo	Cu	Ti	Nb	Ta
I	0.025	0.010	0.39	0.033	0.004	0.35	16.12	0.25	0.025	0.050	<.001	0.43	0.010	0.16
J	0.024	0.010	0.39	0.032	0.004	0.35	16.16	0.25	0.025	0.050	<.001	0.43	0.010	0.34
K	0.024	0.010	0.39	0.032	0.004	0.35	16.08	0.25	0.025	0.050	0.004	0.43	0.011	0.57
L	0.023	0.014	0.47	0.034	0.004	0.42	15.64	0.29	0.020	0.043	0.015	0.25	0.010	0.90
M	0.024	0.017	0.47	0.033	0.004	0.44	15.09	0.29	0.018	0.043	0.029	0.18	0.010	1.68
N	0.024	0.018	0.47	0.024	0.004	0.46	15.10	0.23	0.010	0.037	0.072	0.16	0.010	2.56

Table 4 presents creep life to 1% and 2% elongation values for a series of 16% chromium steels with sufficient titanium content to provide theoretical stabilization and with niobium additions ranging from about 0.5 to 1.5 effective atom fraction. A lower degree of improvement in creep life is evident

TABLE 4 16% Chromium Alloys With Niobium Additions and Titanium Stabilization

			Hours to Creep at 871°C - 8.274 MPa							
Alloy	Effective Nb Content (Wt %)	Effective Atom Fraction Nb	Annealing Temperature (°C)							
			1010		1038		1066		1093	
			1%	2%	1%	2%	1%	2%	1%	2%
O	0.42	0.45	33	43	42	60	60	80	13	25
P	0.61	0.66	148	195	155	208	130	172	65	89
Q	0.80	0.86	107	123	222	274	130	153	158	231
R	1.00	1.08	113	140	230	279	240	298	272	325
S	1.20	1.29	51	69	69	77	56	75	56	78
T	1.40	1.51	23	33	21	29	28	40	36	42

Compositions

Alloy	C	N	Mn	P	S	Si	Cr	Ni	Al	Mo	Cu	Ti	Nb
O	0.028	0.011	0.39	0.028	0.003	0.41	16.19	0.27	0.029	0.031	0.020	0.36	0.42
P	0.029	0.015	0.39	0.028	0.003	0.39	16.27	0.27	0.025	0.031	0.020	0.32	0.61
Q	0.030	0.015	0.38	0.027	0.003	0.39	16.16	0.27	0.026	0.031	0.020	0.30	0.80
R	0.026	0.011	0.37	0.030	0.003	0.38	16.11	0.26	0.032	0.041	0.020	0.36	1.00
S	0.027	0.011	0.37	0.030	0.003	0.38	16.03	0.26	0.024	0.041	0.020	0.35	1.20
T	0.028	0.011	0.37	0.030	0.003	0.38	16.01	0.26	0.022	0.040	0.020	0.33	1.40

in these data and the superimposed effect of annealing temperature can again be seen. Figure 2 shows a graphic representation of the response surface generated by the time to 2% creep elongation values when plotted against effective niobium content (wt %) and annealing temperature. Although lower creep life values are obtained, the combination of lower cost and lower atomic weight provides greater cost effectiveness for niobium as an alloying element than tantalum.

Table 5 presents creep life data for 16% chromium steels with sufficient titanium content to provide theoretical stabilization and with zirconium additions ranging from about 0.5 to 1.2 effective atom fraction. Very little effect is noted from either zirconium content or annealing temperature. A similar study with vanadium additions again showed little effect.

TABLE 5 16% Chromium Alloys With Zirconium Additions and Titanium Stabilization

Hours to Creep at 871°C - 8.274 MPa										
Alloy	Effective Zr Content (Wt %)	Effective Atom Fraction Zr	Annealing Temperature (°C)							
			1010		1038		1066		1093	
			1%	2%	1%	2%	1%	2%	1%	2%
U	0.49	0.537	6	10	7	12	8	15	8	15
V	0.78	0.855	5	12	5	12	5	12	10	18
W	0.97	1.06	11	35	7	16	10	25	15	34
X	1.10	1.21	13	30	10	23	10	20	47	105

Compositions

Alloy	C	N	Mn	P	S	Si	Cr	Ni	Al	Mo	Cu	Ti	Zr
U	0.025	0.014	0.35	0.029	0.0057	0.38	16.09	0.23	0.038	0.042	<0.001	0.22	0.49
V	0.027	0.012	0.40	0.030	0.006	0.40	16.05	0.27	0.26	0.073	0.001	0.34	0.78
W	0.027	0.060	0.33	0.026	0.0058	0.45	15.84	0.23	0.034	0.042	<0.001	0.29	1.01
X	0.027	0.011	0.40	0.030	0.006	0.40	15.93	0.28	0.27	0.095	0.002	0.33	1.10

Whittenberger, Oldrieve and Blankenship (1978) have shown that 16% chromium, 2% aluminum ferritic stainless steels with tantalum additions of 0.45% and 1.25% exhibited improved 800°C stress rupture and creep properties with increasing tantalum when compared to a similar composition without the tantalum addition. The same properties at 1000°C, however, were not improved by tantalum addition. All three materials were annealed at 997°C and all three of these alloys contained sufficient titanium to accomplish stabilization.

Takeyama (1970) and co-workers found age hardening in Fe-Ta and Fe-Nb system alloys with small amounts of tantalum or niobium. The hardening resulted from precipitation of Fe₂Ta or Fe₂Nb (MgZn₂ type) Laves phases when aging at temperatures from 600°C to 700°C after quenching from 1300°C.

Speich (1962) evaluated age hardening from precipitation of Laves phases from iron-niobium and iron-titanium solid solutions. Solubility of titanium in α -iron being much higher than that of niobium, the titanium content necessary for effective age hardening is so great that the alloys would be difficult to melt commercially.

Dunning (1980) also shows Laves phase precipitation hardening in Fe-Ti, Fe-Mo and Fe-W alloys to require large amounts of the secondary element,

thus leading to practical melting and fabrication difficulties. Fe-Ta, Fe-Nb and Fe-Hf alloys, however, require only smaller secondary element additions to produce precipitation hardening.

Pearson (1967) shows no simple iron-vanadium Laves phase to form and the rather questionable existence of an iron-zirconium Laves phase which might not produce precipitation hardening as indicated in the phase diagram presented by Shunk (1969).

It can safely be concluded that the improved creep properties demonstrated result from Laves phase precipitation at the testing temperature. The annealing temperature effect noted appears to be that of the temperature necessary to produce near complete solution of the Laves phase. A practical limit on this solution temperature is imposed by very rapid grain growth which takes place at solution temperatures near 1100°C and which adversely affects cold formability of the steel products.

BRAZING WETTABILITY

Fabrication of heat exchangers and exhaust system components may often involve brazing. One of the more common and least expensive brazing filler metals is oxygen-free copper. Attempts to furnace braze components made from the ferritic stainless steels with copper have revealed problems which are attributed to poor wettability. One solution involving copper plating of the stainless steel has major cost disadvantages. Using a cold wall vacuum furnace and a 1.27 cm thick plate fixture to provide temperature uniformity, 3.8 cm dia. x 0.51 mm thick discs of various ferritic stainless steels were tested with a small piece of 2.57 mm dia. oxygen-free copper wire placed on end at their center. After exposure to a brazing cycle with a maximum temperature of 1121°C, wettability was evaluated by measuring the diameter(d) and height(h) of the drop obtained and calculating a parameter d^2/h . Values of d^2/h were found to be largely unaffected by niobium or tantalum content when used as stabilizing elements. Values of d^2/h , however, decreased with increasing titanium content when this element was added for stabilization. An essentially non-wettable surface oxide film develops with titanium contents of 0.12% or above and lower titanium contents of about 0.01% are required for desirable wettability in these ferritic stainless steels.

CATALYST SUBSTRATES

Automotive exhaust system emissions in the U.S. are presently controlled through the use of catalytic converters in which the noble metal catalysts are washed onto the surface of ceramic substrates. Development of a metallic substrate for the catalysts presents important advantages in fabricability, vibration and impact tolerance, and weight savings. Using an alloy commonly known as Fecralloy (16%, Cr 5% Al, 0.3Y) which produces an adherent alumina scale, Chapman (1982) and others (1981) at General Motors Corp. have developed treatments to cause the alumina surface oxide to form as thin whiskers growing roughly perpendicular to the metal surface. Figure 3 shows an example of the whisker configuration obtained.

Unfortunately, yttrium is extremely expensive, has a limited production and because of its reactivity presents grave recovery problems in melting. In fact, no method is presently available to recover yttrium values in remelting of scrap. Consequently, development of less expensive alloys with adher-

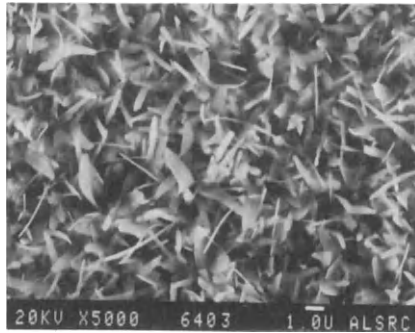


Fig. 3. Al_2O_3 whiskers grown on the surface of Fe-Cr-Al-rare earth alloy.

ent whisker growing capabilities is desirable. Alloys meeting this requirement were developed using the described whisker growing techniques in combination with a resistance heated oxidation test modified from ASTM specification B78-59T only in that a strip sample 0.051 mm x 4.76 mm in section was used instead of a round wire and a test temperature of 1260°C was applied. Samples were heated to temperature for two minutes and cooled to room temperature for two minutes alternately until failure.

It was found that alloys with from 12-23% chromium, 3-8% aluminum and small additions of cerium and/or lanthanum would grow the desired adherent Al_2O_3 whisker configuration and exhibited useful oxidation resistance. A useful melting addition for the rare earths is the relatively inexpensive mixture known as mischmetal and an optimum dissolved total rare earth metal content appears to be about 0.02% by weight.

Only a few of the possible property effects of the reactive elements as alloy additions have been explored and further developments in this field may be expected from the interactions of melting and alloy technologies.

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The Influence of Metallurgical Aspects on the Pitting Corrosion Behaviour of High Alloy Stainless Steels

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ABSTRACT

The resistance of high alloyed stainless steels to pitting corrosion is determined by the electrochemical test method. The pitting corrosion resistance decreases with increasing temperature, though differently for the various steel types. The linear correlation between the Cr and Mo content and the pitting potential according to the so-called pitting index factor (Wirksumme) $\% \text{Cr} + 3.3 \times \% \text{Mo}$ describes the results in the range of lower pitting index values as expected. At higher values and higher electrolyte temperatures deviations occur, but the increase of the pitting potential is still monotonic. Additionally, the effect of heat treatment and welding on the pitting resistance is determined. With increasing heterogeneity the pitting potential is shifted to less noble potentials. Thus, the weld seam is preferentially attacked because of its solidification structure.

KEYWORDS

Pitting Corrosion, Stainless Steels, Electrochemical Test Method

INTRODUCTION

Modern chemical and thermal processes call for ever increasing resistance to corrosion of materials to obtain high space-time yields under extreme reaction conditions. In many cases, traditional stainless steels have reached the limit of their application so that in this sector, a further development of the steels towards higher resistance to corrosion is aimed at (Horn, Kuron and Gräfen, 1977a, b). The susceptibility to corrosion of stainless steels lies mainly in the field of localized corrosion attack, e.g. pitting corrosion, crevice corrosion, stress corrosion cracking. This localized corrosion attack is primarily caused by chloride ions which are present in many processes as almost all chlorides are easily soluble in water. Typical examples in this connection are the cooling and waste water sections of chemical plants as well as seawater technology. Also with media where dew point conditions may occur in combination with chloride ions, localized corrosion may easily arise. As any material used in the chemical industry must be weldable, it is necessary to determine the corrosion properties of the structural zones subjected to heat influences, too.

Within the framework of this report, the pitting corrosion resistance of the following steels will be discussed:

TABLE 1 Chemical composition of tested material

VDM- Designation	German Materials No.	Other Standards	C	Cr	Ni	Mo	Mn	S	P	Other
Cronifer 1810Ti	1.4571	AISI 316Ti	0.045	16.7	10.7	2.12	1.55	0.012	0.022	0.41Ti
Cronifer 1713LCN	1.4439	AISI 317	0.018	17.4	13.3	4.28	1.53	0.011	0.024	0.167N
Cronifer 1925LC	1.4539	UNS 08904	0.012	20.7	24.8	4.72	1.34	0.004	0.022	1.43Cu
Cronifer 1925hMo	1.4529	Al 6x	0.015	20.6	24.9	5.90	1.41	0.010	0.018	1.67Cu
Cronifer 2328	1.4503	-	0.018	22.7	26.6	2.71	0.74	0.008	0.023	2.70Cu
Cronifer 2205LCN	1.4462	AF 2205	0.013	22.3	5.50	2.84	1.80	0.015	0.024	0.12 N

All stainless steels listed above form a natural oxide film which passivates these alloys. This oxide film is a protective layer which may be formed in various ways, e.g. rolling skin, oxidizing action of the pickling agent, electrochemical polarization (Uhlig 1979). The passive layer cannot be regarded as completely homogeneous since the configuration of the microstructure influences the properties of the oxide film. Structural heterogeneities such as grain boundaries, precipitations and inclusions change the diffusion conditions on the surface and are reflected in the properties of the passive layer. On chloride ion attack, it is particularly at these weakened points that destruction of the passive layer and thus localized corrosion attack is favoured.

This type of corrosion attack depends on several parameters (Horn, Kuron and Gräfen, 1977a.)

properties of the electrolyte

concentration of the chloride ions
concentration of impurities
Redox potential
(concentration of oxidizing media,
e.g. O₂)
temperature
flow velocity

material properties

alloy composition
surface condition
cold deformation
homogeneity of the microstructure
(annealing)

The so-called pitting corrosion potential is a measure of localized corrosion. This electrochemical potential is determined via potential-current density curves. Following a change in potential towards the more noble potentials in the passive range of the potential-current density curves, there will be a premature steep rise in current density if pitting corrosion is in evidence, the current density thus being a parameter for metal dissolution.

DESCRIPTION

For experimental purposes, the pitting corrosion potential is normally measured using either the potentiodynamic method where the potential is shifted continuously and the current is recorded or the potentiostatic method where measurements are made point by point. In both cases the current is recorded as a function of potential. A 0.5 n NaCl solution ($\approx$ 3% solution) is used as

an electrolyte. The concentration of its impurities (oxygen influences are eliminated by scavenging with nitrogen) remain constant as well as the surface finish of the samples. Thus, the only variables are the temperature and material analyses and/or the microstructure.

For the high alloy stainless steels, listed in Table 1, the pitting corrosion potential was measured both by the potentiostatic and the potentiodynamic method. These measurements showed that the pitting corrosion potentials determined by the respective methods matched each other well. Moreover, additional influences of the microstructure on pitting corrosion resistance due to heat treatment, e.g. sensitizing and solution annealing as well as welding, were measured.

TEST RESULTS

The characteristic shape of the potential-current density curves is shown in Fig. 1 whereas Fig. 2 shows a summary of the results for all steels tested in the as-received condition. The different shape of the pitting corrosion potential curves as a function of temperature are indicative of different properties with regard to pitting corrosion resistance. Those materials whose pitting corrosion potential lies above the curve for the Redox potential of the electrolyte are considered as resistant to pitting corrosion.

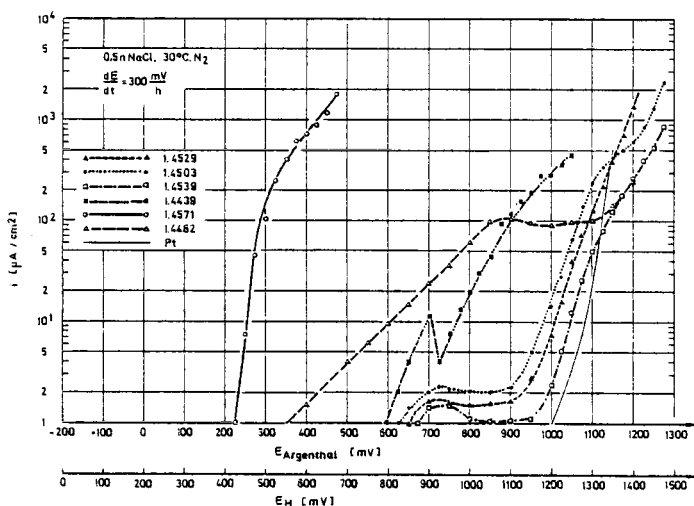


Fig. 1: Current-density potential curves of the different stainless steels at 30°C

The pitting corrosion properties of heat-treated sheet metal were investigated. Two stainless steels, 1.4571 and 1.4539, were used. Fig. 3a-d shows the microstructures of 1.4571 in the as-received condition, after solution annealing and after sensitizing (650°C, 2 h) as well as the heat-affected zone (HAZ) of the weld (matching filler metal). In the as-received condition, individual ferrite lines as well as some precipitations at the grain boundaries - probably carbides - can be seen (Fig. 3a) whereas these structural features are no longer found after solution annealing (Fig. 3b), i.e.

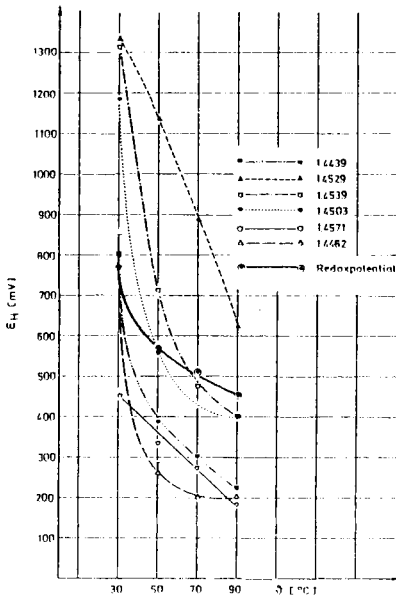


Fig. 2: Pitting potential as a function of temperature

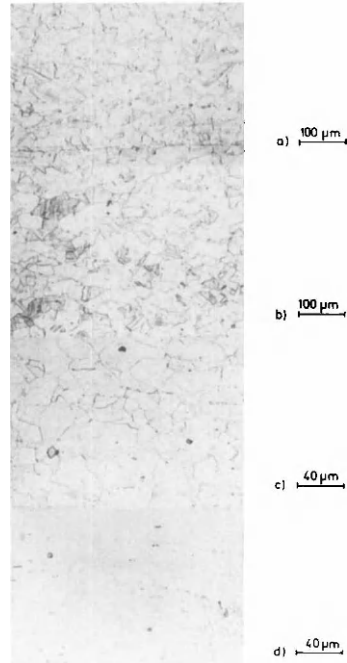


Fig. 3: Microstructure of stainless steel 1.4571 (SS316Ti)
 a) as-received c) sensitized
 b) solution annealed d) weld and HAZ

the structure is almost homogeneous. In the sensitized condition (650°C, 2h) heavy carbide precipitations are found at the grain boundaries (Fig. 3c). The welded specimen exhibits an austenitic-ferritic weld structure. There are only few grain boundary precipitations in the heat-affected zone (Fig. 3d). The microstructure of 1.4539 (Fig. 6) does not exhibit any precipitations at the grain boundaries in the as-received condition (Fig. 6a). Similar observations were made even after sensitizing annealing (Fig. 6b). The weld shows a typical dendritic structure which is purely austenitic. The grain boundaries of the base metal are free from precipitations. The results of the corresponding electrochemical measurements are shown in Fig. 4 and 5.

DISCUSSION OF RESULTS

As a general rule, the pitting corrosion potential of the individual high alloy stainless steels decreases with increasing temperature, as Fig. 2 substantiates. This can be explained by the increasing adsorption capacity and the accelerated reaction. At elevated temperatures, the pitting corrosion potentials of most of the materials examined remain below the Redox potential curve of the electrolyte and are therefore considered as only partially resistant to pitting corrosion (e.g. 1.4503, 1.4539) or as non-resistant (e.g.

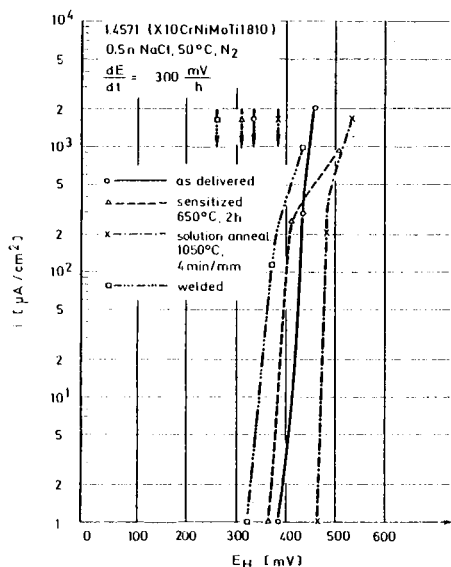


Fig. 4: Potentiodynamic and potentiostatic pitting potentials as a function of treatment of 1.4571(SS316Ti) at 50°C

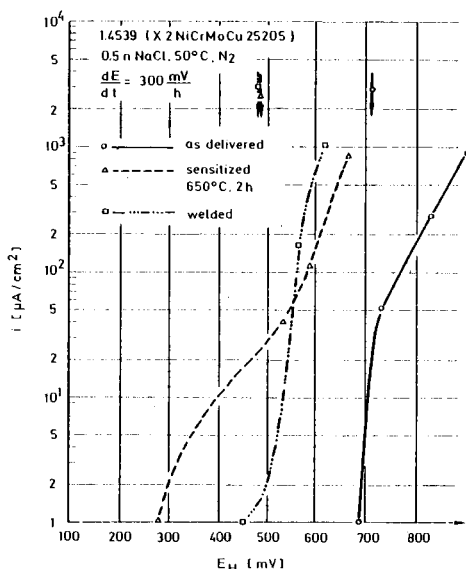


Fig. 5: Potentiodynamic and potentiostatic pitting potentials as a function of treatment of 1.4539 at 50°C

1.4571, 1.4462) under the specified test conditions. On the other hand, the resistance of high-molybdenum stainless steel 1.4539 lies above this limiting curve so that this type of steel is resistant under the specified test conditions. In this connection, the influence of the microstructure has, however, to be taken into consideration since precipitations and inclusions will considerably decrease the pitting corrosion potential.

In the publication of Lorenz and Medawar (1969), steels with different chromium and molybdenum contents have been examined for pitting corrosion resistance. These authors have introduced the term pitting index (Wirksumme) in the discussion of pitting corrosion of steel:

$$\text{pitting index (Wirksumme)} = \% \text{ chromium} + 3.3 \times \% \text{ molybdenum}$$

If the pitting corrosion potentials from Fig. 2 are plotted against the pitting index, the following curves are obtained for the individual temperatures (Fig. 7). At lower values of the pitting index a linear correlation can be found for the different temperatures, especially for 50°C. For higher chromium and molybdenum content a deviation is observed, however, the curves are still monotonic increasing. Whether the pitting index-formula which was introduced by Lorenz and Medawar (1969) for more or less standard stainless steels is also valid for the very highly alloyed stainless steels remains to be clarified by further experiments. According to Fig. 7 a stainless steel can be considered pitting resistant when its pitting potential lies above the corresponding Redox potential. From this relationship, certain criteria for material selection can be obtained. At given concentrations and temperature, a material with a specific pitting index is required.

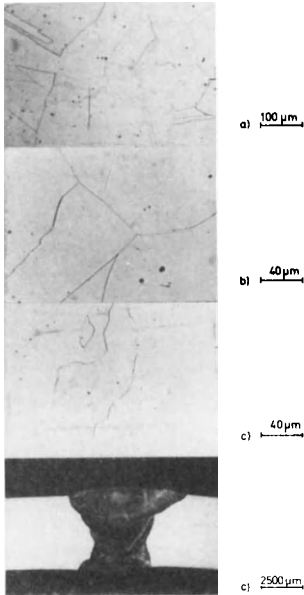


Fig. 6: Micrographic structure of stainless steel 1.4539

- a) as-received c) weld and HAZ
b) sensitized d) weld
650°C/2h

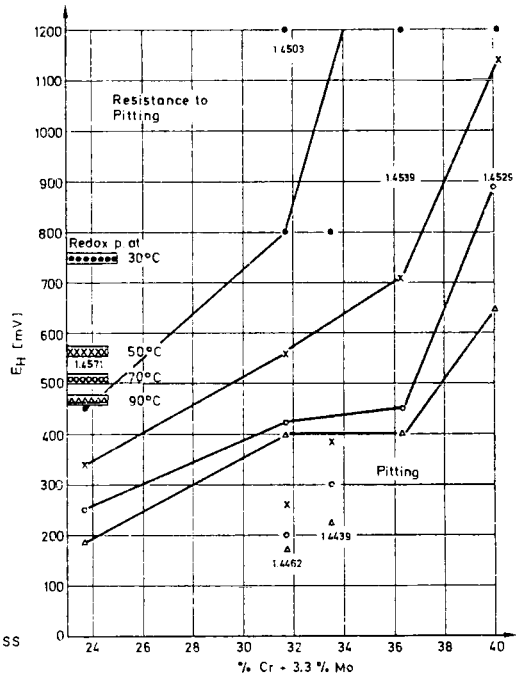


Fig. 7: Pitting potential as a function of the pitting index (Wirksumme) for different temperatures

The order of the pitting corrosion potentials after the different heat treatments of both tested alloys 1.4571 and 1.4539 (Fig. 4, 5) shows that the pitting corrosion potential becomes less noble, i.e. corrosion resistance decreases, as the heterogeneous constituents of the microstructure increase. Obviously, precipitations and phase boundaries favour local corrosion attack.

Concerning the pitting corrosion behaviour of welded material a remarkable difference in the E-i-curves is observed (Fig. 4, 5). Although a sufficiently alloyed matching filler metal has been chosen in both cases, the defects in the passive layer caused by the inhomogeneities - ferrite in 1.4571 and microsegregations in 1.4539 - make the weld more reactive because of the adverse effect on the oxide film and thus facilitates localized corrosion. In practice, however, the influence of the surface effect which has been eliminated here, has also to be taken into account since the susceptibility to pitting corrosion increases with increasing surface roughness.

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Properties and Applications of a Highly Alloyed Ferritic Stainless Steel

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ABSTRACT

"Superferrite" (28% Cr-4% Ni-2.5% Mo-Nb) is a newly developed ferritic stainless steel with outstanding corrosion resistance especially in hot chloride-containing media. This advanced stainless steel grade is intended for severely corrosive applications, e.g. in sea water desalination, cooling units for coastal power plants, phosphoric acid production, pulp and paper bleach plants and urea service.

KEY WORDS

High chromium ferritic steel, chloride corrosion resistance, weldability

INTRODUCTION

In general, the corrosion resistance of stainless steels in chloride-containing solutions will be enhanced by increasing the chromium and molybdenum content. Using multiple regression analysis, it was found that, e.g. the pitting potential - a criterion of chloride corrosion resistance - is a function of the so-called efficiency sum viz. % Cr + 3.3% Mo (Fig. 1). Thus for some years the two important development directions of highly corrosion resistant steels have been, for the austenitic grades, the alloying of higher molybdenum contents up to the solid solubility limit of about 6%, and on the other hand, the development of high chromium ferritic steels with molybdenum and nickel additions.

Because of the very low solubility of carbon and nitrogen in a ferritic steel, it is difficult to obtain a structure without brittle chromium-rich carbides and nitrides causing intergranular corrosion and resulting decrease in toughness. To suppress this kind of precipitation the total amount of these interstitials must be kept at a very low level and moreover fixed as stable carbonitrides by titanium or niobium.

Depending on the alloying contents, detrimental intermetallic compounds can occur during thermal treatments like welding or hot working. In steel types containing relatively high molybdenum percentages, the matrix can precipitate the molybdenum-rich Chi-phase. High chromium containing steels can be im-

paired by chromium-rich sigma-phase formation and, at temperatures below 550°C, by substructural decomposition of the ferrite, the so-called 475°C-embrittlement (Fig. 2). All of these precipitation processes result in a

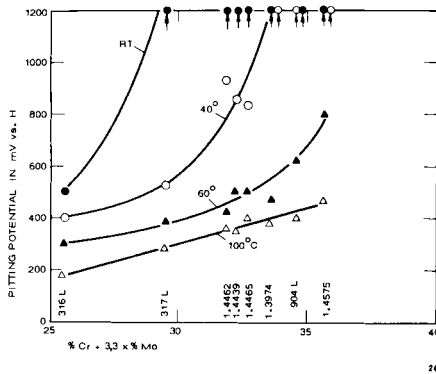


Fig. 1. Dependence of pitting potential on the "efficiency sum" in aerated 3% Sodium Chloride Solution

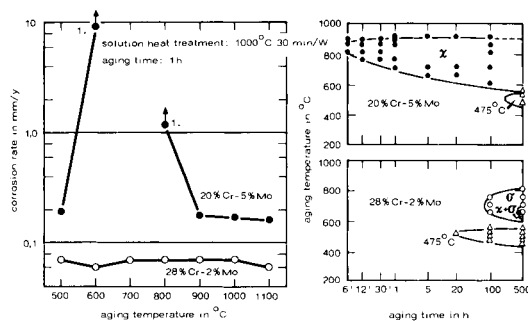


Fig. 2. Influence of annealing temperature on precipitation behaviour and intergranular corrosion susceptibility (Huey test)

decrease in toughness and corrosion resistance. However, the occurrence of the hexagonal sigma-phase, which is incoherent with the cubic ferrite structure, is less deleterious than the cubic, partially matching phase. This fact and the strong tendency of molybdenum to cause ingot segregation are reasons for selecting a 28% Cr - 2% Mo steel type from a great number of alloy combinations. A further addition of about 4% Ni results in an increase in toughness, strength and corrosion resistance but also in accelerated precipitation behaviour. However, the critical incubation times of decomposition

processes are sufficient to suppress decay of the steel's good properties during high temperature operations. The total amount of carbon and nitrogen is limited to 0.045% and fixed by niobium; titanium additions, in contrast to niobium, accelerate the precipitation reactions (Fig. 3) and decrease the notch impact toughness even in the solution annealed state.

This steel, designated X 1 CrNiMoNb 28 4 2 and known as "Superferrite", with the German DIN. Material number 1.4575, has the nominal composition in weight percent:

C	Cr	Ni	Mo	N	Nb
≤ 0.020	27.0/29.0	3.5/4.0	2.0/3.0	≤ 0.030	> 10 x (C + N)

MECHANICAL PROPERTIES

Due to its high alloying content, this steel grade exhibits remarkably high strength properties at room temperature

0.2% offset yield strength MPa	tensile strength MPa	elongation %	long.	trans.
> 500	600-750	> 20	> 16	

Compared with standard austenitic steel grades this material has twice the yield strength and this advantage is maintained at higher temperatures (Fig.4). Consequently, thinner sections can be designed for engineering applications.

As a result of the extra low and fixed carbon and nitrogen contents, "Superferrite" shows an exceptionally good notch impact toughness even at lower temperatures (Fig. 5); its transition temperature from ductile to brittle is distinctly lower than that of most commercially available ferritic stainless steels such as AISI 430.

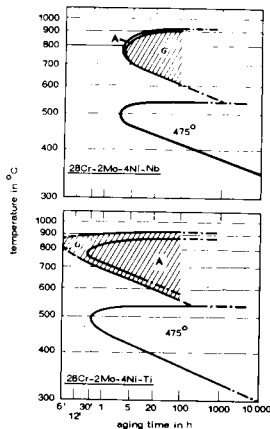


Fig. 3. Isothermal TTP diagrams of stabilized steels containing 28%Cr, 2%Mo and 4%Ni

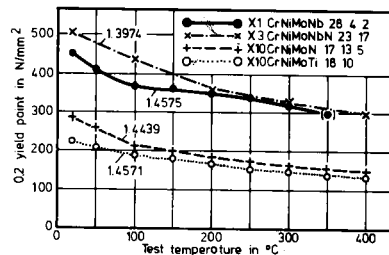


Fig. 4. "Superferrite" X 1CrNiMoNb 28 4 2 guaranteed 0.2 yield point (Comparison with austenitic steels)

COLD WORKING

Due to its low work-hardening rate compared with that of austenitic grades, "Superferrite" shows a good cold workability. Deep drawing is illustrated in Figure 6; the largest part has been deep drawn in six operations without intermediate annealing. Stretch drawability is limited due to the relatively small difference of 0.2% yield and tensile strength. Cold upsetting operations have been carried out with more than 80% deformation without any appearance of cracking (Fig. 7). Thus "Superferrite" is very suitable for the manufacturing of cold headed bolts and nuts and other comparable applications.

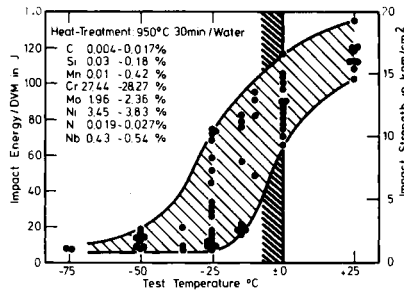


Fig. 5. Dependence of notch impact toughness on test temperature

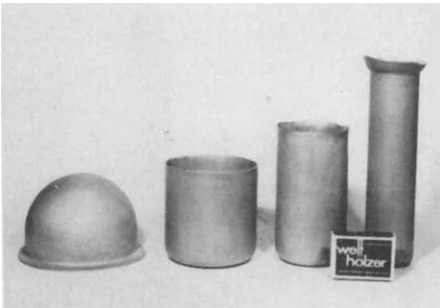


Fig. 6. Shaped parts from REMANIT 4575, without intermediate annealing deep drawn by 6 draws (Total drawing ratio $\beta_{tot} = 4.5$)

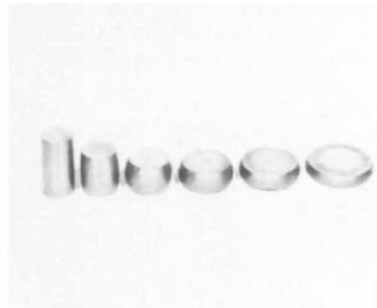


Fig. 7. Cold headed specimens of 15 mm diameter bar material (initial height 30 mm)

WELDING

Limited by grain coarsening, "Superferrite" can be joined with matching filler metal up to about 15 mm. As a consequence of the extremely low carbon and nitrogen contents, it must be welded under inert gas shielding conditions. TIG process with pure argon is recommended. Longitudinally

welded tubes exhibit remarkably good mechanical properties (Fig. 8). Pressure tested specimens show expansions of more than 30% without failure and tube pieces can be double flattened without cracking; free bending at small radii was possible without formation of wrinkles. Figure 9 illustrates a matching filler weld joint of 12 mm (0.5 in) production sheet which has been tested for intergranular corrosion. Neither cracks nor intergranular attack has been observed. Heavy gauges can be welded with intermediate layers of duplex or austenitic electrodes containing some percentages of ferrite and covered with two layers of an adequate corrosion resistant material like Inconel 112 or alternatively a matching filler wire.

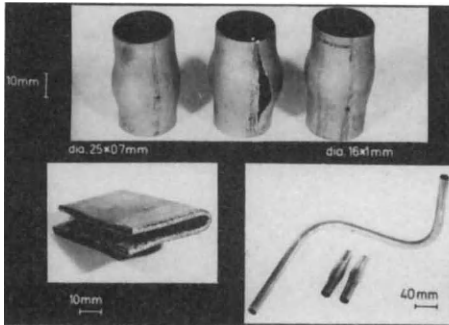


Fig. 8. "Superferrite" X1CrNiMoNb 28 4 2 (welded tubes dia. 25x0.7 mm; dia. 16x1 mm) Bending, double-flattening, tube expansion

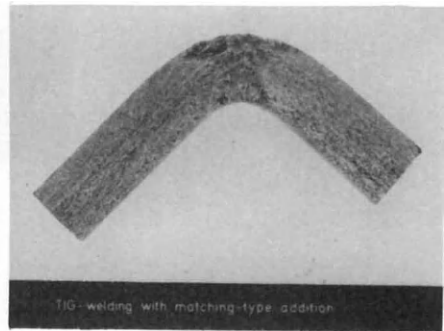


Fig. 9. REMANIT 4575 / 12 mm sheet Test for intergranular corrosion (Streicher test) after welding

CORROSION RESISTANCE

"Superferrite" exhibits no intergranular corrosion even after sensitising heat treatments such as 1 h annealing in the temperature range of 500-1000°C.

Due to its high chromium content together with the molybdenum addition the pitting and crevice corrosion behaviour is excellent. In an aerated 3% sodium chloride solution, "Superferrite" is resistant against pitting up to the boiling point (Fig. 10), whereas high alloyed austenitic grades become susceptible at lower temperatures.

Longitudinally welded tubes were exposed in 10% seawater brine in a test loop for 13 000 hours at 130°C and about 10 000 hours at 150°C without failing under these highly corrosive conditions. Resistance against stress corrosion cracking has been tested at U-bent specimens half immersed in boiling seawater and 15% seawater brine (Fig. 11). Under conditions of salt formation on the protruding parts of the specimens, the material was exposed to highly concentrated chloride solutions. After 1000 and 6000 hours, respectively, the nickel-containing "Superferrite" showed no sign of corrosion, whereas the nickel-free experimental heat sample was attacked by crevice corrosion under the salt incrustations.

The general corrosion resistance of "Superferrite" in acids is excellent. For example, in wet process raw phosphoric acid with high chloride and fluoride levels, in which high alloyed austenitic grades suffer severe weight losses, "Superferrite" exhibits even better corrosion behaviour than

the nickel base alloy NiCr 20 Mo 15 (Fig. 12).

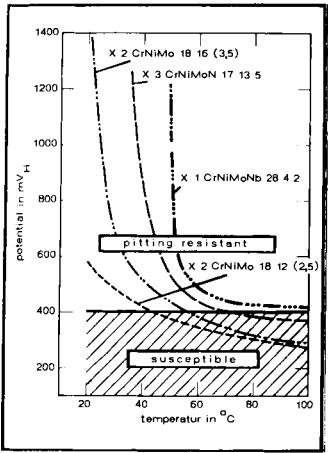


Fig. 10. Comparison of pitting susceptibility of austenitic steel grades and niobium stabilized 28%Cr-2%Mo-4%Ni-Steel

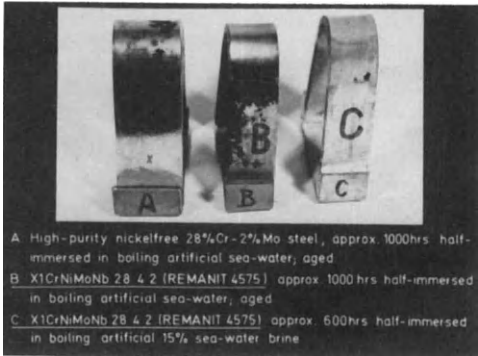


Fig. 11. Stress-corrosion hack specimens from "Superferrite"

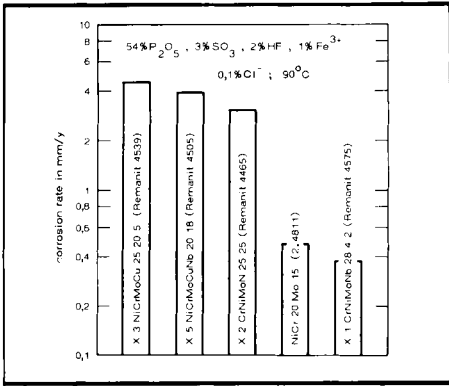


Fig. 12. Corrosion resistance of several high alloyed austenitic grades and "Superferrite" X1CrNiMoNb 28 4 2 in wet process phosphoric acid

APPLICATIONS

As a consequence of its outstanding chloride corrosion resistance, "Superferrite" is very suitable for seawater and desalination plants. Out of production heats, items such as water boxes, heat exchangers and superheaters have been built and successfully tested (Figs. 13 and 14). Urea service

tubes, which have been in use since 1974, show no evidence of corrosion attack in the stripper. This steel grade is a strong candidate for coastal power plants, the pulp and paper industries, the chemical and petrochemical industries. It can be used under severe corrosion conditions like seawater desalination at high temperatures, pulp bleach liquors, phosphoric acid processors and urea synthesis in which many commercially available high alloyed stainless steel grades fail.

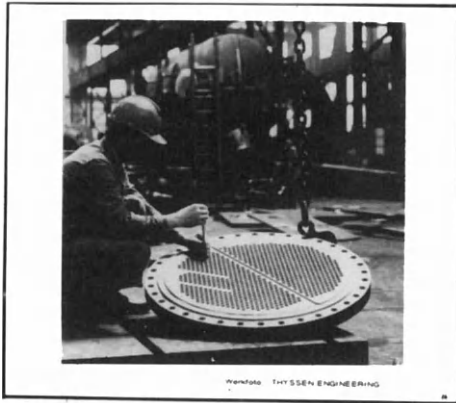


Fig. 13. Explosion cladded tube plate
(1280 mm ϕ)
100 mm Bulk Material :
20 MnMoNi 5 5 (1.6310)
15 mm Clad Material :
X1CrNiMo 28 4 2 (1.4575)

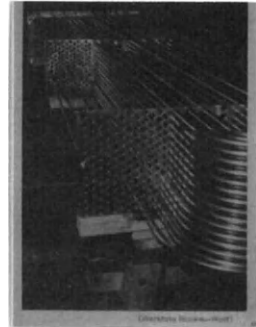


Fig. 14. Superheater of a 500m³/d
(130 000 gal/day) sea-
water distillation plant
"Superferrite" tubes
23x1 mm rolled in 25 mm
"Superferrite" plate

The Effect of Replacing Molybdenum with Vanadium on the Corrosion Resistant Properties of Stainless Steels

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ABSTRACT

The effect of replacing molybdenum with vanadium, both fully and partially, on the corrosion resistant properties of wrought ferritic, and wrought and cast austenitic stainless steels is examined. All alloys contained approximately 18% chromium with the austenitic alloys based on Types 304L and CF-8 respectively. The ferritic alloys contained chromium and 1-4% vanadium; the wrought austenitic alloys up to 6% vanadium and 2% molybdenum (not in combination); and the cast austenitic alloys up to 6% vanadium and 1.5% molybdenum, separately and in combination. Corrosion testing involved anodic polarization in H_2SO_4 and determination of the pitting potential in 0.1N NaCl. Vanadium was found to improve the pitting resistance of all alloys in NaCl, and generally had a beneficial effect on the passivation characteristics of the ferritic and wrought austenitic alloys in H_2SO_4 . The element had a detrimental effect on passivity in the cast austenitic alloys, a fact possibly related to the higher carbon and nitrogen level and the formation of detrimental precipitating phases (e.g. carbides). Molybdenum was found to be more effective than vanadium on a weight-for-weight basis in conferring corrosion resistance.

KEYWORDS

Molybdenum replacement; vanadium; ferritic; austenitic stainless steels; corrosion properties; potentiodynamic testing; H_2SO_4 ; pitting potential.

INTRODUCTION

Molybdenum has a very beneficial effect on the corrosion resistant properties of stainless steels, in particular the resistance to pitting corrosion and to sulphuric acid. There are several factors which have encouraged the development of a local substitute for molybdenum, these being that South Africa must import all her requirements of the metal, the importance of the metal as an alloying element in stainless steels and high-strength, low-alloy steels, the highly fluctuating price of the metal, and lastly but perhaps most importantly, the abundance in South Africa of the metal vanadium which is one of the most promising substitutes for molybdenum.

The literature contains several references to the fact that vanadium improves the pitting resistance of stainless steels (Tomashov and others, 1964; Bieffer, 1970; also Climax Molybdenum, unpublished data), particularly in the concentration range 2-5%. An additional advantage of vanadium in ferritic stainless steels is the improvement it confers on the impact properties, an aspect in which these steels are very deficient (Aslund, 1977; Davies and Robinson, 1982).

The object of the present investigation was to examine the effect of replacing molybdenum with vanadium, both fully and partially, on the corrosion properties of ferritic and austenitic stainless steels. Polarization tests were conducted to determine the resistance to pitting in a NaCl solution, and the passivation characteristics studied in H_2SO_4 . An alloy containing 18-19% chromium was used as a base for alloying additions.

EXPERIMENTAL PROCEDURES

Materials. The compositions of the alloys tested are listed in Table 1. The wrought ferritic and austenitic stainless steels were both prepared by vacuum induction melting, the base composition being respectively a low-interstitial

TABLE 1 Chemical Composition of the 18-19% Chromium Stainless Steels Examined in this Study

Classification	Percentages		ppm	
	Vanadium	Molybdenum	Carbon	Nitrogen
<u>Ferritic Alloys</u>				
(18% chromium)				
1 V	1.12	-	50	44
2.6 V	2.67	-	100	57
4 V	4.00	-	80	69
<u>Wrought Austenitic Alloys</u>				
Base alloy (Type 304L)				
(18%Cr - 9% Ni)	0.13	0.11	190	270
2 V	2.05	0.09	280	360
4 V	3.70	0.08	190	330
6 V	5.65	0.13	230	360
1 Mo	0.12	1.04	240	310
2 Mo	0.09	1.97	170	390
<u>Cast Austenitic Alloys</u>				
Base alloy (Type CF-8)				
(19% Cr - 11% Ni)	-	-	570	300-400
2 V	2.10	0.80	490	
4 V	4.10	0.25	500	
6 V	6.04	0.13	530	
3 Mo	0.09	2.91	350	
2 V - Mo	2.10	1.62	570	
2.7 V - Mo	2.69	1.41	480	

Minor element concentrations (P, S, Si, etc.) in the austenitic alloys are as reported for the base Type alloys. For the ferritic alloys the levels were somewhat lower, viz. P = 0.012%, S = 0.008%, Si = 0.05%.

element 18% chromium alloy and Type 304L. The ferritic alloys were hot-rolled from 1050°C to a thickness of 12mm before being annealed at 825-875°C for 30 minutes, and water quenched, while the wrought austenitic alloys were hot-rolled from 1200°C to a thickness of 12mm, followed by a solution treatment at 1050°C for 30 minutes and water quenching. A Type CF-8 alloy (19% Cr - 11% Ni) was used as the base composition for the cast austenitic alloys and preparation involved argon induction melting, casting and a solution treatment at 1050°C for 2 hours, followed by water quenching.

Pitting Tests. Determination of the pitting potential involved anodic polarization in a deaerated 0.1N NaCl solution at a temperature of 30°C. The sample was allowed to stabilize for one hour in the NaCl solution before commencing at a scanning rate of 200 $\mu\text{V/s}$ from the free corrosion potential. The actual pitting potential was taken at a value corresponding to a current density of 10 $\mu\text{A/cm}^2$, as suggested by Truman (1978).

Passivation Tests. Passivation characteristics were determined using accepted potentiodynamic testing procedures involving polarization in deaerated 1N H_2SO_4 (for the ferritic and wrought austenitic alloys) and 2N H_2SO_4 (for the cast austenitic alloys). The same size samples and preparation and running procedures as for the determination of the pitting potentials were followed with the exception that cathodic activation was carried out before anodic polarization. In the case of the wrought alloys the samples were cathodically activated at -650 mV (versus the SCE) before the stabilization period, whereas for the cast alloys the polarization run was commenced at 200 mV below the free corrosion potential.

RESULTS AND DISCUSSION

The data obtained for three selected points on the anodic polarization curve in H_2SO_4 and for the pitting potential in NaCl, are given in Table 2. Plots examining some trends from the data are shown in Figures 1 and 2.

Pitting Results. Examination of Table 2 shows that vanadium increases significantly the pitting potential in NaCl, thus confirming in detail the results reported by other workers. The pitting potential increased continuously in the austenitic alloys as the vanadium level was raised above the base alloy composition. Although a base alloy was not examined in the case of the ferritic alloys, the same trend is envisaged. A comparison with the basic austenitic alloys containing molybdenum showed that this element was more beneficial than vanadium on a weight-for-weight basis by a factor of about two. A comparison of the vanadium-bearing ferritic alloys with Type 444 stainless steel, an 18% Cr - 2% Mo - Ti stabilized alloy with an interstitial element level about 2 - 3 times that reported for the ferritic alloys here, also showed molybdenum to be more effective than vanadium. SEM examination of the alloys, combined with EDX analysis, showed that pitting was initiated at inclusions such as silicates, oxides and sulphides.

The combination of vanadium with molybdenum also had a beneficial effect on the pitting potential in the cast austenitic alloys, in particular when combined in the proportion 2.7% vanadium and 1.4% molybdenum. The alloy with this combination had a pitting potential almost as high as the 6% vanadium alloy, again showing the greater effect of molybdenum.

Passivation Results. The anodic polarization results obtained in H_2SO_4 for the wrought vanadium-bearing ferritic and austenitic alloys differ significantly from those obtained for the cast austenitic alloys. Whereas vanadium had a generally beneficial effect in promoting passivity in the wrought

alloys, it was detrimental in the cast materials. The most noticeable effect of vanadium in the ferritic and wrought austenitic alloys was in reducing the critical density and potential for primary passivation (Fig. 1). On balance, the effect on the passive region was beneficial (i.e. the passive potential range was extended and the passive current density lowered), except in the ferritic alloys where vanadium appeared to lower the breakdown potential. This trend, as shown in Fig. 1, is due to incipient breakaway of the trans-passive region.

TABLE 2 Anodic Polarization Results in H_2SO_4 and 0.1 NaCl, at 30°C

Alloy	I_c^*	E_{cp}	I_p	E_p	I_b	E_b	E_{pit}^{**}
<u>FERRITIC ALLOYS (1N H_2SO_4)</u>							
Type 430	18766	-411	24	-178	3.9	+713	-58
1 V	36621	-423	19	-263	7.8	+720	+200
2.6 V	19549	-435	18	-274	7.9	+587	+285
4 V	10351	-451	15	-292	6.3	+451	+504
<u>WROUGHT AUSTENITIC ALLOYS (1N H_2SO_4)</u>							
Base alloy	1610	-270	49	-92	65	+779	+201
2 V	1140	-325	23	-123	13	+820	+210
4 V	1030	-329	18	-133	11.1	+790	+229
6 V	841	-350	20	-160	9.5	+795	+232
1 Mo	80	-280	6.1	-115	8.5	+825	+262
2 Mo	96	-273	6.3	-170	5.8	+820	+281
<u>CAST AUSTENITIC ALLOYS (2N H_2SO_4)</u>							
Base alloy	45	-262	4.7	-100	4.0	+871	+143
2 V	51	-251	4.9	-86	4.9	+771	+214
4 V	126	-258	6.0	-100	7.5	+700	+293
6 V	879	-267	15	-93	8.5	+450	+379
3 Mo	18	-239	4.5	-100	4.0	+871	+421
2V-Mo	12	-219	4.7	-79	5.4	+771	+285
2.7V-Mo	17	-219	5.1	-66	4.7	+714	+345

* Refer to Fig. 1 for abbreviations. I in $\mu\text{A}/\text{cm}^2$, E in mV.

** E_{pit} = pitting potential (mV) in 0.1N NaCl.

The potentials reported are relative to the Standard Calomel Electrode, with each result being the average of 1-4 determinations.

A basic, low-interstitial, 18% chromium ferritic alloy without vanadium was not examined in this study but comparison of the critical current density with results for Type 430 and other 18% chromium alloys (Fig. 2) shows that vanadium is in fact detrimental up to a concentration of several percent. An increase in vanadium beyond the 1% level, however, was found to be beneficial in reducing the critical current density.

A comparison of the vanadium- and molybdenum-bearing wrought austenitic alloys shows that molybdenum was in most cases more beneficial than vanadium, especially in reducing the critical current density (Fig. 2). Molybdenum, however, was not as effective as vanadium in reducing the critical potential for primary passivation.

The effect of vanadium in the cast austenitic alloys was to increase the

critical current density (Fig. 2) and to contract the potential range of the passive region and move it to higher current values. As was the case for the ferritic alloys, vanadium in the cast alloys decreased the breakdown potential in H_2SO_4 . The detrimental effect of vanadium in the cast alloys may be due to the high carbon level of 550ppm (relative to the wrought austenitic alloys) causing the precipitation of some harmful phase, such as a carbide. Tomashov and others (1964), however, found vanadium to be beneficial with a carbon level of 360ppm. It is possible that the formation of ferrite in the cast alloys is contributing in some way to the poorer passivation characteristics shown, although this is not the case for the wrought austenitic alloys which show a similar increase in ferrite phase with increasing vanadium content. Microprobe analysis has confirmed the results of previous work (Forbes-Jones and Kain, 1975; Dundas and Bond, 1975) that ferrite is enriched in chromium, molybdenum and vanadium relative to the austenite.

An important difference between molybdenum and vanadium as alloying elements is that molybdenum occurs largely in solid solution whereas vanadium occurs both in solid solution and as a precipitate (hence the use of vanadium as a stabilizer by Aslund, 1977). More research is needed on the nature of precipitating phases as related to the vanadium and carbon and nitrogen levels to clarify the results in the austenitic stainless steels.

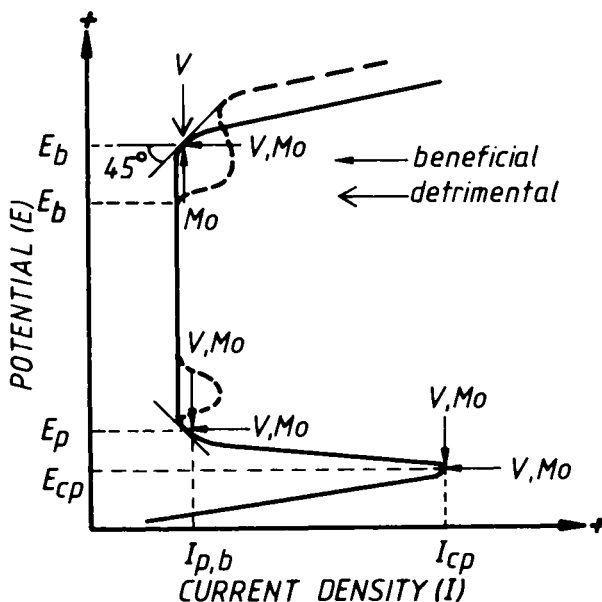


Fig. 1. Effect of vanadium and molybdenum on the passivation characteristics of wrought ferritic and austenitic stainless steels in 1N H_2SO_4 (from this study).

cp = critical values for primary passivation;
p = primary values for passivation;
b = breakdown values.

CONCLUSIONS

Vanadium is found to improve the pitting resistance of ferritic and austenitic stainless steels in NaCl, and the passivation characteristics in general of the wrought ferritic and austenitic alloys in H_2SO_4 . The element has a detrimental effect on passivity in H_2SO_4 in the cast alloys possibly due to the high carbon and nitrogen level which is leading to the formation of harmful precipitating phases. More research is needed to clarify this point.

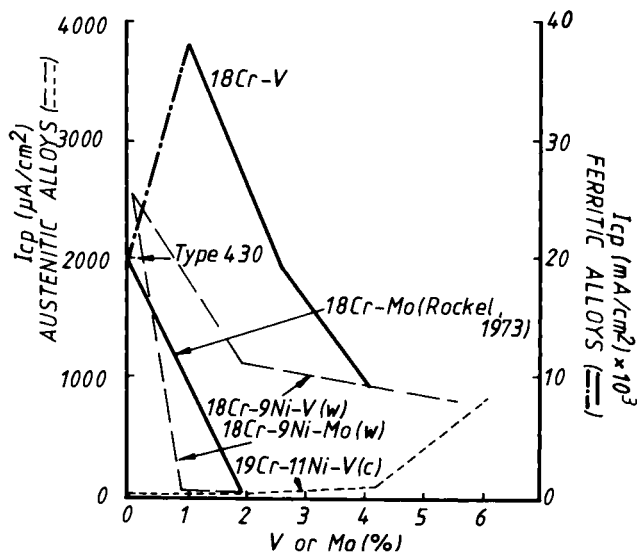


Fig. 2. Effect of vanadium and molybdenum on the critical current density (I_{cp}) for 18-19% chromium stainless steels in 1N H_2SO_4 (2N H_2SO_4 for cast alloys).

(w) = wrought alloys; (c) = cast alloy.

ACKNOWLEDGEMENTS

Acknowledgement is made to the C.S.I.R. and Middelburg Steel and Alloys for financial support and to the University of the Witwatersrand for permission to publish this paper.

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The Structure of Rapidly Solidified Nickel-base Alloys

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ABSTRACT

The rapid solidification of nickel-base superalloys is currently being extensively studied in the search for superior gas-turbine materials. Initial results suggest that marked improvements in formability and mechanical properties can be achieved, compared with conventional material. The aim of this paper is to describe the development of the observed solidification structures in some rapidly solidified commercial superalloys, and to explain the subsequent development of fine γ' precipitates during heat treatment. Preliminary data from an investigation of some simple model nickel alloys will also be presented.

KEY WORDS

Rapid solidification. Nickel-based superalloys. Spinodal decomposition.

INTRODUCTION

The major benefits to be gained from the rapid solidification processing (RSP) of nickel superalloys are the development of a chemically homogeneous structure and improved workability (in alloys difficult to process by conventional wrought methods).

In addition to these immediate benefits, RSP allows a wider range of alloy compositions to be considered since in many systems large increases in solute solubility limits can be achieved. This provides more material for subsequent precipitation. The nature of the precipitation reactions is also modified because of the small grain size, the increase in 'quenched-in' vacancy concentration and the increase in chemical activity of the elements in solid solution. Other effects of rapid solidification (such as the formation of new metastable or amorphous phases) are not important in the production of nickel-base superalloys, for which an f.c.c. matrix is desired.

The present paper describes results of a study of the structures

and properties of some rapidly quenched commercial nickel-based superalloys, which are currently cast or wrought, together with data from a preliminary investigation into some simple model nickel alloys.

EXPERIMENTAL PROCEDURE

Commercial alloys were provided in the form of 10 mm diameter extruded rod by Henry Wiggin Ltd., Hereford, U.K. Model alloys were cast as 10 mm dia. ingots from pure elements in an argon arc furnace. The analyses of all the alloys are presented in Table I. (The alloy APK I has been developed by Henry Wiggin Ltd., for argon gas atomisation at relatively low quench rates (Williams, 1977)).

TABLE I Analyses of Nickel Alloys in Weight % (Major Elements Only)

Designation	C	Ti	Al	Mo	Cr	Co	Nb	Ni
Nimonic 80A	0.1	2.7	1.6	-	21	2	-	balance
APK 1	0.03	3.6	4.1	5.2	16	15	-	"
IN 100	0.18	4.7	5.5	3.0	10	15	-	"
IN 792 LC	0.10	4.2	3.2	2.0	13	19	-	"
JV 1	-	5.63	-	-	-	-	-	"
JV 2	-	-	5.63	-	-	-	-	"
JV 3	-	3.0	3.0	-	-	-	-	"
JV 4	-	-	-	-	-	-	2.7	"
JV 5	0.1	-	-	-	-	-	2.7	"

RSP was performed using both melt spinning (MS) and pendant drop melt extraction (PDME) (Pond, Maringer and Mobely, 1974), in a chamber, evacuated to 10^{-2} Pa prior to backfilling with helium gas. Details of this apparatus and its application to nickel alloys have been described elsewhere (Wood, Bingham and Bee, 1978). The PDME technique provided wire of ~ 50 μ m dia. which is suitable for X-ray analysis and, after thinning to produce a small radius tip, for field ion atom probe analysis. Melt spinning through a 1 mm dia. nozzle produced ribbon ~ 3 mm wide which could be electrolytically polished for transmission electron microscopy (carried out in a Philips EM 301). The overall solidification structures could also be studied by scanning electron microscopy (in a Philips 501B) on ribbons back-etched using aqua regia in ethanol. Two types of atom probe field ion microscope were employed. In both cases, atoms on the surface of a small radius tip are field evaporated (ionised) by an intense electric field. This beam of ions is then mass analysed by a time-of-flight spectrometer. The first instrument enables analyses from small areas (1-2 nm dia.) to be made, and a progressive plot of composition vs. time (depth of evaporation) allows a narrow cylinder of material along the fibre axis to be sampled. The resultant composition profile has a resolution of ~ 1 nm. In the second instrument ions with the same time-of-flight are accepted, from an area 30 - 35 nm dia., in an image-forming spectrometer to produce elemental maps. The individual ionic resolution is again ~ 1 nm, although local differences in surface radius (due to particles or grooves) change the local magnification (thus giving images which suggest particles are larger than their actual size). Details of these techniques and their errors have been

published elsewhere (Southon and colleagues, 1975; Waugh and Southon, 1979).

Room temperature tensile tests were performed on a small low-load servo-controlled Instron machine fitted with a special cradle for gripping fine wires. The cross-sectional area of the fracture surfaces was measured in a scanning electron microscope.

RESULTS AND DISCUSSION

(A) Commercial Alloys

a) As-quenched structures. Investigations of highly alloyed stainless steels produced by gun splat quenching demonstrated that a variation in solidification structure could be observed in single samples due to changes in local cooling conditions (Wood and Honeycombe, 1974; Wood and Sare, 1975). A similar range of structure is found in nickel alloys, which also undergo no subsequent solid state phase change. The terms 'micro-crystalline' and 'dendritic' have recently been introduced to describe grains that have developed through a planar front or dendritic growth mode respectively (Holiday, Cox and Patterson, 1978). A typical mixed micro-structure is shown in Fig. 1. The ratio of these constituent morphologies would be expected to depend on composition, cooling rate and the local undercooling prior to crystallisation. However, Kadalbal, Montoya and Kataris (1978) have plotted cooling rates on a typical growth rate - thermal gradient graph for electron-beam glazed beads in Ni-Al-Cr alloys. This work showed that while the balance between the proportion of micro-crystalline and dendritic grains can be seriously affected by small changes in R and ρ (where R = growth rate in $M.S^{-1}$, and ρ = thermal gradient in Km^{-1}), it is independent of cooling rate ($\rho.R$). In the various methods used for RSP, some techniques (such as glazing) allow high heat transfer coefficients (h) and thus give large values of ρ , but small undercoolings (ΔT). For other techniques, the opposite is true. Since the limiting conditions for planar and dendritic growth are also dependent on the partition coefficient and diffusivity of solute atoms in the liquid, it is not surprising that there is considerable variation in the structures reported for any given alloy and between different alloys.

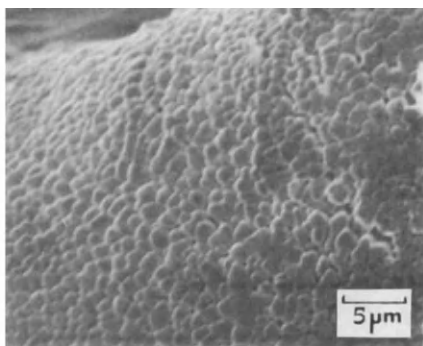
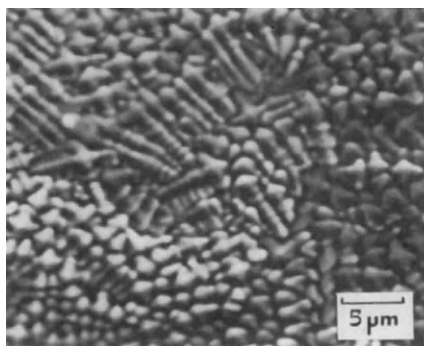


Fig. 1. Typical mixed solidification structure (SEM). Fig. 2. As-quenched APK1 structure (SEM).

In the present study, RS APK 1 was found to be microcrystalline throughout its cross-section (Fig. 2). In the absence of dendrite arms, these grains sometimes contain arrays of dislocations which form low angle or 'cell' boundaries (Fig. 3). By contrast, argon gas-atomised APK 1 powder is entirely dendritic (Williams, 1977) with a secondary dendrite arm spacing of $\sim 2 \mu\text{m}$, which is consistent with the lower cooling rate achieved. In Nimonic 80A, rapid solidification produced a mixed microstructure, but with a secondary dendrite arm spacing of $\sim 0.5 \mu\text{m}$.

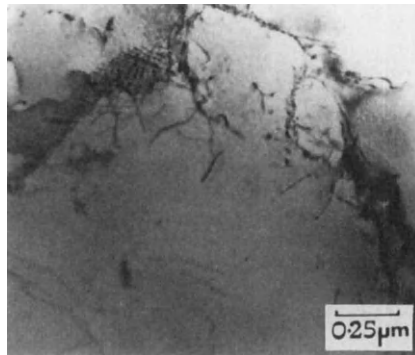


Fig. 3. As-quenched APK 1 (CTEM).

After solidification, a number of reactions can occur during the subsequent solid state part of the quenching cycle. These are

- (i) precipitation of carbides at grain boundaries,
- (ii) matrix precipitation of carbo-nitrides,
- (iii) matrix precipitation of ordered γ' : $\text{Ni}_3(\text{Al,Ti})$,
- and (iv) the formation of pre-precipitate modulated structures.

(i) and (ii) Carbide precipitation. Grain boundary carbides were found in high carbon alloys (IN 100 and IN 792) and occasionally in the inter-dendritic regions of Nimonic 80A. Similar structures have also been reported in these and other alloys by other workers (Davies, Shohoji and Warrington, 1981). The presence of such precipitates, randomly distributed on boundaries does not lead to embrittlement of the material.

Matrix carbides occurred in all the commercial alloys and some have been analysed using the FIM atom-probe. In Nimonic 80A, the particles were found to be homogeneous up to the particle-matrix interface and were of the type $(\text{Ti,Cr})_3(\text{C,N})_2$. By contrast, the precipitates in APK 1 were determined to have an approximate composition $(\text{Ti,Cr})(\text{C,N})$. In the absence of a statistically significant sample it is not possible to comment on this apparent discrepancy. However, wide variations in the stoichiometry of carbide particles in rapidly-quenched alloys might be expected due to differences in local vacancy concentration, associated with solute segregation.

(iii) and (iv) γ' precipitation and spinodal decomposition. Alloys

containing large concentrations of titanium (IN 100 and IN 792) exhibited significant matrix precipitation of ordered γ' . The measured particle size was 10 - 20 nm for IN 100 (Fig. 4), while in IN 792 the scale of the precipitate was an order of magnitude smaller. In Nimonic 80A there was no evidence of any matrix precipitate in the as-quenched material.

Between these two extremes are the structures observed in APK 1, which displayed a mottled contrast (Fig. 5), but there were no ordering reflections in the diffraction patterns indicative of precipitate formation.

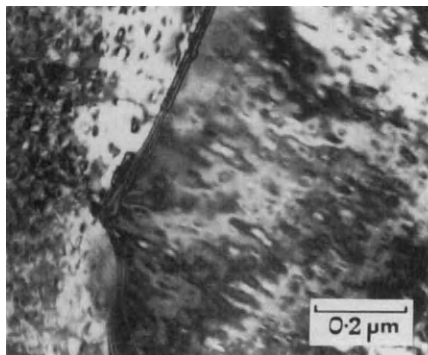


Fig. 4. As-quenched IN-100 (TEM)

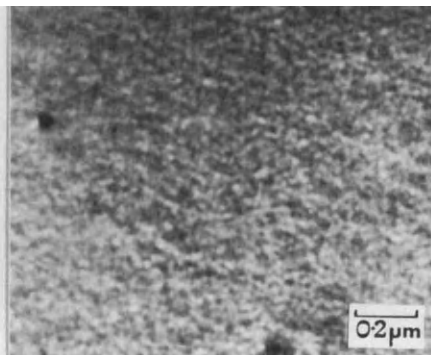


Fig. 5. As-quenched APK 1 (CTEM)

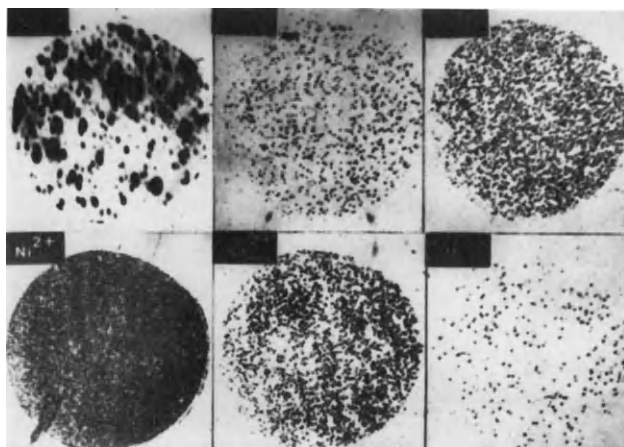


Fig. 6. Elemental Map of as-quenched APK 1 (atom probe)

Elemental images from PDME wire (Fig. 6) revealed slight partitioning (banding) in Ni and Cr concentrations. (There is also banding in the Ti and Al images, but this is more difficult to observe.) The Cr-depleted

regions were found to be 10 nm long by 5 nm wide, with no distinct boundary between matrix and 'particles'. Atom probe traces obtained by evaporation along the wire axis direction gave the following observations:

- (a) the Al- and Ti-rich regions are spaced at 10 - 20 nm,
- (b) the matrix Cr content rises to 20 at.%, but only falls to 7 at.% in the Ti,Al-rich regions,
- (c) Mo partitions with Cr,
- and (d) in the (Ti + Al)-rich areas, their combined concentration is 25 at.%, which is that necessary for γ' formations.

(b) Heat-treated structures. Initial interest in these alloys was centred on the disordered modulated precipitates found on ageing Nimonic 80A at 973K (Wood and colleagues, 1979). Atom probe evidence showed that the first formed precipitate was rich in chromium. With continued holding at temperature, Cr diffused into the matrix and the precipitates then ordered to become γ' . A similar sequence has been observed on ageing the initial modulated microstructure in APK 1 (Wood and colleagues, 1980). Progress of this reaction can be seen in more detail from atom-probe elemental images (Figs. 7a,b) which show the gradual development of γ' precipitates in APK 1.

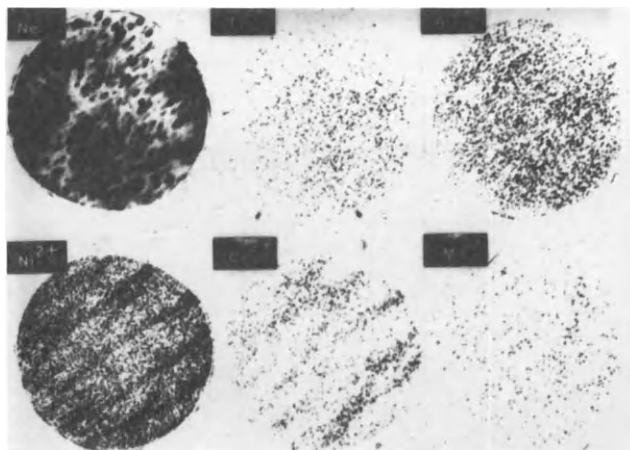


Fig. 7a. APK 1. Heat treated for 1.2×10^3 s at 1033 K.

Clearly defined particles are observed after 9×10^3 s (Fig. 7b) at 1033 K, although partitioning is obvious after 1.2×10^3 s (Fig. 7a). At this stage, the chromium level in the particles has dropped from the as-quenched value of 7 at.% to the equilibrium 3 at.% for γ' . It is also obvious from transmission electron microscopy studies that ordered γ' precipitates had developed after 1.2×10^3 s (Fig. 8).

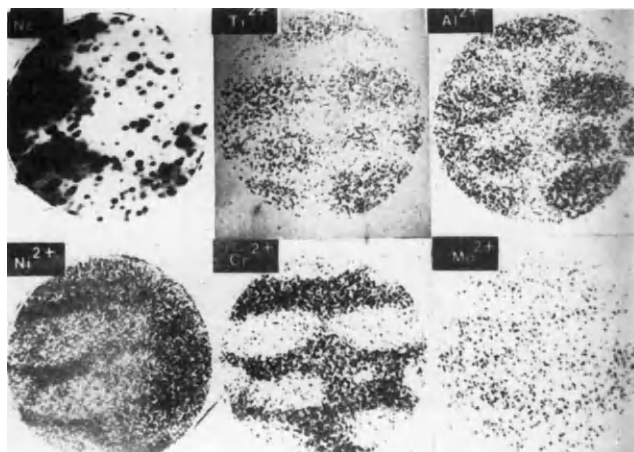


Fig. 7b. APK 1. Heat treated for 9×10^3 s at 1033 K.

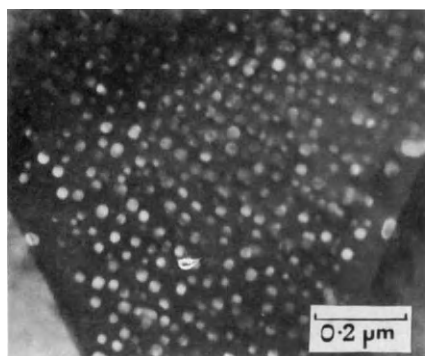


Fig. 8. APK 1. Heat treated for 9×10^3 s at 1033 K.
(CTEM: CDF)

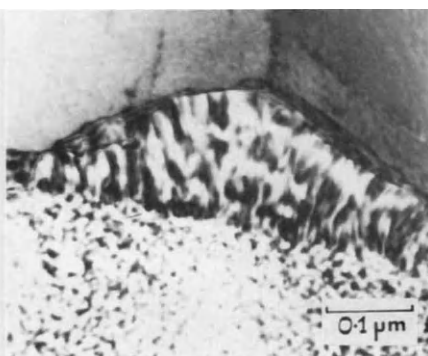


Fig. 9. Nimonic 80A. Heat treated for 3×10^2 s at 1033 K.
(CTEM)

(c) Mechanical properties. The extremely fine γ' precipitates in APK 1 lead to exceptionally high tensile strengths in excess of 2000 MPa, compared with 1200 MPa for as-quenched samples. Alloys with higher carbon contents (such as Nimonic 80A) also develop grain boundary films of $\gamma' + M_{23}C_6$ (Fig. 9) by a discontinuous reaction. This leads to a marked loss of strength due to low resistance to crack propagation. However, there is evidence that at slower quench rates, where dendritic growth occurs in these alloys, these deleterious grain boundary films are not developed (Davies, Shohoji and Warrington, 1981).

(A) Experimental Alloys

In the model alloys JV1, 2, 4 and 5 there was no evidence of any matrix precipitate in the as-quenched material. However, Alloy JV3 developed a complex microstructure (Fig. 10) similar to that observed in the spinodal decomposition of β brass (Kubo and Wayman, 1979). There is evidence of both precipitation in two directions and domain walls. The diffraction patterns from these regions (Fig. 11) not only show weak ordering reflections (due to the presence of ordered γ' precipitates), but also strong reflections at $g = (1/3, 1/3, 1/3)$ and $(2/3, 2/3, 2/3)$. These are unexpected results, since according to the appropriate phase diagram (Betteridge and Heslop, 1974) this alloy should be single phase. Further investigations are currently in progress to explain this phenomenon. Some clue to what might be occurring may be found from alloy JV2, which contains only nickel and aluminium. In its as-quenched state, there is extensive faulting in the structure (Fig. 12) which is not typical of normal solidification structures (cf. Fig. 1). Although JV3 does not exhibit this gross faulting, and appears well-behaved in all other respects, there is frequent evidence of streaking in its diffraction pattern which may be indicative of a faulted microstructure.

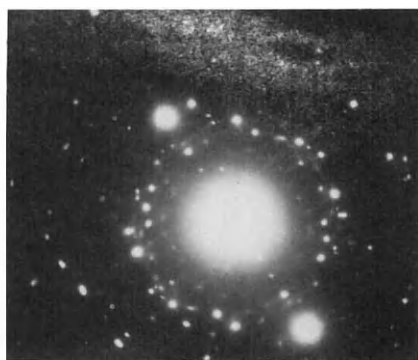
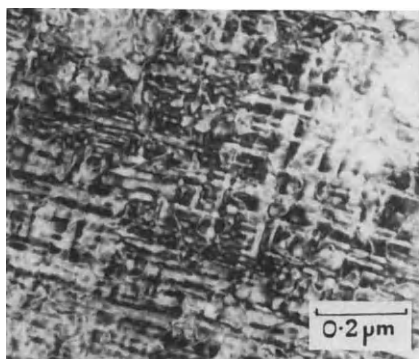


Fig. 10. As-quenched Ni-3Ti-3Al (CTEM) Fig. 11. The same alloy (SADP)

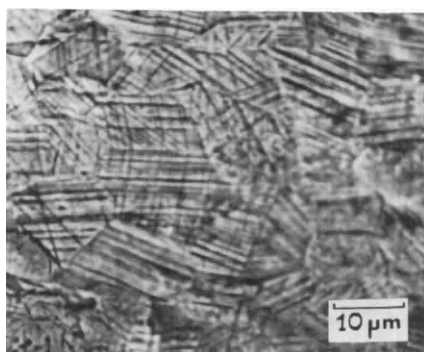


Fig. 12. As-quenched Ni-6Al. (SEM)

Based on these preliminary observations, and the results of the current study of the heat treatment of these high purity alloys, it is hoped to gain further insight into the mechanisms of γ' precipitation in nickel-base alloys.

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Microstructure and Creep Behaviour at Elevated Temperature of Unidirectionally Solidified Eutectic Nickel-base Superalloys

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ABSTRACT

Ni-W, Ni-W-Al, Ni-Mo and Ni-Mo-Al eutectic alloys were subjected to a process of unidirectional solidification (UDS) with a view to a composite of ductile matrix containing fibres or lamellae of comparatively high strength.

The post-UDS structure of the Ni-W eutectic consisted of a Ni(W) solid solution γ -matrix, reinforced with W(α) fibres (or lamellae at high solidification rates), in addition to which it contains semicoherent Ni_4W -(β) precipitates in the matrix. The transition from a fibrous to a lamellar morphology will be discussed. The microstructure of the Ni-W-Al eutectic consists of a γ matrix reinforced with Ni_3Al (γ') fibres. In the Ni-Mo eutectic system the post-UDS microstructure consists of alternating NiMo- δ lamellae in a γ -matrix which contains Ni_3Mo and Ni_4Mo precipitates. The Ni-Mo-Al eutectic after UDS consists of a γ/γ' matrix reinforced with Mo-(α) fibres. The orientation relationships between the phases in each case were determined by electron diffraction or X-rays (Laue back reflection technique).

The creep behaviour of the binary specimens was examined under constant and increasing load at 930-1000°C. Observations of the fracture surface and microstructural changes during the creep process were examined by SEM and TEM.

KEYWORDS

Unidirectional eutectic alloys; in situ composite materials; creep resistance at high temperature; Ni-W, Ni-Mo, Ni-W-Al and Ni-Mo-Al eutectics.

INTRODUCTION

Unidirectionally solidified eutectics have considerable potential for elevated temperature applications, mainly because of the high inherent strength and microstructural stability.

The strengthening phase in the form of lamellae or fibres is generated in situ during the solidification process. The low-energy interphase boundaries possess good stability at high temperatures. These alloys also exhibit greatly improved creep strength.

The eutectics chosen for this investigation were the binaries Ni-W and Ni-Mo and the ternaries Ni-W-Al and Ni-Mo-Al. This study concentrated mainly on the morphology and microstructure after UDS and after creep testing as well as the creep behaviour.

EXPERIMENTAL PROCEDURE

Unidirectional Solidification. The unidirectional process was carried out by a Bridgman-type technique, whereby the solidification front is advanced by means of a temperature gradient shifted along the vessel which contains the liquid alloy. The device consisted of a double-walled copper cylinder with an alumina crucible in the interior space, relative to which the cylinder moves at a variable speed (thereby controlling the solidification rate) - and water flowing between the concentric walls (Fig. 1). (For a detailed description of the equipment, see Zuta (1980).)

Homogeneous alloys of eutectic composition were prepared from high-purity powders by arc melting. Melt composition for the Ni-W eutectic: Ni-54.5 w/o, W-45.5 w/o; for Ni-Mo eutectic: Ni-53 w/o, Mo-47% (Hansen, 1958); for Ni-W-Al eutectic: Ni-79 w/o, W-10 w/o, Al-11 w/o (Budberg, 1958); and for Ni-Mo-Al eutectic: Ni-62 w/o, Mo-32.3 w/o; Al-5.2 w/o (Henry, 1976). Master ingots were remelted and directionally solidified into ϕ -12.5 mm bars of 25 cm length. The range of solidification rates in the present study was 3-30 mm/h and the temperature gradient 105°C/cm throughout. The alloy is held in a liquid state, under vacuum 1-3 hours for complete homogenization and degassing prior to the solidification process itself, which takes place in an argon atmosphere.

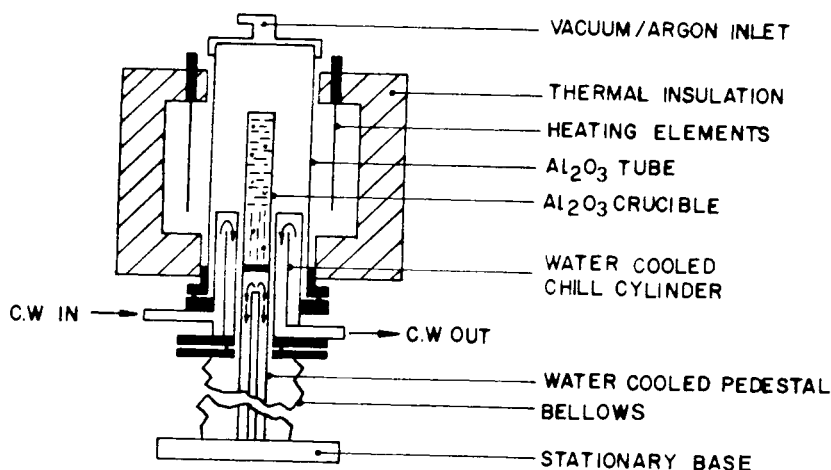


Fig.1. Scheme of the unidirectional solidification device.

Creep testing. The creep tests were carried out in a "Satec" machine under constant and variable load at 920-1000°C in an argon atmosphere. Some of the Ni-W creep tests were preceded by 24 hours solution treatment at 1030°C followed by quenching.

Metallography. Standard techniques of optical metallography were employed for examination of the unidirectionally solidified structure. The microstructural features before and after the creep process were determined by means of scanning and transmission electron microscopy. The specimens for TEM were prepared by the standard technique of electropolishing and ion milling.

RESULTS AND DISCUSSION

Metallography

Binary eutectics. The eutectic systems Ni-W and Ni-Mo after UDS are composites consisting of a solid solution matrix reinforced with fibres (Ni-W) or lamellae (Ni-Mo). In addition to this morphology the matrix in both systems contains intermetallic precipitates. In the Ni-W system the Ni(W) matrix contains W fibres (square, circular or hexagonal cross section) (see Fig. 2a) while in the Ni-Mo system the Ni(Mo) matrix contains NiMo lamellae (see Fig. 2b).

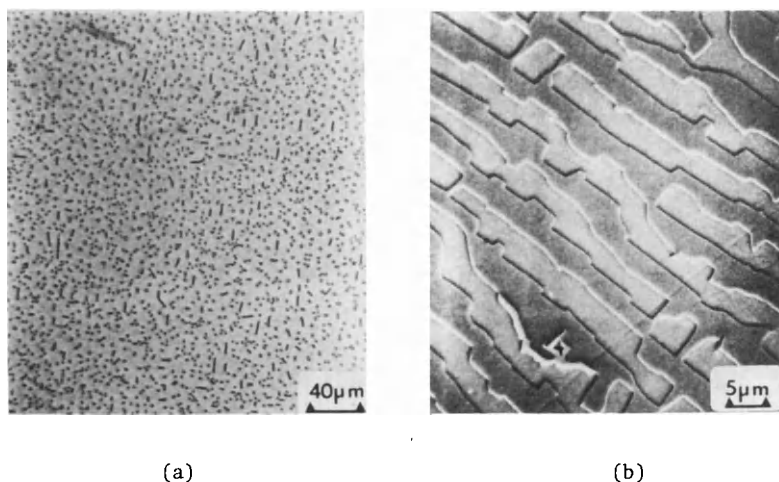


Fig. 2. Morphology after UDS. Section transverse to the solidification direction a) Ni-W eutectic with fibrous structure (optical micrograph); b) Ni-Mo eutectic with lamellar structure (scanning micrograph).

The calculated volume fraction of the W fibres is 5.7% and the calculated volume fraction of the NiMo lamellae is 40%. In the Ni-W system as the growth rate increases, transition from a fibrous to a lamellar morphology sets in, as observed also by Kurz & Lux (1971) for the same system, by

Livingstone (1970) for the Au-Co and by Street (1962) for the Al-Al Ca. This transition is attributable to the tendency of the system to lower the supercooling of the solidification interface, which in turn provides the energy required for build-up of the interphase boundaries and for diffusion of atoms in the liquid, thus creating the concentration gradient between the phases. It can be shown that in the Ni-W system the surface energy of the fibrous structure is only 0.42 of that of its lamellar counterpart at the same spacing (Zuta, 1980). On the other hand, the diffusion energy for the fibrous structure is always higher than that for the lamellar one, since the average diffusion distances of the W atoms and the Ni atoms in fibrous structures are 3.1 and 4 times higher respectively than those of the W and Ni atoms in the lamellar structure. At relatively low solidification rates, the total energy for the fibrous structure is lower than that for the lamellar; but as the rate increases, the dimensions of the fibres and the corresponding interphase distance decrease (Tiller, 1958; Jackson & Hunt, 1966), and the contribution of the curvature to the surface energy increases until the total-energy relationship is reversed to favour the lamellar structure.

Electron-diffraction analysis indicated that Bain type orientation relationships exist between the Ni(W) matrix and the W fibres or lamellae. The growth direction of the W phase is $\langle 111 \rangle$, while its $\langle 100 \rangle$ direction is parallel to that of the matrix.

In the Ni-Mo system the growth direction of the NiMo phase is $[001]$.

The following crystallographic relationships were concluded:

$$\begin{array}{lcl} [001]_{\text{NiMo}} & || & [112]_{\text{Ni}} \\ [100]_{\text{NiMo}} & || & [11\bar{1}]_{\text{Ni}} \\ [010]_{\text{NiMo}} & || & [1\bar{1}0]_{\text{Ni}} \end{array}$$

The Ni(W) matrix contains coherent $\text{Ni}_4\text{W}(\beta)$ precipitates (Fig. 3) of the D_{1a} type which have a tetragonal fcc structure with orientation relationships to the Ni(W) matrix identical to those of Ni_4Mo precipitates (Fig. 4) which exist in the Ni-Mo system and were also investigated by Rudel, Delavignette and Amelinckx (1968) and by Okamoto & Thomas (1971).

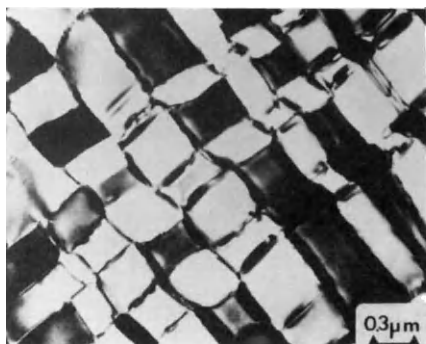


Fig. 3. The Ni_4W precipitates.

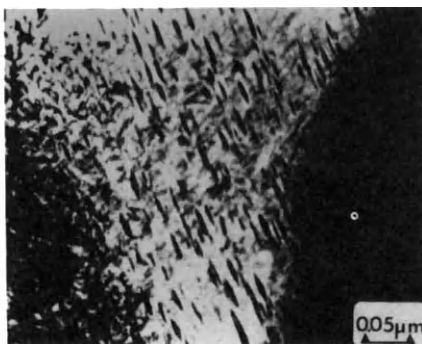


Fig. 4. The Ni_4Mo precipitates.

In addition to the Ni_4Mo precipitates two other kinds of precipitates exist in the Ni-Mo system - Ni_3Mo and Ni_2Mo . During cooling of the ingot after the solidification, exposure to high temperature is not long enough to obtain the stable phases predicted by the phase diagram, i.e. appearance of Ni_3Mo . Instead, one obtains a metastable solid solution $\text{Ni}(\text{Mo})$ with embedded precipitates of Ni_4Mo and Ni_2Mo each with its different superlattice structure. Only with highly magnified observations and careful study of the specimen can traces of Ni_3Mo be detected. The appearance of Ni_3Mo is accompanied by shear along the atomic densely populated planes of the matrix. Metallography shows it as bands of hexagonal phase inside the lamellae of the fcc phase. Actually, they appear as stacking faults in the $(111)_{\text{FCC}} = (002)_{\text{CPH}}$ planes in alternating arrangements.

The ternary eutectics. The eutectic composition in the Ni-W-Al system, determined according to Budberg (1958) was found as Ni-79 w/o, W-10 w/o Al-11w/o with two phases present at room temperature, $\gamma\text{-Ni(W)}$ and $\gamma'\text{-Ni}_3\text{Al}$. The post-UDS structure consisted of a γ matrix reinforced with γ' fibres, which (unlike the Ni-W system) are circular in cross-section throughout (Fig. 5). No precipitates were found in the matrix, but are not ruled out in the fibres in view of certain contrast effects in the TEM examination. The matrix fibre semi-coherent interfaces contain a network of dislocations (Fig. 6).

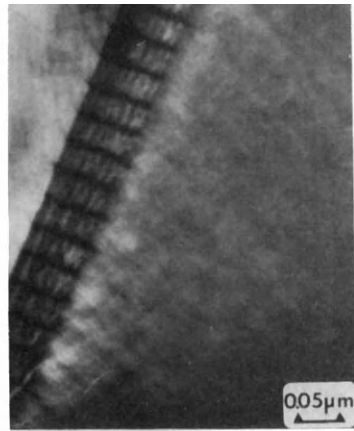
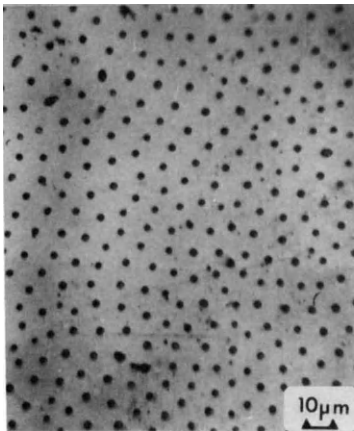


Fig. 5. Ni-W-Al eutectic after UDS. Fig. 6. The interphase boundary between the fibres and the matrix. (Ni-W-Al).

The UDS microstructure of the Ni-Mo-Al eutectic consist of three phases:

- (a) $\gamma\text{-Ni}$ -base solid solution, face centered cubic; has substantial solubility for both Al and Mo.
- (b) γ' - based on Ni_3Al , ordered bcc (L1_2); has a narrow variation about stoichiometry and limited solubility for Mo.

(c) α -solid solution of Mo; has about 10 a/o solubility for Al while that for Ni is only about 1 a/o.

The γ/γ' matrix is reinforced by Mo(α) fibres which have square cross-sections.

Creep

The creep resistance of the Ni-W and the Ni-Mo specimen was found to be influenced by the solidification rate and to improve with decreasing fibre or lamellar spacing (increasing growth rate).

Typical results are given in Table 1.

TABLE 1 Results of Creep Test

Specimen No.	Growth Rate [mm/h]	Temp. [°C]	σ MPa	$\dot{\epsilon}$ [h^{-1}]	Ultimate Creep Strain [%]	Rupture Life [h]	Rupture Stress MPa
Ni-W-1	10	980	188.5	$4.16 \cdot 10^{-4}$	3.04	52	194.2
Ni-W-2	9	970	192.8	$13.26 \cdot 10^{-4}$	6.1	46	213.2
Ni-W-3	8	920	192.8	$10.6 \cdot 10^{-4}$	10.6	156	204.43
Ni-Mo-1	10	980	200	$35 \cdot 10^{-4}$	2.9	74	211.8
Ni-MO-2	20	1000	150	$3.7 \cdot 10^{-4}$	4.1	99	168.4

Creep testing of specimens with increasing load were also conducted. The dependence of the steady-state creep rate on stress was determined. Using the creep equation $\dot{\epsilon} = B\sigma^P$ where B and P are material constants, values of P=6 and P=5 were determined for the Ni-W specimens at 960°C. The higher value of P belongs to the specimen which solidified at a slower rate and due to this has a greater interfibre distance. A similar test was conducted with Ni-Mo specimens at 1000°C. The value of the exponent P was 8.

The matrix-fibre (lamellae) interfaces are subject to high stresses, due to differences in ductility and in thermal expansion coefficients between the phases. The interfaces are sources of dislocations and microtwins. In the Ni-Mo system twinning takes place in the NiMo lamellae (Fig. 7). In the Ni/W system the microtwins observed in the {111} planes and penetrating both the Ni(W) phase and the Ni_4W precipitates, Fig. 8.

As regards the heat treatment (24 hours at 1030°C followed by quenching), the resulting system consists again of a Ni(W) matrix plus W fibres or lamellae, but without any Ni_4W precipitates. Subsequent creep tests showed reduction of the creep rate with time in the steady-state creep region, following which the rate begins to increase. The reduction of the creep rate is attributable to reprecipitation of Ni_4W particles during the creep test. The increase of $\dot{\epsilon}$ is due to coarsening and coalescence of the precipitates.

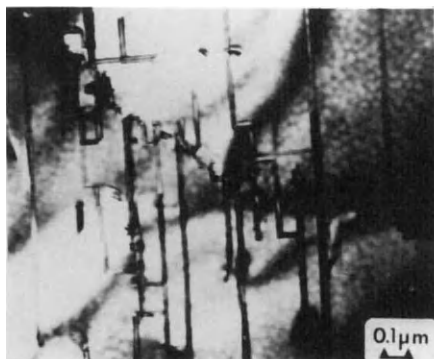


Fig. 7. Twinning in the NiMo intermetallic.

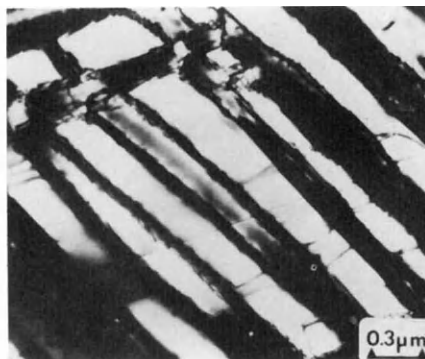


Fig. 8. Microtwin penetrating Ni(W) matrix and Ni₄W precipitates

Acknowledgement

The authors gratefully acknowledge the financial support of the Ministry of Research and Technology (BMFT) W. Germany and Inst. für Werkstoff Forschung of DFVLR Köln.

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Microstructural Basis of Strength and Toughness in Hardmetals

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ABSTRACT

By considering results of recovery experiments and observations of deformed structures and fractures, it is shown that various microstructural requirements for obtaining strength and toughness in WC/Co hardmetals can be explained by simple analogue models based on fibre-composites and statistical theory. The propensity for microcracking, and the work-hardening capacity of the binder phase are important parameters in determining the resistance to overload fracture.

KEYWORDS

Hardmetals, tungsten carbide, cobalt, strength, toughness, recovery, fracture, microstructure, contiguity, microcracks, fibre-composite, statistical, work hardening.

INTRODUCTION

The present paper illustrates how hardmetal behaviour can be modelled analogically in a form which could be developed fundamentally or empirically to identify metallurgical factors of importance in determining strength and toughness. The basic premises are that the WC/Co microstructure consists of two interpenetrating structures of WC and the binder phase, bound together by a very strong WC/binder-phase interface. The models are based on two important corollaries: (i) when a hardmetal undergoes a large permanent strain, both the binder-phase and the WC structure will be permanently strained (but not equally), (ii) fracture planes through the hardmetal must pass through binder-phase regions and the WC structure.

DEFORMATION

When WC/Co hardmetal specimens are annealed at 700°C for 4h after undergoing strain in compression, there is a height recovery as shown in Fig. 1. (Almond, 1982). To provide a rigorous explanation for this phenomenon would involve solving the load transfer relationships, which determine how stresses and strains are partitioned between the constituents of a

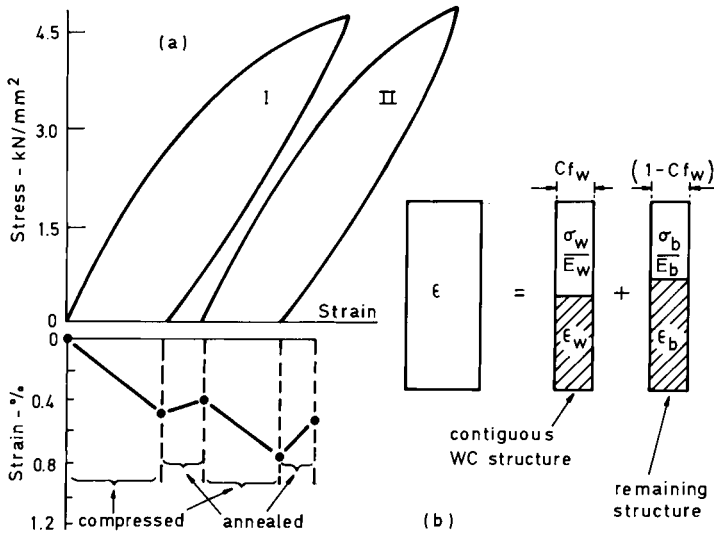


Fig. 1. (a) Stress-strain curves and height recovery measurements for an 11% Co/WC hardmetal subjected to two alternate cycles of compression and annealing at 700°C. (b) Independent parallel fibre model for explaining recovery phenomenon.

composite microstructure. This approach, with approximations, is reasonably successful for fully-elastic and fully-plastic deformation (Gurland, 1979), but a three-dimensional finite element analysis would be needed for elastic-plastic conditions (Sundström, 1973). A semi-quantitative explanation can be made by adopting an analogue model in which the specimens consist of independent parallel fibres of the contiguous WC structure and the binder phase plus non-contiguous WC. Thus in an 11 wt% Co/WC hardmetal specimen the permanent strain after compression ϵ^c was 0.0046, while the residual strain after annealing ϵ^a was 0.0028. Since the total strains in the parallel fibres would be equal, the total strains in the constituents would be:

$$\epsilon^c = \frac{\sigma_w^c}{E_w} + \epsilon_w^c = \frac{\sigma_b^c}{E_b} + \epsilon_b^c \quad (1)$$

$$\epsilon^a = \frac{\sigma_w^a}{E_w} + \epsilon_w^a = \frac{\sigma_b^a}{E_b} + \epsilon_b^a \quad (2)$$

where ϵ , σ , E , and superscripts c and a denote permanent strain, residual stress, Young's modulus, compressed and annealed states, respectively; subscripts w and b refer to the contiguous WC and the remaining structure respectively.

If it is assumed that recovery occurs by reverse plastic flow of the binder phase as a result of creep at 700°C under the action of residual stresses

in the WC structure, then if σ_D^a is negligibly small at 700°C, and there is no reversed permanent deformation of the WC structure, it follows that:

$$\sigma_W^a/E_W = 0; \quad \epsilon^a = \epsilon_W^a = \epsilon_W^C; \quad \sigma_W^C = E_W(\epsilon^C - \epsilon^a) \quad (3)$$

Consequently, there would be a permanent strain of 0.0028 combined with a residual stress of 1.27 kN/mm² in the contiguous WC structure with a value of 707 kN/mm² for E_W . Since the compressive strains were measured after unloading the specimens, the residual stresses would be distributed in proportion to the effective cross-sections of each constituent fibre, such that:

$$Cf_W \sigma_W^C + (1 - Cf_W) \sigma_b^C = 0 \quad (4)$$

where f_W and C refer to the volume fraction and contiguity of the WC structure respectively, and were measured as 0.82 and 0.6 for the specimen in Fig. 1. These values give a σ_b^C of 1.23 kN/mm² which is similar in magnitude to results derived from other recovery measurements, but is higher than would be expected in relation to the flow stress of WC-Co binder-phase alloys at small strains (Roebuck and Almond, 1981).

MICROSTRUCTURAL CONSIDERATIONS

In the fibre-composite analogue, the assumption that deformation is concentrated in the contiguous WC component enables high stresses and large permanent strains to be explained in the WC structure. To explain such stresses at a microstructural level by early models, it would have been necessary to assume that the stresses generated during constrained yielding of thin layers of binder-phase (Drucker, 1965) would be sufficiently high to initiate plastic deformation of WC grains. In constrained yielding of macroscopic metallic layers of thickness t and width a between rigid endpieces, the flow stress is raised by a factor of $(1 + a/3t)$ (Almond and co-workers, 1982) and since the microscopic equivalent of a/t would be approximately f_W/f_b , the flow stress of constrained binder regions in, for example, an 11wt% Co/WC hardmetal (18 vol%Co) would be about 1.26–2.5 kN/mm² relative to a uniaxial value of 500–1000 N/mm².

Consequently, in this and more rigorous models, the existence of stress concentrations needs to be invoked to explain experimental observations of plastic strain in WC grains, if estimates of 4.5–6.7 kN/mm² for the flow stress of WC are correct. In crystallographic terms, plastic deformation in compressed hardmetals occurs on $\{01\bar{1}0\} \langle 2\bar{1}\bar{1}3 \rangle$ slip systems in WC grains, and intergranular microcracks are nucleated at slip band intersections at high strains (Figs. 2a–b). However, the predominant site for microcracking is at WC/WC interfaces, and by analysing the results for a 11wt% Co/WC hardmetal tested in compression (Roebuck and Almond, 1979), it was found that the fraction of interfaces cracked, F , observed the following dependence on strain, ϵ^d , (Fig. 2c).

$$F = 1 - \exp - \left[\frac{\epsilon^d - 0.002}{0.0392} \right]^{1.7} \quad (5)$$

FRACTURE

When WC/Co hardmetals are tested in tension, the strength is often lowered by the initiation of fracture at pores, inclusions and coarse WC grains.

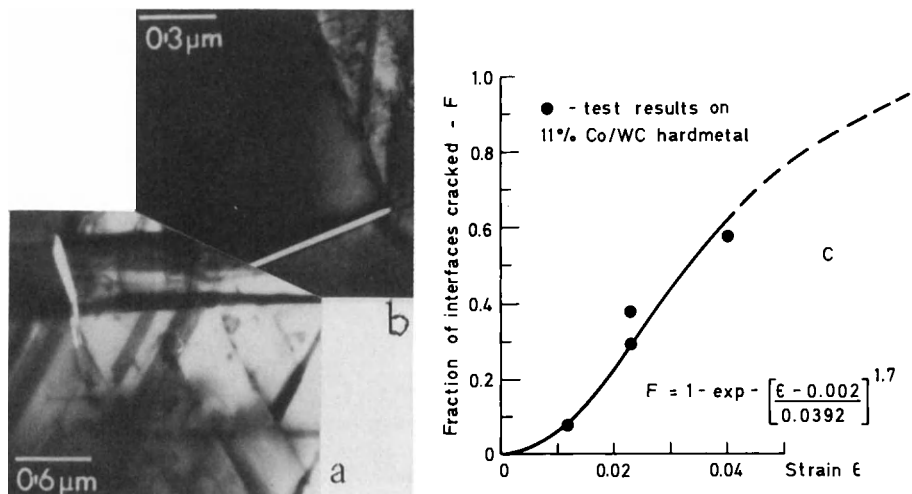


Fig. 2. (a) Microcrack at slip band intersection, and
 (b) Microcrack at WC/WC interface in 11%Co/WC hardmetal;
 (c) Fraction of WC/WC interfaces cracked versus compressive strain in 11%Co/WC hardmetal.

However, these defects are usually too widely separated to affect the growth of large pre-existing cracks which normally show no preference for either the binder-phase or WC constituents but tend to travel intergranularly along WC/WC interfaces (Lea and Roebuck, 1981). Arrested cracks do not exhibit a well-defined crack tip nor a uniquely located plastic zone; rather they consist of interlinked fractured regions interrupted by ligaments of binder phase (Fig. 3a). This configuration resembles that of cracks in composites of ductile fibres in a brittle matrix (Evans and co-workers, 1977) but unlike the latter, the hardmetal structure has a capacity for generating stable microcracks which probably provide an extra source of toughness.

Multi-Ligament Model

Thus in a simplified model, the crack consists of three zones: (A) the completely separated structure, (B) the ligament-zone where a large number of binder phase regions are strained but still intact, and (C) the process zone, where the hardmetal structure is intact, but there are some WC/WC interface-cracks (Fig. 3). In zone B, the crack faces are held together by binder ligaments strained by various amounts ranging from the failure strain, ϵ_f , in the zeroth ligament, to the yield strain in the m 'th ligament. Crack growth by a unit increment (equal to the ligament spacing) involves straining each successive ligament by a strain increment equal to that experienced by its neighbour in the previous growth increment. Consequently, the energy W involved in unit crack growth in an m -ligament system is the same as that for unit crack growth achieved by straining a single ligament to fracture, which is the model usually used for hardmetals. Thus, to obtain improved toughness it is necessary to maximise W or to introduce another energy dissipation mechanism. The second objective seems to be achieved in WC/Co hardmetals with a resultant n -fold increase in W , by the crack being periodically diverted onto parallel planes so that ligaments

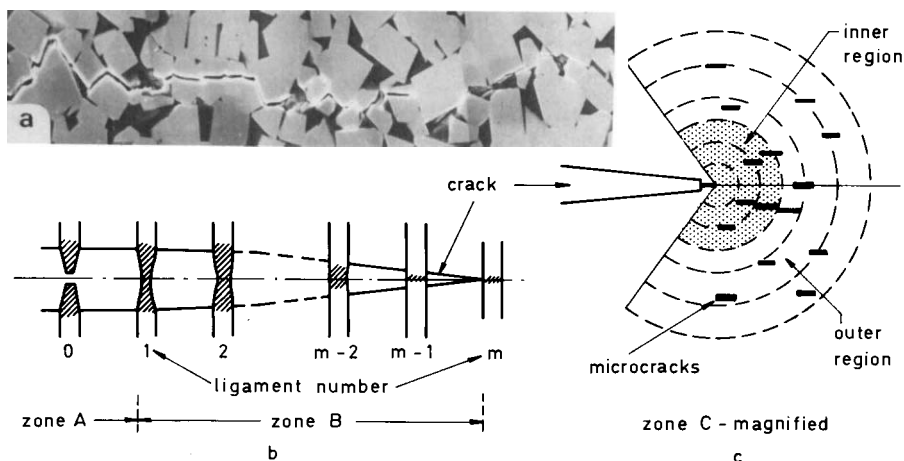


Fig. 3. (a) Arrested crack in 11%Co/WC hardmetal;
 (b) Multi-ligament model of crack path;
 (c) Process-zone at crack tip showing simplified tensile-stress/ failure probability contours and microcracks (based on Evans 1977).

are being strained simultaneously on n parallel planes. The precursors for crack branching will be microcracks initiated in the process zone C. The magnitude of W can be increased by inhibiting necking of the ligaments by using a binder phase with a high work hardening capacity so that deformation penetrates to the maximum possible depth below the fracture surface. Similarly, Hahn and Rosenfield (1968) found that in some steels and aluminium alloys, the plastic zone size and the K_{IC} fracture toughness were proportional to a work hardening index N .

A further improvement in toughness can be obtained by altering the microstructural dimensions. Thus, in the planar intersection of a crack with the microstructure, the areal fractions A_i of each constituent are equal to their volume fractions, f_i , such that: $A_b = f_b$. However, associated with each intersected binder phase region, there is a ligament of depth λ equal to the binder region dimensions. Consequently, for a given hardmetal composition, the volume of binder phase deformed during crack propagation and the fracture toughness G_{IC} value should be proportion to λ , and this is observed experimentally. Combining these observations, the multi-ligament model predicts that for a given binder phase content, G_{IC} will be proportional to $nN\lambda W$, which differs from previous values by a factor nN (Almond, 1982).

An explanation for the high intrinsic toughness of WC/Co hardmetals emerges from applying the ligament model to microcracks. Thus, if the microcracks are smaller than the ligament spacing, each increment of crack growth will involve straining an additional ligament, and growth will be increasingly difficult until the stable crack size of m -ligaments is reached. The process resembles the increased resistance to crack growth with increase in applied load in some metals, which is explained in terms of a rising R -curve which describes the increasing difficulty of fracturing material at the crack tip ahead of an advancing crack (Turner, 1979). The existence of a microstructural version in WC/Co hardmetals, explains their high tolerance for microcracks and contributes towards their good thermal shock

resistance, compared with that of other hardmetals.

Process Zone

The sequence of microcrack formation in the process zone has a major influence on subsequent crack propagation and fracture toughness. The positional incidence of WC/WC interface cracking can be calculated by deriving an equivalent expression to equation 5, but expressing the results in tensile stresses rather than strains. Then by using standard expressions for the tensile stress field around a crack, contours for the probability of microcracking can be calculated for different distances from the crack tip. The process zone can be further sub-divided into an inner and outer region (Fig 3c) with microstructurally dependent dimensions (Evans and co-workers, 1977). Formation of microcracks in the outer region increases the material's compliance (decreased effective elastic modulus) with a consequent decrease in the crack opening displacement and an increase in toughness. The cracks also provide potential sites for crack branching. However, in the inner zone a high density of microcracks is a disadvantage if they are contiguous with the main crack and serve only to lengthen it. Hence, high WC contiguity should be avoided. The radius of the inner zone is dependent on the stress intensity factor, K_I , and consequently it would be expected that the tendency for microcracking and crack branching would be different in simple overload fracture from that in fatigue or stress corrosion. This has not yet been tested, although differences in fracture-surface morphology have been observed in overload and fatigue fracture, as shown in Fig. 4 (Almond and Roebuck, 1980).

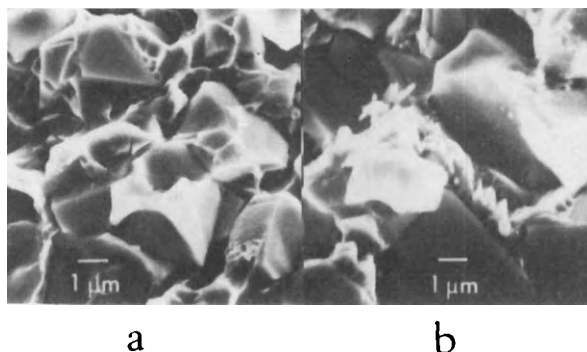


Fig. 4. Electron micrographs of fracture path in fatigue specimen of coarse-grained 11wt%Co/WC hardmetal showing (a) unstable crack propagation and (b) fatigue crack growth.

From a metallurgical viewpoint, to increase toughness it is necessary to design a microstructure which produces a favourable microcrack distribution function. The requirements are similar to those for toughening the multi-ligament model, in that the binder phase should have a high work hardening capacity so that plastic strain is distributed as widely as possible in the microcracked region. Also, the binder-phase regions should have a high failure strain but it is not yet clear whether this property can be predicted accurately from uniaxial tensile tests on binder phase alloys (Roebuck and Almond, 1979). Implicit in all these considerations is that the binder phase should form a very strong interface with the WC structure, and it should not exhibit a tendency for cleavage fracture, either in the form of microcracking or as an extension to the main crack.

CONCLUSIONS

The results of recovery experiments are consistent with a fibre composite model of a WC/Co hardmetal, in which the contiguous WC structure supports high stresses and undergoes permanent deformation in compression. The existence of a recovery effect needs to be taken into account when considering the dimensional stability of hardmetal tools or precision parts that are subjected to cold work and exposed to high temperatures.

By using a multi-ligament model for the crack configuration it is shown that toughness can be increased by increasing the binder-phase spacing, and by using a binder phase with a high work hardening capacity, which also assists in producing microcracking at WC/WC interfaces. Controlled microcracking improves toughness by blunting the main crack and by promoting energy dissipation by crack branching. At a microstructural level, the high toughness of WC/Co hardmetals is probably due to a high tolerance for the existence of microcracks, which encounter increased resistance to growth until they have strained sufficient binder-phase ligaments to assume the stable macroscopic crack configuration.

The practical relevance to improving hardmetals or developing substitutes is that wide binder-phase spacing, controlled microcracking, and a binder metal with high work hardening capacity produce high toughness in overload fracture, and resistance to thermal shock, fatigue and stress corrosion. A highly continuous WC network is needed to obtain the maximum fibre strengthening effect, while the contiguity should be of a form that avoids providing low energy fracture paths and inhibiting other energy dissipation processes.

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Magnetic Properties of the Cobalt Matrix in WC-Co Compacts

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ABSTRACT

A series of sintered WC-Co hardmetals containing 3 to 25 wt% Co and a presintered (i.e., compressed but unsintered) hardmetal containing 8 wt% Co were studied by measuring their magnetic properties in a Foner magnetometer. Internal demagnetising factors (N_{if}) of the hardmetals were obtained from inverse slopes of anhysteretic magnetisation curves after correcting for external demagnetising factors. The very small magnitudes of N_{if} of sintered materials confirm that Co is not present as discrete particles but as a continuous interlinked network of ferromagnetic thin films resembling a ferromagnetic sponge. The decrease in coercivity (H_c) occurring on densification is ascribed to magnetostatic interactions between newly bonded Co films. Whereas the H_c of the continuous matrix depends on the mean Co layer thickness the remanence ratios (j_r), after correction for an external demagnetising factor, depend on the thickness of the thickest Co films present. Relationships between Co content and/or WC grain size and some magnetic properties (N_{if} , H_c , and j_r) are established. Some mechanical properties are considered.

KEYWORDS

Ferromagnetic sponge; internal demagnetising factor; anhysteretic magnetisation; densification; coercivity; remanence; hardmetals.

INTRODUCTION

Cobalt in WC-Co cemented compacts is the phase which binds refractory WC powders, on sintering at about 1450°C, into very hard materials. The Co content can be varied from 3 to 25 wt% and WC grain sizes can range from 0.2 to 5 μm . The ferromagnetism of Co lends itself to the development of non-destructive quality control tests. Although such tests are widely applied in practice, the mechanism giving rise to the observed parameters is not unambiguously known. An important aspect of magnetic measurements is the role played by demagnetising fields, $H_d = N_e M$, where M is the measured

magnetisation per unit volume at applied field H and N_e the geometrical demagnetising factor of the specimens which can be calculated or read from graphs, (Stoner, 1945), for ellipsoidally shaped specimens. The magnetisation of the magnetic fraction, $M/(1-V)$, written as M_f , requires that the associated demagnetising factor N_{ef} be defined as $N_e(1-V)$ so that H_d remains unaltered. V is the non-magnetic volume fraction.

Internal demagnetising factors N_i arising from discrete particles, voids or non-magnetic inclusions in heterogeneous materials in the interior of the specimens, can only be obtained by experiment. There are a few theories applicable to heterogeneous materials (Néel, 1948; Humphreys and Rhodes, 1964) but these hold for large applied fields and although these theories have been studied experimentally for WC-Co (le Roux and McLachlan, 1982), this paper will deal only with results obtained from low field anhysteretic measurements, as outlined by Berkowitz (1969) and Kneller (1969). The inverse anhysteretic slope for $H \rightarrow 0$ is:

$$H/M_a = \chi_a^{-1} = N_T = N_e + N_i \quad (N_e \ll N_i) \quad (1)$$

where H is the applied field, M_a the measured anhysteretic magnetisation, χ_a the anhysteretic susceptibility, N_T and N_i the total and internal demagnetising factors, respectively. For the magnetic fraction, eq. (1) becomes, on multiplying by $(1-V)$:

$$H/M_{af} = \chi_{af}^{-1} = N_{Tf} = N_{ef} + N_{if} \quad (N_{ef} \ll N_{if}) \quad (2)$$

The factors affecting N_{if} depend on the magnetic particle shape, on the degree of particle interconnectivity and on the magnetic fraction. When the particles are spherical and isolated from each other $N_{if} \approx 1/3$. This decreases to $\sim 1/30$ in a continuously interconnected sponge, where N_{if} is due to voids. The intermediate state depends on the magnetic fraction and on the extent of agglomeration of ferromagnetic particles which occurs even in dilute mixtures. The external geometric demagnetising factors N_{ef} also change through the range $1/3$ to $1/30$ according to specimen shape, dimensional ratio and magnetic fraction. Inverse anhysteretic slopes provide a total demagnetising factor N_{Tf} and to find N_{if} , N_{ef} should be duly taken into account.

This paper presents some measurements of N_{if} as well as an analysis of the remanence ratios and coercivities of sintered and presintered materials. A comparison with previous measurements on WC-Co (Kranz, 1956) has been made.

EXPERIMENTAL

Apparatus and Measurements

Magnetisation (M - H) curves were measured using a vibrating sample magnetometer, (Foner, 1959; Doyle, 1975). The magnetisation of the specimens was determined by comparison with very pure nickel standards with similar specimen shapes. The error of the measurements was maintained at less than 1%. By winding a set of coils around the pole pieces and driving these with a variac and transformer, ac fields of up to 0.0995 MA/m peak to peak were obtained. This allowed a point by point plotting of anhysteretic curves (Berkowitz, 1969). All anhysteretic measurements were made for applied field values of $|0.199|$ MA/m.

Specimens

A series of WC-Co specimens with a constant coarse grain size of 2-4 μm were sintered at about 1450°C. They were supplied in the form of rods 7 (or 10) mm in diameter from which sets of discs 0.5, 1.0 and 1.5 (or 0.7 and 1.4) mm, were sliced on a diamond saw and, with the exception of a single WC8wt% Co presintered sample, were all examined in the as-sintered condition. A similar series of WC-8Co hardmetals with grain sizes varying from (2-4) to ($\frac{1}{2}$ -2) μm and one presintered sample were also examined. The densities of all specimens were measured by the suppliers. Sintered specimens are nearly twice as dense as presintered specimens. All sintered specimens were etched by standard techniques to remove surface damage to a depth of about 20 μm . The applied field was in the plane of the discs. Although ellipsoidal specimens were preferable this requirement could not be met as the extreme hardness of the material makes machining difficult and although shaping of such thin specimens before sintering is possible, surfaces not representative of the bulk material could occur in variable thicknesses. Spark erosion has been found to cause some permanent damage to a depth of at least 50 μm in Co, (le Roux, unpublished). The effects of ellipsoidal shapes were controlled by keeping the disc-shaped specimens thin. For either very thin specimens or low Co content, N_{ef} is very small. As tabulated N 's do not take sharp corners into account an error of 1-3% for $N_{\text{ef}} < N_{\text{if}}$ has been estimated from the small variations in the results for changes in N_{e} (or N_{ef}) in particular grades. When $N_{\text{ef}} \approx N_{\text{if}}$ the error is about 10%.

TABLE 1 Measured Magnetic Properties of WC-Co Hardmetals

Spec. wt% Co	N_{ef}^a	$(N_{\text{ef}} + N_{\text{if}})^b$	N_{if}^c	M_r/M_s^d	WC grain size μm	H^e A/m
3	0.003	0.0312	0.0282	0.144	2-4	12 800
	0.005	0.0250	0.0200	0.146		
7	0.007	-	-	0.117	2-4	8 040
	0.012	-	-	0.104		
	0.016	-	-	0.108		
8(J8-1)	0.007	0.0312	0.0242	0.108	2-4	6 760
(J8-2)	-	-	-	0.108	1-4	6 760
(469)	-	-	-	0.120	1-3	7 480
(592)	-	-	-	0.126	1-2 $\frac{1}{2}$	7 800
(70/1)	-	-	-	0.156	$\frac{1}{2}$ -2 $\frac{1}{2}$	10 000
(891)	-	-	-	0.164	$\frac{1}{2}$ -2 $\frac{1}{2}$	11 500
(62/1)	-	0.0288	0.0218	0.165	$\frac{1}{2}$ -2	10 800
(890)	-	-	-	0.167	$\frac{1}{2}$ -2 $\frac{1}{2}$	10 700
10	0.008	-	-	0.111	2-4	7 080
	0.016	-	-	0.095		
	0.022	-	-	0.093		
20	0.017	0.0355	0.0185	0.094	2-4	5 650
	0.032	0.0424	0.0104	0.074		
25	0.020	0.0317	0.0117	0.095	2-4	5 410
	0.039	0.0440	0.0050	0.067		
(J8-1) ^g	0.004	0.111	0.107	0.0434	2-4	7 321

a, b, c, geometric, total, internal demagnetising factors of magnetic fraction, respectively; ^d remanence ratios; ^e coercivity; ^g presintered specimen

RESULTS

The magnetisation curves were recorded and analysed. The remanence M_r and coercivity of each specimen were obtained from the intercepts made by hysteresis loops on the M_r and H axes, respectively. The inverse anhysteretic slopes were measured for specimens containing low (3, 8) and high (20, 25) wt% Co having the same grain size. Included in this is one presintered specimen. These are listed in Table 1 and plotted in Figs. 1 and 2. High field measurements have been made for all these specimens but are reported elsewhere (le Roux and McLachlan, 1982).

Internal Demagnetising Factors

To assess the significance of the observed values of N_{if} , they have been compared with the classical results obtained, using eq. (2f), by Forrer, Baffie and Fournier (1944); Gerlach, Rennenkampf and Brill (1948); and Kranz (1956) for ferromagnetic particles of various shapes and concentration embedded in a non-magnetic medium as shown in Fig. 1. The presintered specimen lies close to the curve for pressed Co, Fe and Ni powders whereas the sintered specimens lie close to the curve for WC-Co hardmetals reported by Kranz. The difference between sintered and presintered specimens is large suggesting that the sintered materials with small N_{if} have continuously interlinked networks of thin Co films whereas presintered materials have only partial networks.

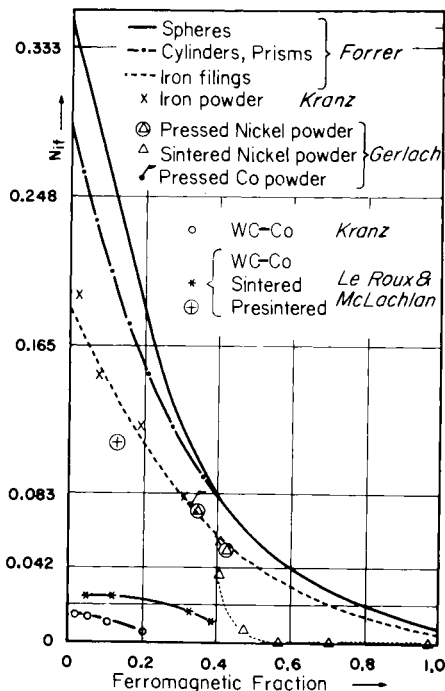


Fig. 1 N_{if} as a function of $(1-V)$
(After Kranz (1956))

Coercivity of Sintered Materials

The structure of the Co matrix may be seen in SEM micrographs (Tillwick, 1972; Tillwick and Joffe, 1973) and measurements made on small arbitrarily selected surface areas show that WC-3Co, WC-7Co and WC-25Co (constant grain size of 2-5 μm) contain Co layers of area $\geq 1\mu\text{m}^2$ on 3%, 7% and 30%, respectively, of the surface area examined. On decreasing the WC grain size, the Co layers are decreased in thickness but increased in number (Kreimer, 1968). A model of the Co sponge may therefore be visualised as a system of thick Co layers connected to each other through thick and thin layers. The decreasing Co content causes connecting layers to become thinner and thick layers to occur less frequently. In fine-grained material Co layers are more uniformly thin.

The specimens examined are divided into two sets in one of which the Co content varies while the WC grain size remains constant and in the other the Co remains constant while the WC grain size varies. The coercive force increases linearly with the inverse of the mean Co layer thickness $\bar{\ell}_{\text{Co}}^{-1}$, (Tillwick and Joffe, 1973; Exner and Fischmeister, 1966). The increase in H_c for both sets of specimens is in agreement with previous observations showing a correlation with inverse layer thicknesses. H_c increases exponentially with decreasing Co volume fraction for a constant WC grain size and $\bar{\ell}_{\text{Co}}^{-1}$ varies from about 0.3 to 1.0 μm for 3 - 25Co, (Tillwick, 1972).

Remanence Ratios of Sintered Materials

The observed values of the remanence ratios ($M_r/M_s = j_r$) are strongly dependent on N_{ef} . Intrinsic remanence ratios, characteristic of each specimen, can only be determined for samples with zero N_{ef} and these are obtained by

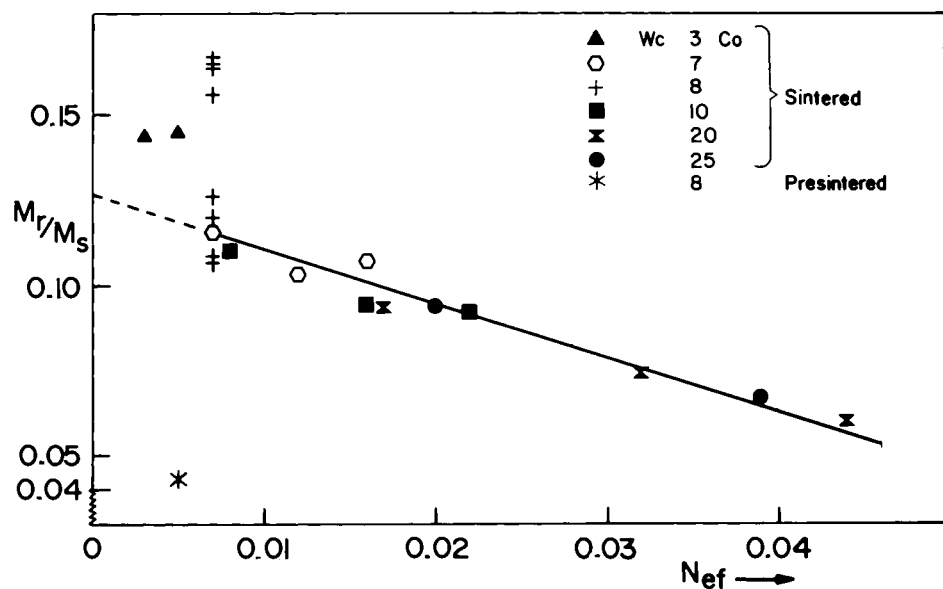


Fig. 2 Remanence Ratios as a function of N_{ef}

extrapolating N_{ef} to zero as in Fig. 2. A straight line is obtained which, on extrapolation, puts j_r equal to a constant of about 0.13 for all specimens with a constant grain size, excepting only WC-3Co where $j_r > 0.13$. Fine-grained WC-8Co also has $j_r > 0.13$. The constant magnitude of j_r is clearly insensitive to the varying $\bar{\ell}_{Co}^{-1}$, showing that there is no simple correlation between j_r and ℓ_{Co} . The thin layered WC-8Co and WC-3Co show that j_r is not always constant but increases when grain size decreases or when the Co content is very small. A constant j_r was reported by Kranz (1956) for WC (1 - 12 wt%)-Co hardmetals where $j_r = 0.38$. The large H_c 's for these specimens show that both the grain size and $\bar{\ell}_{Co}$ are small. The very thin layers cannot therefore be responsible for $j_r = 0.13$. It is concluded that the thickest layers determine j_r which varies inversely with the thickness of these thickest layers. In coarse grained assemblies magnetisation reversal is expected to occur mainly by domain wall motion (Kneller, 1969; Berkowitz, 1969). The reversal mechanism could be nucleated in the thickest layers and this mechanism could be transmitted to and through neighbouring thin layers by magnetostatic interactions.

Remanence and Coercivity of Presintered Materials

For presintered WC-8Co, also a coarse grained specimen, $j_r \ll 0.13$. This small j_r is associated with a large N_{ef} which in turn is associated with discrete Co particles. The coercive force decreases on sintering and densification. Because the Co is spread into thinner layers on sintering the H_c is expected to increase, but as the layers are also becoming interconnected the magnetostatic interactions, occurring between close packed ferromagnetic particles, will cause the H_c , as well as N_{ef} , to decrease (Bean 1955). The observed 10% decrease can be regarded as a resultant of these two competing processes.

CONCLUSIONS

The magnetic properties described can be used as non-destructive quality control tests. All properties measured provide structural information which, taken together, can help to characterise the material. The internal demagnetising factor describes the state of interconnectivity of ferromagnetic Co. The remanence and coercivity are measures of the thickest and average Co layers, respectively, and provide information on the range of layer thicknesses present. Since mechanical properties of thick and thin layers are different, the wide range of layer thicknesses usually present in hardmetals is a sign of non-uniform mechanical properties in these materials. The wider the range between thick layers with the properties of bulk Co, and the thinnest layers with the properties of thin film Co, the more pronounced will be the non-uniformity of the mechanical properties. Since layer thicknesses are largely determined by WC grain sizes, there is a built-in obstacle to attaining a uniform state although, with a careful choice of grain size, the non uniformity can be minimised. There is another factor contributing to the non uniform state. Ferromagnetic particles tend to agglomerate resulting in Co-rich and Co-lean regions. The preparation and milling methods of WC and Co powders in production will have to be modified to take account of this factor.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge their indebtedness to : Professor F.R.N. Nabarro, F.R.S., for his help in clarifying many ideas; Boart Hardmetals

(Pty) Ltd., for specimens, and Boart Research Centre for financial sponsorship and their continuing interest in this research.

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ACKNOWLEDGEMENT OF COPYRIGHT PERMISSION RECEIVED.

The authors acknowledge with thanks the receipt of permission from:

- (1) SPRINGER-VERLAG, Heidelberg, West Germany, for data due to Kranz (1956);
- (2) JOURNAL DE PHYSIQUE, Les Ulis Cedex, France, for data due to R. Forrer, R. Baffie and P. Fournier (1944);
- (3) DR RIEDERER-VERLAG GmbH, Postfach 447, 7000 Stuttgart 1, W-Germany (ZEITSCHRIFT FÜR METALLKUNDE) for data due to W. Gerlach, J.V. Rennenkampf and A. Brill (1948).

The Palmqvist Test and its Applications in WC-Co Alloys

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ABSTRACT

The literature on Palmqvist tests in WC-Co alloys has been reviewed. The possible applications of the test have been discussed and a new empirical relationship between Palmqvist toughness and bulk toughness has been proposed.

KEYWORDS

Surface toughness, cemented carbides.

INTRODUCTION

The Palmqvist test consists of producing cracks on a highly polished surface by means of a Vickers indenter and in using the length of the cracks as an indirect measure of resistance to surface crack propagation. The cracks, which are called Palmqvist cracks, are produced at the corners of the Vickers indentation (Palmqvist, 1962). In WC-Co alloys having cobalt content ≥ 6 wt % Palmqvist cracks are the only cracks formed around Vickers indentations (Perrott, 1977); therefore they account for all the fracture energy dissipated during the indentation process.

PALMQVIST CRACKS

Metallographic investigations have shown that Palmqvist cracks are nucleated just below the corners of Vickers indentations. In WC-Co their depth is approximately equal to the depth of the indentation, while their length (i.e. the length of the cracks' traces on the indented surface) can be much larger than the length of the diagonals of the indentation (Perrott, 1977). The cracks lie on planes defined by the diagonals and the apex of the indentation and propagate entirely within the plastically deformed region surrounding the indentation.

Almond and Roebuck (1979) have shown that Palmqvist cracks in WC-Co propagate both during the loading and during the unloading of the indenter. The ratio between growth in loading and growth in unloading increases with increasing cobalt content in the material. According to the results of Perrott's ana-

lysis (1977) of the stress distribution around Vickers indentations, during loading the free surface of the plastically deformed zone surrounding the indentation is under a tensile hoop stress, while the free surface of the elastically deformed zone surrounding the "plastic" zone is under compression. When the indenter is unloaded the compressive elastic strains are removed and crack growth continues, driven by the tensile residual stresses.

PALMQVIST TOUGHNESS

Palmqvist was the first to observe that a linear relationship exists between the sum of the lengths of the four cracks at the corners of Vickers indentations ($\Sigma \ell$) and the load, P , applied to the indenter:

$$\Sigma \ell = a_1 P - a_2 \quad [1]$$

where a_1 and a_2 are constants which depend on the composition and the microstructure of the material. a_1 decreases with increasing cobalt content while a_2 increases (Palmqvist, 1962).

The potential of the parameter a_1 as an indirect measure of the work required to produce cracks was not fully appreciated until Exner (1969) proposed to define $W = 1/a_1$ as "the crack resistance" of the material (W was later called "Palmqvist toughness"). Exner's work awoke interest in the Palmqvist test not only because he defined W but mainly because he established the conditions under which the Palmqvist crack length is reproducible. Exner (1969) proved that Palmqvist cracks have a constant length at a given load and in a given material only if the compressive stresses introduced by grinding are completely removed from the surface to be indented, either by prolonged polishing or by annealing. Exner (1969) concluded that prolonged polishing also leads to the disappearance of the constant a_2 from Eq. [1]. Recent work (Luyckx, 1982) has confirmed that the value of a_2 depends on the preparation of the indented surface, at least for cobalt contents of up to ~ 9 wt%. The value of a_1 , however, seems to be independent of the degree of polishing, within reasonable limits (Luyckx, 1982). Since the parameter of interest is a_1 ($a_1 = 1/W$), the surface preparation for Palmqvist tests seems not to be as critical as was believed up to now.

It has been established that Palmqvist toughness, $W = 1/a_1$, increases with increasing cobalt content (Viswanadham and Venables, 1977; Warren and Matzke, 1981; Dawihl and Dworak, 1976), carbide grain size (Zum Gahr and Fischer, 1981) and mean free path (Zum Gahr and Fischer, 1981; Peters, 1979). Peters and Cooper (1978) reported that $\Sigma \ell$ (see Eq. [1]) increases with decreasing carbon content, as did Suzuki and co-workers (1969), and attributed this to the increase in the amount of tungsten dissolved in the binder, the fracture of their samples being intergranular. Sadahiro (1979), on the other hand, found that W is independent of carbon content.

It is interesting to note that W does not change after hot isostatic pressing (Sadahiro, 1979), therefore it must be independent of porosity.

CORRELATIONS WITH OTHER TOUGHNESS PARAMETERS

The Palmqvist toughness has the dimensions of an energy per unit area and therefore attempts have been made to relate it to the energy release rate, G_{IC} , of fracture mechanics. Exner and co-workers (1978) and Perrott (1978) found experimentally that the relationship between W and G_{IC} is linear only up to $G_{IC} \approx 0.2$ kJ/m² and $W \approx 1$ MJ/m². Peters (1979) established the empirical relationship $W = 5.74 \times 10^3 G_{IC} - 8.63 \times 10^4$, which is valid only for cobalt contents ≤ 10 wt% and agrees quantitatively with the results of both

Exner and co-workers and Perrott.

Attempts have also been made to find a simple relationship between K_{IC} , the bulk fracture toughness, and W , the Palmqvist toughness, which is sometimes referred to as "the surface toughness", although much of the energy expended in plastic deformation in the indentation process is not directly related to the Palmqvist cracks. The experimental methods to determine K_{IC} are generally costly, therefore the simple Palmqvist test would be a convenient replacement. It has been found experimentally (Dawihl and Dworak, 1976) that K_{IC} and W are not linearly related, and indeed K_{IC} and W have different dimensions. Warren and Matzke (1981) have recently proposed the semi-empirical relationship $K_{IC} = 0.087\sqrt{HW}$, where H is the hardness of the cemented carbide. This relation is dimensionally acceptable and appears to agree with experimental results up to $K_{IC} \sim 18 \text{ MN m}^{-3/2}$, i.e. for most commercial grades. Niihara and co-workers (1982) have established a correlation between a normalized fracture toughness/hardness parameter and the relative length of Palmqvist cracks and indentation size. This correlation agrees with experimental results up to cobalt contents of at least 15 wt%, but is of less practical value than Warren and Matzke's correlation (1981), since it involves parameters which are difficult to determine with precision.

Viswanadham and Venables (1977) found a linear relationship between $1/W$ and the hardness, H . When plotting $1/K_{IC}$ against H , using results at constant grain size which were published by Chermant and Osterstock (1976) and Pickens (1977), we found a monotonic correlation, which may be linear (bearing in mind the errors involved). It is possible, therefore, that at constant grain size W and K_{IC} are related in the following way:

$$\frac{1}{W} = \frac{\alpha}{K_{IC}} + \beta \quad [2]$$

α and β being constants. Work is in progress to verify this relationship.

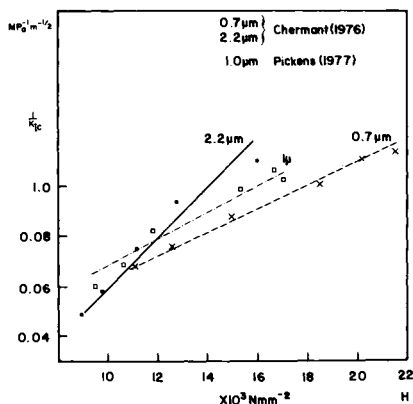


Fig. 1. A linear relationship may exist between $1/K_{IC}$ and H (see text). The K_{IC} and H values have been taken from Chermant and Osterstock (1976) and Pickens (1977).

APPLICATIONS AND DISCUSSION

Palmqvist tests are often used to measure qualitatively the toughness of WC-Co (see, for example, Knotek and co-workers, 1981). However, relationships such as the ones proposed by Warren and Matzke (1981) and by Niihara and co-workers (1982) suggest that these tests may provide also a quantitative measure of K_{IC} , at least within the range of materials for which the relationships have been proved valid.

The main objections to the acceptance of the Palmqvist test as a standard test have been: a) the Palmqvist crack length, Σl , depends on the surface preparation of the specimen; b) the preparation of the specimen surface is time consuming; c) the test can only be used for grades having a cobalt content not higher than 10-15 wt% (depending on grain size); d) the test has no theoretical basis. However: a) the parameter of interest is not Σl but W , which is independent from surface preparation within reasonable limits (Luyckx, 1982); b) the cost of surface preparation is offset by the small size and the small number of specimens required; c) grades containing up to 10-15 wt% Co include the majority of commercial grades; d) the standard industrial test presently used, the TRS test, has no stronger theoretical basis than the Palmqvist test as far as measuring toughness is concerned (Pickens, 1977), however useful it is in other aspects.

An advantage of the Palmqvist test, when compared with other mechanical tests, is its sensitivity to small effects. For example, Palmqvist cracks measurements have shown changes in WC-Co samples after compression, which had not been shown by hardness or TRS measurements (Exner and Gurland, 1970; Contre and co-workers, 1971; Luyckx, 1981). Suzuki and co-workers (1969) found that Σl (see Eq. [1]), is more sensitive than hardness to small variations in bending strength. Almond and Roebuck (1981) showed that at low temperatures hardness does not vary with carbide grain size while Σl does. The ability of showing up small changes in microstructure and composition makes the Palmqvist test a potential valuable tool in material development.

The main application of the test, however, should be in the indirect determination of surface toughness, which is a critical property of most WC-Co components, independently from bulk toughness. At cobalt contents ≥ 6 wt% it is likely that correlations exist between Palmqvist toughness and wear mechanisms involving fracture, since the Palmqvist cracks are the only cracks nucleated by indentations (Perrott, 1977). It would be, of course, of practical importance to determine such correlations.

As a conclusion, Figs. 2 and 3 summarize results from different authors in the form of Σl vs. P plots, obtained from Palmqvist tests. In Fig. 2 results are compared which were all obtained from 6 wt% Co grades having similar fine grain size. The slopes of the three curves are the same, which indicates that the surface toughness, W , of the three grades is the same. In contrast, the results in Fig. 3, which were obtained from nominally similar coarse grained grades, do not agree. Both the two 9 wt% Co grades (lines A and B) and the two 11 wt% Co grades (lines C and D), have very different surface toughness. As mentioned above, the discrepancy can be a reflection of small differences in the microstructure (e.g. different grain size distribution or tungsten concentration in the binder) which may not be revealed by other mechanical tests. Fig. 3, therefore, suggests a further application of the Palmqvist test: in the choice of the most suitable material among nominally equal grades.

ACKNOWLEDGMENTS

The author wishes to thank Professor F.R.N. Nabarro and Dr. G.J. Rees for their very helpful criticism and suggestions, Dr. R. Warren (Chalmers University, Göteborg), Mr. R. Cooper and Dr. C.T. Peters for useful comments. It is also gratefully acknowledged that this work has been sponsored by Boart International Ltd., South Africa.

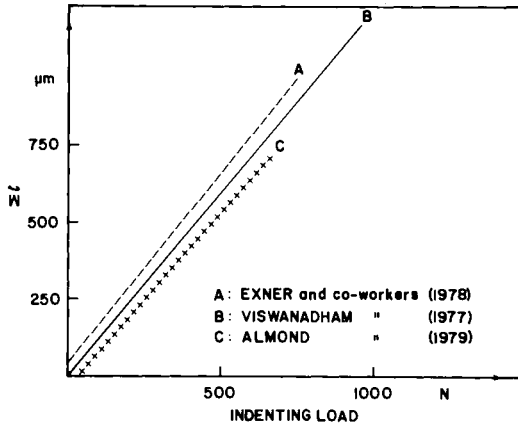


Fig.2. Results obtained by different authors from 6 wt% Co samples having similar fine grain size. The sum of the Palmqvist cracks, $\Sigma \ell$, has been plotted against the indenting load, P . There is good agreement among the values of W obtainable from the three graphs.

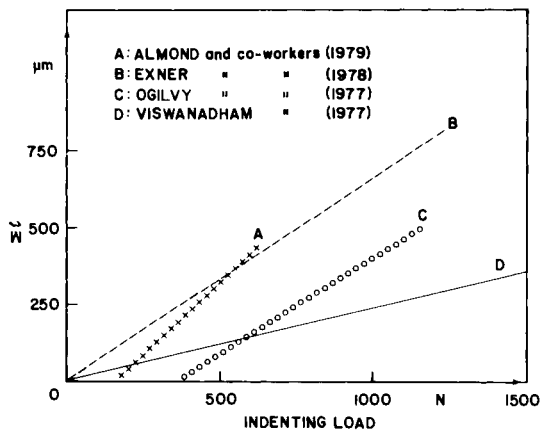


Fig. 3. Results obtained by different authors from 9 wt% Co samples having fine carbide grain size (A and B) and from 11 wt% Co samples having coarse grain size (C and D). The W values obtainable from these graphs vary considerably from author to author.

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The Inter-relation of Microstructure, Toughness and Fatigue Crack Growth Behaviour in WC-Co Hardmetals

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ABSTRACT

Utilising the double torsion test specimen geometry, the toughness and fatigue crack propagation behaviour of WC-Co hardmetals have been studied as a function of Co-content and grain size and have been shown to respond identically to microstructural manipulation. Fractographically, the two crack processes are indistinguishable and mechanistically cyclic crack growth occurs by static modes of fracture such as cleavage and microvoid coalescence. A procedure is thence indicated whereby fatigue crack propagation rate can be estimated through a knowledge of the more readily measured fracture toughness.

KEY WORDS

Fracture. Hardmetals. Fatigue crack propagation. Fracture toughness.

INTRODUCTION

For many engineering materials fatigue crack growth plays a dominant role in determining component life. In general terms this is also true for many applications of tungsten carbide-cobalt (WC-Co) hardmetals, which are used almost universally in variable loading situations.

Often, fracture toughness values for materials are either commonly available or can be determined by standard laboratory procedures. Corresponding fatigue crack propagation data, however, are much less available and this applies particularly to nominally 'brittle' materials, for which conventional test geometries are totally inappropriate. WC-Co hardmetals typify this situation. There is a wealth of information on fracture toughness but only limited work has been directed at measuring fatigue crack growth and identifying the mechanisms of cyclic crack propagation.

The object of this paper is to report on a study aimed at evaluating the important microstructural parameters controlling the fatigue process in hardmetals, in comparison with those affecting conventional strength and

toughness properties, with a view to exploring unifying factors in structure-property relationships in these materials and thereby identifying possible predictive procedures.

EXPERIMENTAL PROCEDURE

The most rational and widely used approach to the problem of dealing with fatigue is the determination of cyclic crack growth rate as a function of operating stresses and prevailing flaw sizes, i.e. the stress intensity range (ΔK). The data obtained not only characterises the alloys tested but enables a fracture mechanics evaluation of a component's expected service performance.

A wide variety of specimen types can be used to obtain fracture and fatigue data. The majority of these, however, have been developed for, and are ideally suited to, relatively ductile materials. While most are satisfactory for determining fracture toughness values in brittle materials, slow crack growth measurements present a more difficult problem. These materials are generally very load sensitive and the stress intensity has to be carefully controlled to prevent premature fast fracture. For this reason the 'constant-K' geometries, summarised by Evans (1974) are preferred.

The double torsion test technique, in particular, first proposed by Outwater and Jerry (1966), has recently gained popularity and has been used quite extensively by various authors to measure fracture toughness and to obtain slow crack growth data in brittle materials subjected to both monotonic and fatigue loading. The major advantages are that the specimen geometry is relatively simple and easy to manufacture. The specimen consists essentially of a thin, flat rectangular plate with a starter notch cut into one end (Fig. 1). The co-linear point loads applied at the notched end effectively cause opposing torsional moments on each side of the plate resulting in crack propagation down the centre line of the specimen. Detailed discussion and analysis can be found elsewhere (Fry, 1982).

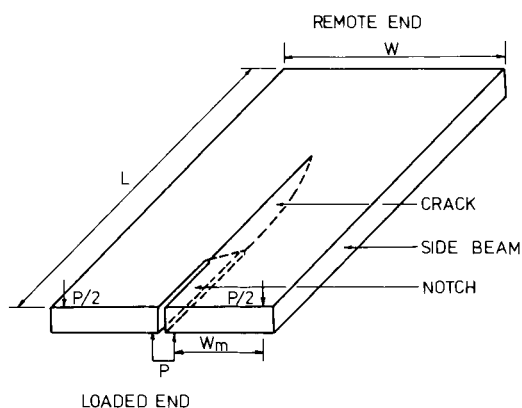


Fig. 1: Basic geometry and terminology used in the double torsion test.

Tests with this geometry in sintered WC-Co samples were carried out on a 50 kN capacity ESH Universal servo-hydraulic testing machine. Fatigue crack growth data were obtained using cyclic sinusoidal loading at a frequency of 5 Hz. Continuous crack length measurement was essential and this was made using an optical travelling microscope and dye penetrant. (Appropriate precautions were taken to ensure that the dye selected did not lead to corrosion effects.) The position of the crack tip was easily identified by smearing a thin layer of dye on the surface of the specimen and then applying a fatigue load. As the crack opens and closes under the cyclic load the dye could be seen 'pulsing'.

In many applications of WC-Co alloy components (drill bits, dies, anvils, rolls, etc.) the load is either on or off, i.e. an R-ratio (P_{min}/P_{max}) of zero is appropriate. A low R-ratio was therefore selected so that crack growth effects observed would be consistent with those anticipated under conditions commonly encountered in practice. When using the double torsion test it is undesirable to have impacting of the load points which may cause the specimen to shift out of alignment. A constant minimum load of 0,1 kN was therefore maintained while the maximum was varied to obtain the stress intensity range required, giving an R-ratio of less than 0,1 (actual values 0,03 - 0,08).

The 'constant-K' characteristic of the double torsion geometry is particularly advantageous in that it enables numerous results to be obtained from one specimen. Six different alloys with a range of cobalt content and grain size were tested, and the relevant microstructural parameters are detailed in Table I.

TABLE I DETAILS OF ALLOYS TESTED

Alloy (Producer's designation)	Cobalt vol. fraction f_{Co}	WC ($\bar{d}$) measured [μm]	Contiguity	Nominal mean free path [μm]	True mean free path [μm]	Hardness VPN [$kg\ mm^{-2}$]
* +						
S6(F)	0,101	1,0	0,50	0,093	0,186	1541
S10(F)	0,164	1,1	0,36	0,216	0,328	1377
G6(C)	0,101	2,9	0,50	0,327	0,654	1377
G10(C)	0,164	3,1	0,36	0,608	0,950	1215
G15(C)	0,237	3,5	0,25	1,090	1,453	1043
25E(C)	0,370	3,2	0,13	1,882	2,163	798

* Cobalt content (wt%)

+ nominal grain size (F = fine, C = coarse)

Nominal mean

$$\text{free path: } \lambda_{nom} = \frac{f_{Co}\bar{d}}{(1-f_{Co})}$$

True mean

$$\text{free path: } \lambda_{true} = \frac{f_{Co}\bar{d}}{(1-f_{Co})(1-C)}$$

RESULTS

Fracture Toughness

Fracture toughness measurements were made on the alloys tested by loading the specimens to failure, under stroke control, at a ramp rate of 0,05 mm/s. Toughness increases approximately linearly with mean free path and decreases as hardness increases, as detailed in Table II.

TABLE II FATIGUE AND TOUGHNESS RESULTS

Alloy (Table I)	K_{IC} ($MNm^{-3/2}$)	m (Figs. 2,3)	ΔK for $da/dN = 10^{-7}$ m/cycle ($MNm^{-3/2}$)	$\Delta K(10^{-7})$ K_{IC}
S6	8,2	19,7	6,6	0,80
S10	9,2	19,2	7,4	0,80
G6	10,0	15,5	7,9	0,79
G10	11,3	15,2	8,4	0,74
G15	13,3	14,2	9,6	0,72
25E	15,7	10,9	11,5	0,73

The fracture toughness values observed are all slightly below those determined by other investigators with respect to both hardness, an easily measured mechanical property, and mean free path, a rather inexact but widely quoted microstructural parameter. This difference may be due to the presence of free graphite in the material tested (Fry, 1982), although there still must be some doubt as to the validity of some precracking techniques used by other investigators. The trend with varying mean free path is, however, entirely consistent with the results of other workers.

Fatigue Crack Propagation

The crack growth rates for the range of alloys investigated are summarised in Fig. 2. For clarity the results for alloy G6 are not included; however, this curve fits between the S10 and G10 data as would be expected.

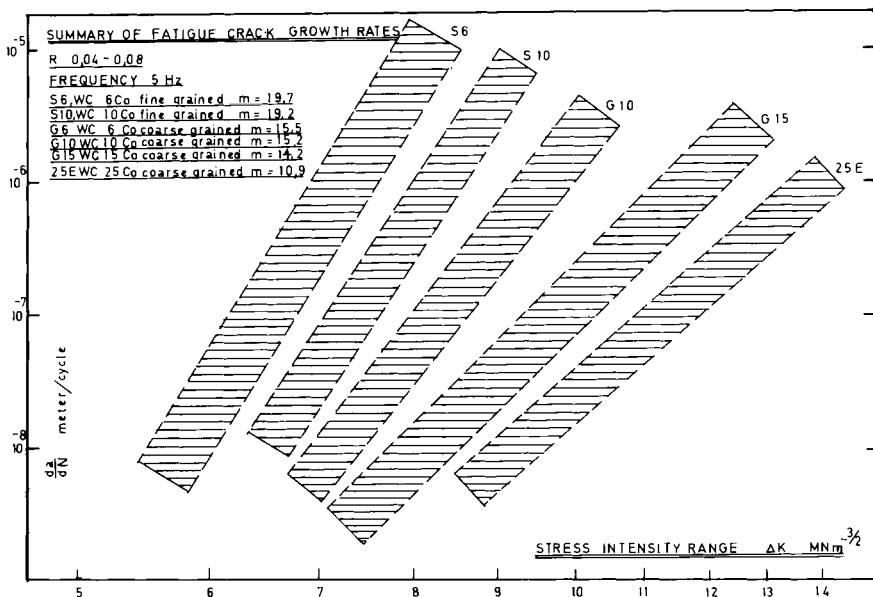


Fig. 2: Summarised results of the fatigue crack propagation behaviour of the alloys tested (for varying grain size and cobalt content).

It is immediately obvious that as the cobalt content and carbide grain size increase, the corresponding fatigue resistance increases. Specifically the results indicate that:

- (i) Fatigue crack growth rates in all alloys tested observe a so-called Paris 'law' dependence of the form $da/dN = C(\Delta K)^m$; there is also a significant dependence on mean stress intensity, discussed elsewhere (Fry, 1982, and Fry and Garrett, 1983).
- (ii) Fatigue crack growth rates decrease as the mean free path of the cobalt binder increases.
- (iii) The values of the exponent 'm' vary in the range 10 - 20, increasing as the mean free path decreases, Fig. 3, correlating with corresponding variations in fracture toughness, Table II.

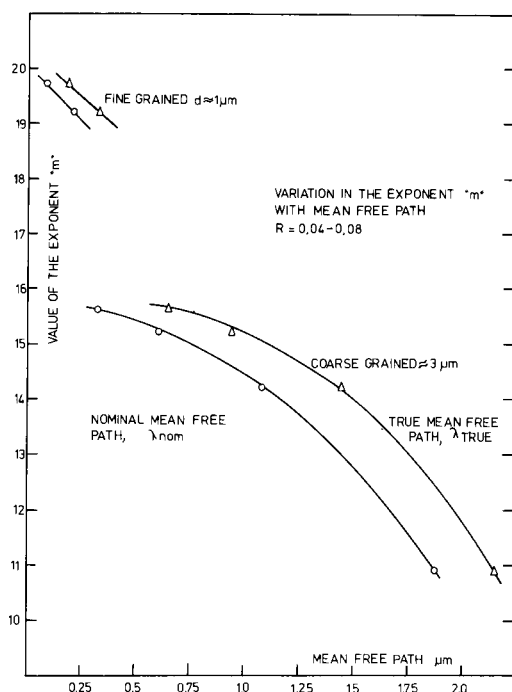


Fig. 3: Variation of fatigue crack growth rate exponent (m) with mean free path (λ) for the alloys tested.

5.3 Fractography

Scanning electron microscopy was carried out on all the grades tested for three different fracture modes:

- (i) Fatigue at R ratio $< 0,02$
- (ii) Fatigue at R ratio $0,6$
- (iii) Fast fracture

Considerable time and attention was paid to the preparation of samples for fractography, which is thought to be responsible for certain contradictions in the literature (Fry, 1982).

Fractographic work showed unequivocally that there are absolutely no distinguishable differences between the fracture surface morphologies of fatigue and fast crack propagation, in any of the alloys tested, Fig. 4. The fracture mode is primarily intergranular with the formation of ductile dimples in the binder phase and, with transgranular cracking of large carbide grains, is characteristic of both the fatigue and fast crack propagation.

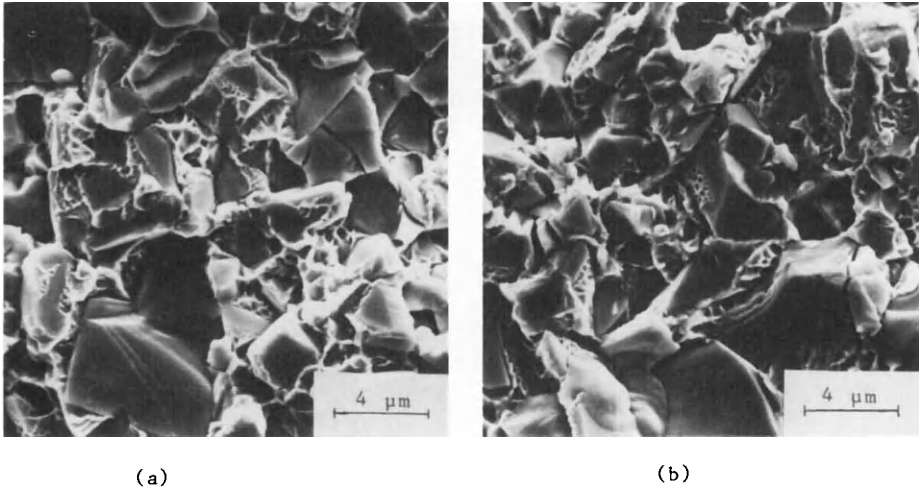


Fig. 4: Identical fracture morphology for fatigue and fast fracture in WC-Co, grade G15 (a) fast fracture, $K_{IC} = 13,3 \text{ MNm}^{-3/2}$; (b) fatigue at $\Delta K = 11,0 \text{ MNm}^{-3/2}$, $R = 0,01$, $da/dN = 1,8 \times 10^{-6} \text{ m/cycle}$).

DISCUSSION

The fatigue crack growth rates determined are slightly greater than results reported elsewhere in the literature for similar alloy compositions (e.g. Evans and Linzer, 1976, Almond & Roebuck, 1980, Lueth, 1981) i.e. crack propagation occurs at lower stress intensity values. The absolute differences are, however, not great and the effects of cobalt content and carbide grain size are in complete agreement.

It is apparent that as the fracture toughness of the alloys increases the resistance to fatigue crack growth also increases. Thus by normalising ΔK for R -ratios $< 0,1$, with respect to the fracture toughness of the alloys, K_{IC} , the fatigue crack propagation rates fall within a reasonably narrow range (Table II).

It may therefore be possible to approximate fatigue crack growth data in WC-Co hardmetal alloys simply by determining the fracture toughness. An 'm' value can then be obtained from Fig. 3 and a crack growth rate from Table II. However, before using such a correlation it is obviously important to consider the mechanistic reasons underlying it.

Firstly, as we have seen, fractographs of fatigue and fast fracture are indistinguishable. Ductile dimples and ligament formation in the cobalt-rich binder and occasional transgranular fracture of the tungsten carbide grains are features characteristic of both fatigue and catastrophic crack propagation.

Detailed evaluation of the nature of fatigue crack propagation in WC-Co (Fry, 1982) has developed on a model originally proposed by Evans, Heuer and Porter (1978) in which binder ligaments spanning the fracture surface behind a crack tip undergo plastic buckling during the unloading half cycle. While

cyclic work hardening and/or a FCC to HCP transformation may contribute to crack growth in the binder phase, consideration of the mechanisms indicates that plastic buckling probably predominates (Fry, 1982). Similarly, on the loading half cycle crack advance can occur by static modes, such as cleavage of the carbide grains and/or microvoid coalescence in the binder phase, until restraint to further crack opening and advance, imposed by the intact and newly-formed binder ligaments, is restored (Fry, 1982).

For these reasons, therefore, it seems reasonable to derive (hard-to-measure) fatigue crack propagation behaviour in WC-Co alloys from the more straightforward fracture toughness test, at least to provide a first estimate of fatigue crack growth under given operating conditions.

CONCLUSIONS

- (i) The double torsion test specimen geometry has been used with success for measuring fatigue crack propagation rates in WC-Co alloys, as a function of grain size and Co-content.
- (ii) When normalised with respect to fracture toughness, the variation in fatigue crack growth rate as a function of microstructure is small.
- (iii) Fractographically, stable fatigue crack growth and fast fracture are indistinguishable.
- (iv) Mechanistically, fatigue crack growth occurs by static modes of material separation and damage due to the cyclic stressing.
- (v) In consequence, fatigue crack propagation behaviour in WC-Co alloys can be estimated from a knowledge of the fracture toughness.

ACKNOWLEDGEMENTS

The financial support of Boart International, the University Research Grants Division of the CSIR, and the University of the Witwatersrand is gratefully acknowledged.

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The Constitution as the Basis for Recent and Future Developments of Wear Resistant Materials

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ABSTRACT

The constitution of wear resistant materials is discussed with regard to the optimization of properties and further developments. Substitution of elements, new compounds, different types of transformations and the adjustment of microstructures are of considerable significance in this field.

KEYWORDS

Constitution, wear resistant materials, new developments, hard metals, ceramics.

INTRODUCTION

Current and future developments in the field of wear resistant materials are influenced by the availability of raw materials, by the energy situation, by new technologies for fabrication and by the increasing need for special materials. Typical objectives of developments are: substitution of scarce raw materials, utilization of inexpensive and readily available materials, material- and energy-efficient design, materials with extremely high wear resistance, optimal adjustment of materials to the particular wear mechanism and to the tool, recycling of used materials. Wear resistant materials are classified by the manufacturer chiefly by hardness and transverse rupture strength. Fig. 1 shows schematically different groups of these materials in a log hardness/transverse rupture strength diagram. The hard metals, divided in hard metals I (carbide rich) and hard metals II (metal rich) are further subdivided into TiC based materials with low strengths and WC based materials with higher strengths. There are the ceramic and nonmetallic refractory materials and the metallic refractory materials (transition metal carbides, nitrides and borides) and the superhard materials. Trends of recent developments are characterized by arrows. The controlled application of phase equilibria in the generally multicomponent systems offers a good basis for many new developments or for the optimization of properties (Holleck, 1982). Key areas relating to phase equilibria in materials development are given in Fig. 2. Some of these will be discussed in more detail in this paper.

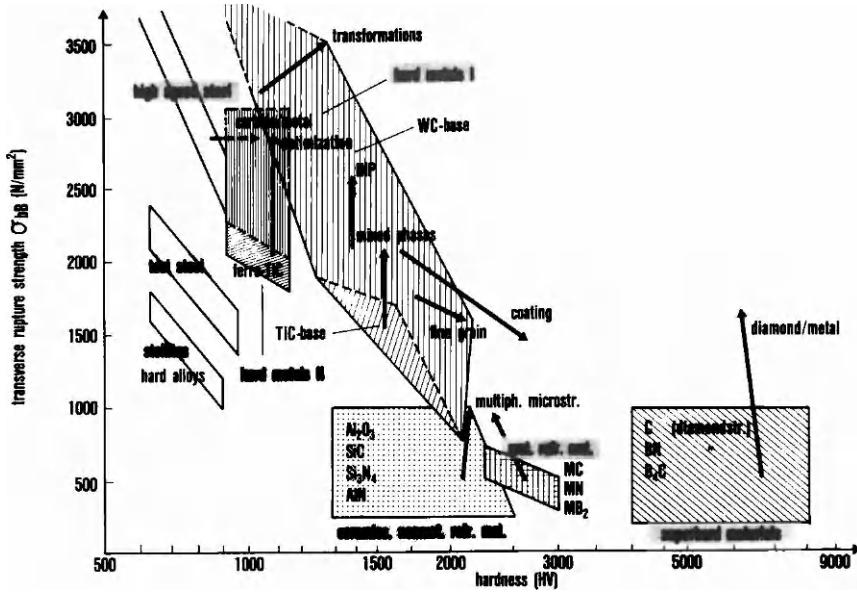


Fig. 1. Wear resistant materials and recent developments (schematically indicated by arrows)

- substitution of elements
e. g. mixed phases
- solid solution hardening
- new compounds
e. g. complex carbides, nonmetallic hard compounds
- optimization of properties by transformations
e. g. order-disorder phenomena, precipitations
- adjustment of microstructure
e. g. eutectic systems, spinodal decomposition, phase decomposition
- dispersion- and composite-systems
- fabrication-technology
e. g. liquid phase sintering
- material fabrication by gas equilibria

Fig. 2. Phase equilibria contributions for the material development

SUBSTITUTION OF ELEMENTS

The substitution of Co by Fe based alloys (Thümmeler, Holleck and Prakash, 1981) as well as the replacement of W by Mo (Holleck, Prakash and Thümmeler, 1981; Holleck, 1979) in conventional WC-Co hard metals are typical examples of new developments. Beside the economic advantage of Fe based alloys compared with Co, an improvement of properties by a martensitic transformation in the binder phase could be achieved. This is demonstrated schematically in Fig. 1

by the arrow indicating the key word "transformations". Figure 3 indicates the difference in fracture toughness between WC-20 Co and WC-20 Fe,Co,Ni (with predominantly Fe and Ni) on the one hand and WC-20 Fe,Co,Ni (with predominantly Fe and Co) on the other.

material	hardness (HV)	fracture toughness K_{IC} [MN/m ^{3/2}]
met. refr. comp.		
TiC	2900	3.8
WC	2300	7.5
hard metals		
Ti(Mo)C-10Ni	1600	10.6
Ti(Mo)C-18(NiCo)	1600	11.7
WC-20Co	1000	16.8
WC-20Fe,Co,Ni	860	23.6
WC-20Fe,Co,Ni	1160	17.7
nonmet. refr. comp.		
SiC	3000	2.8
(Si ₃ N ₄) _{0.1} Co _{0.9} Ni _{0.1}	2900	4.7
AlN	1300	~ 3.0
Si ₃ N ₄	1400	5.0
Al ₂ O ₃	2200	1.9-3.6
nonmet. composites		
Al ₂ O ₃ /TiC	2100	~ 5.0
Si ₃ N ₄ /TiC	1550	8.6
superhard materials		
BN (diamondstr.)	4400	14.8-17.3
C (diamondstr.)	8800	9.7
SiC	5000	6.0

Fig. 3. Hardness and fracture toughness of different wear resistant materials (hard metals: own measurements, other substances: literature values)

Another example of recent developments concerning substitution of elements is the replacement of W by Mo in conventional hard metals. In principle there are two possibilities: the partial replacement by introducing Mo in the hexagonal WC-type phase and the complete replacement by stabilizing a cubic Mo based mixed carbide. Both routes lead to cemented carbides with properties comparable to the WC-Co carbides (Holleck, Prakash and Thümmel, 1981; Holleck, 1979).

SOLID SOLUTION HARDENING

TiC based hard metals, which are very attractive from the economic point of view, are characterized by a relatively low rupture strength (see Fig.1). Both hardness and strength can however be raised by the formation of solid solutions with other carbides. TiC is completely miscible at high temperatures with ZrC, HfC, VC, NbC, TaC, MoC_{1-x} and WC_{1-x} (Holleck, 1981). In practice only MoC_{1-x} and VC play a role as addition carbides. Besides the strengthening effect obtained by the formation of a solid solution, the wetting behaviour with the binder metal and the solubility of carbide components in the binder are also favorably influenced. For TiC-Ni hard metals with a hardness of 1600 HV the fracture toughness K_{IC} can be inferred from crack resistance data to be 8.4 MN/m^{3/2}. (Ti,Mo)C-Ni, and especially (Ti,M)C-Ni,Co (with M = Ta,Mo,W) materials with the same hardness surpass the toughness considerably as shown in Fig. 3.

NEW COMPOUNDS

An obvious and directly constitution related aspect of the material devel-

opment are the discovery and the preparation of new compounds and their application in wear resistant materials. Typical examples are: complex carbides and multicomponent nonmetallic refractories. Only some of the more than 400 complex compounds are investigated in relation to their properties. Studies of the abrasion behavior of Ti_3AlC , Ti_2AlC of Ti_2AlN show remarkable results (Ivchenko and Kosolapova, 1976) which suggest further investigations are warranted.

Taking into account the distribution of elements in the outer shell of the earth, compounds with the elements Al, Si, Mg, Ti, C, N, O are extremely attractive. An example for a nonmetallic quaternary refractory compound with these components are the sialons. The fracture toughness K_{IC} exceeds with about $6 \text{ MN/m}^{3/2}$ the values of the binary compounds SiC, AlN, and Al_2O_3 (Lange, 1980). The same is true for the quaternary carbonitride $(Si_{0.9}Al_{0.1})Co_{0.9}No_{0.1}$ (a solid solution between SiC and AlN) with a remarkably higher toughness than SiC and AlN (Rafaniello, Cho and Virkar, 1981) (see Fig. 3). To assess the potential of similar compounds we need much more knowledge for the multicomponent system Si-Al-O-N-C-B.

OPTIMIZATION OF PROPERTIES BY TRANSFORMATIONS

Transformations in cemented carbide systems have hardly been used up to now. An example for the strengthening of the binder metal phase by martensitic transformation was given previously. Strengthening of the binder phase leads to the possibility for application of materials with higher metal contents compared with the common cemented carbides. Referring to Fig. 1 one changes from the field of hard metals I into that of hard metals II. These materials are much more economical than the hard metals with high amounts of expensive transition metal carbides. Precipitations of carbides and the martensitic transformations are responsible for the strengthening in Fe based binders, whereas precipitations of the ordered γ' -phases have a similar effect in Ni based binders. For the controlled optimization of such metal-rich materials we need much more knowledge of the constitution for the systems multicomponent Fe based and Ni based systems.

Order-disorder phenomena and precipitation mechanisms also offer the opportunity for the strengthening of the carbide phase. Typical microstructures for such transformations in the carbide phase, which are accompanied by a hardness increase of up to 30%, are given in Fig. 4. In ternary carbide systems property changes by different cooling rates indicate a remarkable influence of order phenomena not only in the nonmetal - but also in the metal - sublattice (for instance for the system V-Ti-C) (Hannink and Murray, 1975). Preliminary investigations show, that also the properties of cemented carbides are partly sensitively dependent on the cooling rates.

ADJUSTMENT OF MICROSTRUCTURE

The application of phase equilibria presents manifold opportunities for the formation of favourable microstructures. Examples are eutectic systems, spinodal decomposition or phase decomposition. Fig. 5 shows the microstructures of a eutectic TiC-W hard metal⁺(a), a spinodal (Ti,Mo)C,N-Ni cemented carbide⁺(b), and a phase decomposed Mo_2C -Mo,Pt (c) material (Holleck, 1982).

⁺ We wish to thank Teledyne Firth Sterling for providing us with these cemented carbide samples.

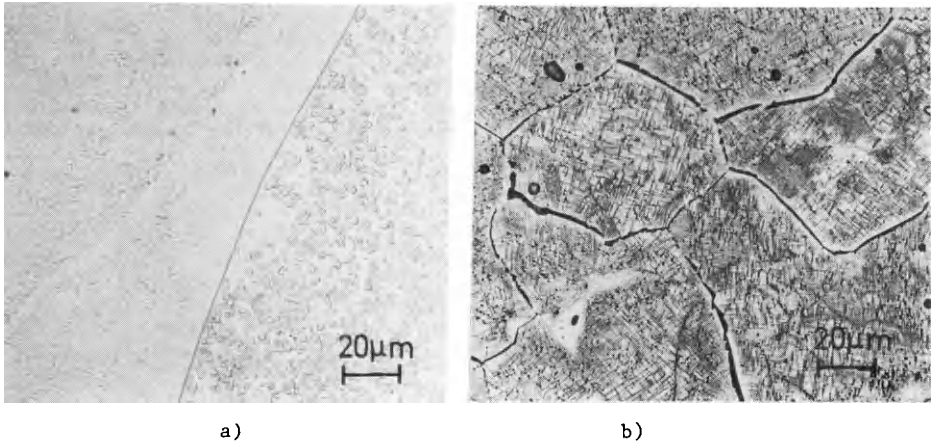


Fig. 4. Microstructures of carbides with precipitation of an ordered phase (a) and a lower carbide phase (b)

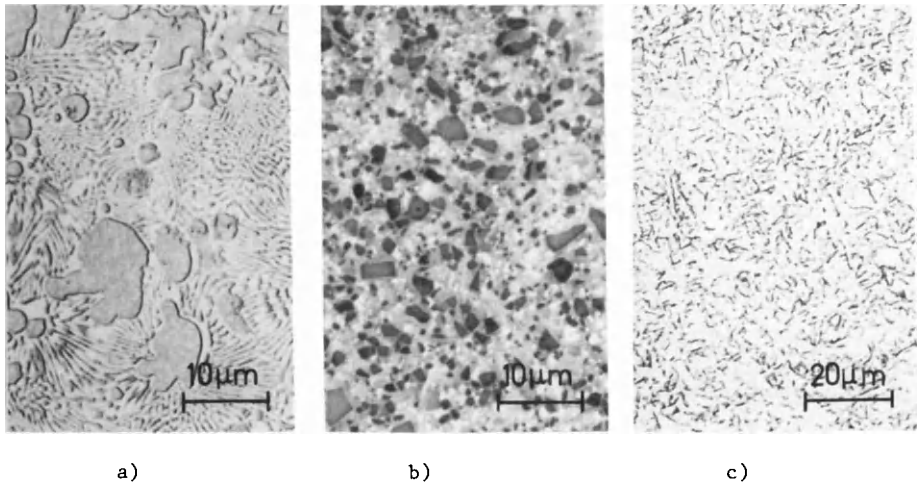


Fig. 5. Microstructures of a eutectic TiC-W hard metal (a), a spinodal (Ti,Mo)C,N-Ni hard metal (b) and a "phase-decomposed" Mo₂C-Mo,Pt material (c)

DISPERSION AND COMPOSITE SYSTEMS

The most common composite system in the field of wear resistant materials are the hard metal systems (Fig. 6). Here we have a combination of a hard carbide and a tough binder phase. Both phases are coexistent and provide best properties only in the dashed region. Also brittle phases can be constituents of materials with remarkable toughness in multiphase, fine grain microstructures. The relation to the constitution is evidenced by the fact, that no reaction should occur between the different phases, and that the structures of these phases provide a fixed minimum strength. The most common materials in this field are the ceramic tool materials based on Al₂O₃

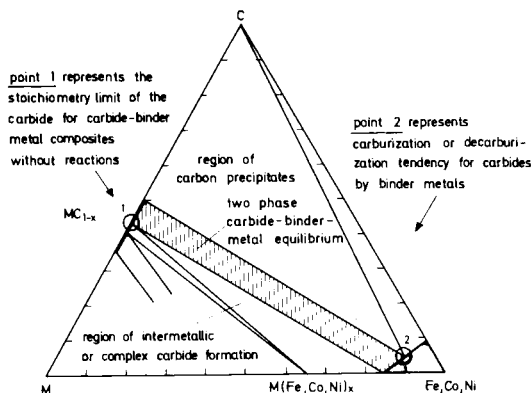


Fig. 6. The constitution of cemented carbides (schematically)

with additions of TiC , TiB_2 , MgO or other phases. Many other combinations are possible such as three phase materials with metallic carbide phases, non-metallic and ceramic refractory phases. For such materials we measured a hardness of 2200 HV and we estimated a fracture toughness of $7.6 \text{ MN/m}^{3/2}$ from crack resistance data.

CONCLUSION

The few examples given in this paper should elucidate that the knowledge of the constitution can be the basis for understanding the wear resistant material properties and their performance in application conditions and that it offers opportunities for further developments. In particular problems of raw materials supply, materials loss by wear, energy consumption and the suitability of new technologies will have a strong influence on these developments. Favourable for a controlled development of wear resistant materials by the application of special phase equilibria are:

- metal-rich hard metals, hardened in the Fe or Ni based binder phase
- carbide-rich hard metals, hardened in the carbide or binder phase by transformations
- multicomponent ceramic systems with optimized microstructure
- polyphase materials based on hard substances such as B_4C , SiC , AlN , Si_3N_4 .

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Wear Properties of Rapidly Solidified Surfaces of a Pseudo-binary Fe-TiC Alloy

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ABSTRACT

The wear behaviour of the steel-base cemented carbide material Ferro-TiC (SK) has been studied following electron beam glazing and tempering treatments. A distinction is made between wear of SK against a moderately hard martensitic stainless steel (17-4 PH), and a hard molybdenum-base high speed steel (M42). The effect of glazing is to produce a three-fold increase in the wear life in tests performed using a fully hardened M42 high speed steel counterface material.

KEYWORDS

Electron beam surface melting (glazing); cemented carbide; microstructural effects, wear characteristics.

INTRODUCTION

When the cemented carbide Ferro-TiC, otherwise known as SK, is subjected to a rapid solidification electron-beam surface melting (glazing) treatment, the original blocky TiC carbides are transformed into a highly refined dendritic structure (Lewis, Gilbert and Strutt, 1981; Strutt, 1977). This feature coupled with a high hardness suggests a possible benefit in terms of improved wear properties. The present study was undertaken to test this proposition. As will be shown, under appropriate conditions, significant improvements in wear resistance due to e.b.-glazing can be achieved.

SPECIMEN PREPARATION

Wear-pin specimens of SK material were glazed using a Carl Zeiss electron beam unit. A beam power density of 10^5 watts/cm² was achieved by setting the power level at 300 watts and by adjusting the focussing to give a measured spot diameter of 0.3 mm. Under these conditions, and with a beam scanning rate of 100 cm/s, a narrow glazed band about 100 μ m in depth was obtained, which experienced an average cooling rate of 5×10^6 °C/s. Continuous surface coverage of glazed material was attained by applying two nearly

equal frequency signals to the X and Y deflection coils, so as to trace out a series of overlapping Lissajous figures (Strutt, 1981), Fig. 1. This particular scanning mode was originally developed for the purpose of solid state transformation hardening of steels, without actual melting (Mayer, Dietrich and Sundermeyer, 1977).

All the material used, whether it was subsequently tested in the unglazed or glazed conditions was initially austenitized at 1050 °C for 5 min, and then quenched in oil at 50 °C. Following this treatment, a few samples were double tempered at 450 °C for 1 hour.

TABLE 1 Major Alloying Elements (wt%) in M42, 17-4PH, and SK (Ferro-TiC)

	Fe	Cr	W	V	Mo	Co	Ti	Mn	Si	C	Ni	Cu	P	Nb/Ta
M42	Bal	3.70	1.36	1.12	9.62	7.88	-	0.24	0.40	1.09	-	-	-	-
17-4PH	Bal	16.5	-	-	-	-	-	0.06	1.0	0.05	4.0	4.0	0.04	0.35
SK	Bal	3.5	-	-	3.0	3.0	21.0	-	-	5.0	0.5	-	-	-

All other elements < 0.01 wt%

WEAR TESTING

Wear tests were carried out in a standardized test machine (Rice, 1979) in which the end of a small cylindrical SK wear pin (3 mm diameter) both impacted and slid across a steel counterface. Tests were performed using two different counterface materials - a moderately hard (400 DPN) martensitic stainless steel (17-4 PH), and a hard (930 DPN) molybdenum-base high speed steel (M42), Table 1. In all tests, the transverse sliding velocity was 8 m.s⁻¹ and the nominal maximum impact stress was 69 MPa at a repetition rate of 800 cycles/min. To determine the extent of wear, pins and counterface samples were weighed before and after testing. Wear pins of SK material in both the unglazed (500 DPN) and glazed (950-1000 DPN) conditions were tested against the two different counterface materials at ambient temperature.

Wear Against a Moderately Hard Steel

Figure 2 shows the general appearance of the microstructure of a glazed SK wear pin after testing. The surface is covered with a thin layer of counterface material (Zone A), which has been transferred onto the pin during testing. Below this layer is a much thicker dendritic carbide region (Zone B), which represents the full extent of the homogeneous glazed material. Zone C is a transition zone of partial glazing, involving melting and re-solidification of the steel matrix only, i.e. without complete dissolution of the original blocky carbides. Zone D is representative of the unmelted parent material. Close inspection of Zone B reveals that it is separable into an upper heat-affected (tempered) deeply etched region 3-4 µm below the surface, and a lower more evenly etched dendritic carbide structure. These microstructural features were rather typical of all glazed and tested wear pins.

Figure 3 compares the microstructures of unglazed and glazed SK wear pins after testing against 17-4 PH. The surface of the unglazed sample is rough, Fig. 3(a), and there is evidence for patchy regions of transferred counter-

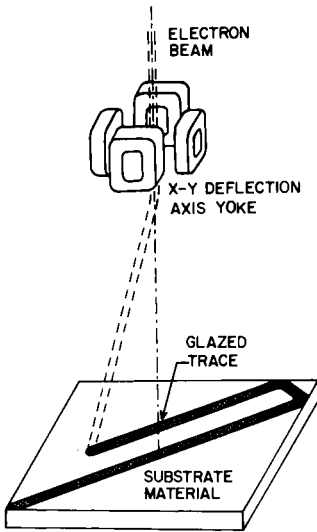


Fig. 1. Schematic of electron beam glazing, utilizing electromagnetic beam deflection.

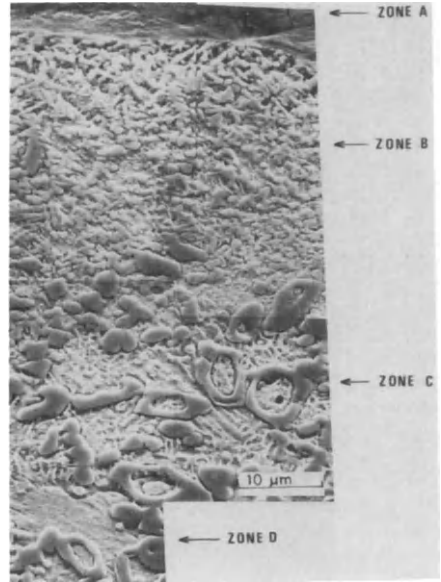


Fig. 2. Electron beam glazed Ferro-TiC(SK) wear pin sectioned parallel to the sliding direction, showing adhered counterface material (Zone A), and sub-surface zones of fully glazed (Zone B), partially glazed (Zone C), and un-melted substrate (Zone D).

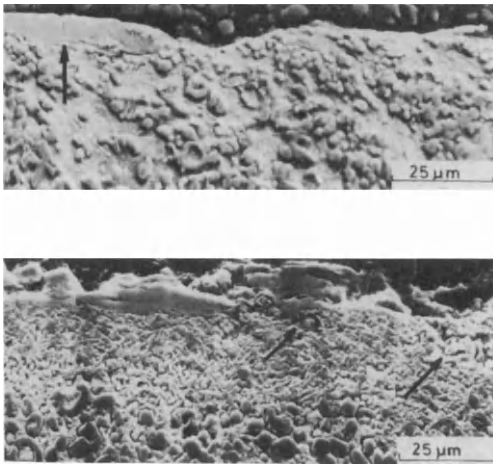


Fig. 3. Comparison of the surface microstructures of unglazed (a) and glazed (b) Ferro-TiC(SK) wear pins, after wear against a moderately hard 17-4 PH steel counterface.

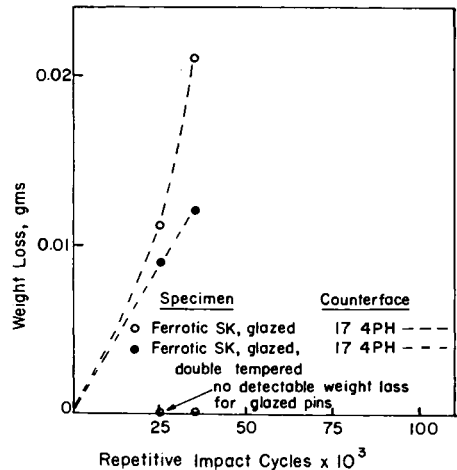


Fig. 4. Weight loss data for glazed Ferro-TiC(SK) worn again 17-4 PH.

face material. Below this there is a region of intense plastic deformation in the sliding direction, which contains small fragmented carbides. The actual amount of plastic strain is estimated from measurements on several micrographs to be >50 %. In complete contrast, in the glazed sample, Fig. 3(b), there is a much greater amount of visible transferred material, but no evidence for significant plastic deformation in the upper part of Zone B. In both cases, there is evidence for cracking in the surface layers, arrows in Fig. 3. These are limited to the transferred material in the unglazed sample, whereas in the glazed sample they extend into Zone B, terminating near its base. Post-glaze tempering treatments to increase martensite ductility did not reduce the propensity for crack formation in the glazed material.

No significant weight changes were recorded for glazed and unglazed pins. On the other hand, metallographic examination provided indirect evidence for more wear of unglazed pins than glazed pins. This is deduced from Fig. 3(a), where carbide particles have clearly worked their way into the adhered material (Zone A). In contrast, the corresponding counterface materials (impact discs) underwent substantial wear, as determined by actual weight losses. Thus, the overall situation can be described as essentially 'one-body wear'. Figure 4 shows plots of the actual experimental weight change data. For completeness, the effect of tempering the glazed pins is included. Tempering reduces the wear rate of the counterface material, which may be the result of more material adhering to the tempered pin.

Wear Against a Hard Steel

Figure 5 compares the microstructures of unglazed and glazed SK wear pins, after testing against M42 high speed steel. The unglazed sample, Fig. 5(a), exhibits some of the features characteristic of wear against the softer 17-4 PH material, Fig. 3(a), such as surface roughness, and near-surface plastic deformation and carbide fragmentation, but there is no indication of pick-up of counterface material. On the other hand, the glazed sample exhibits quite distinctive features, not previously seen in the 17-4 PH case. As shown in Fig. 5(b), the wear surface is smooth, contains no detectable counterface material, and there is no evidence for cracking of the glazed material. Careful examination reveals a small amount of carbide fragmentation, limited to the top 2-3 μm of the glazed region.

Figure 6(a) shows that wear of unglazed SK pins against M42 produces significant weight losses for both pin and counterface materials, i.e. two-body wear, in contrast to the one-body wear characteristic of 17-4 PH. Both tempered and untempered samples wear at a similar rate up to 50,000 cycles, beyond this there is a continued weight loss only for the untempered material. A possible explanation for this behaviour is that a greater amount of M42 counterface material adheres to the tempered wear pin, which gives rise to wear of M42 against M42 in the later stages of testing. A similar two-body wear is found also in the case of the glazed material, Fig. 6(b), except that to obtain a weight loss equivalent to that of unglazed material, Fig. 6(a), it is necessary to increase the test time by a factor of 2.5 (i.e. to 250,000 cycles). In other words, e.b.-glazing in this case increases wear life by 2.5x.

DISCUSSION

The present work shows that electron-beam glazing is capable of improving the wear resistance of a hard cemented carbide material. Although the under-

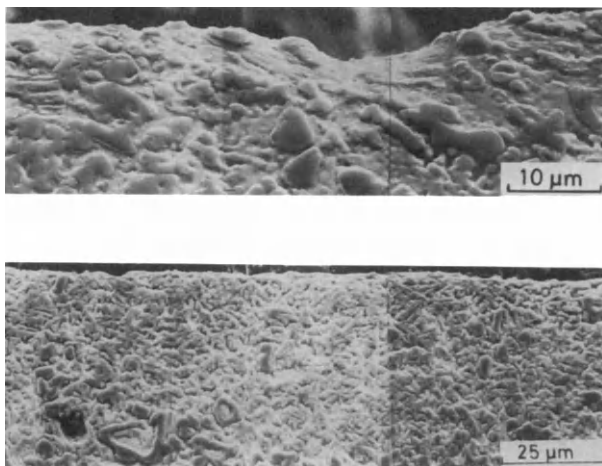


Fig. 5. Comparison of surface microstructures of unglazed (a) and glazed (b) Ferro-TiC(SK) worn against a hard M42 high speed steel counterface.

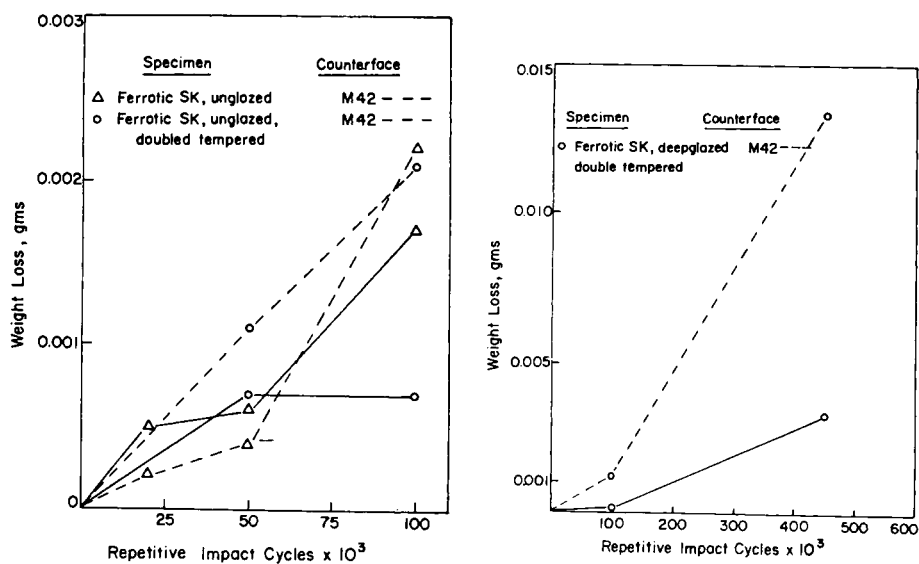


Fig. 6. Weight loss data for unglazed (a) and glazed (b) Ferro-TiC(SK) worn against M42.

lying mechanisms are imperfectly understood, it is believed that the most important factors contributing to improved performance are (i) the high degree of homogeneity of the rapidly solidified material, and (ii) the high yield strength of the ultra-refined microstructure.

Before considering wear of glazed material, it is instructive to consider the degradation process of untreated material. The microstructure of unglazed SK material, Fig. 3(a), after wear against a 17-4 PH steel counterface, is indicative of a situation where fragmented carbide particles tend to align themselves along curved flow lines within a plastic deformation slip field produced by shear along the wear direction. X-ray diffraction analysis of wear debris confirms that small TiC particles are indeed carried from the SK material into the adhered layer.

Observations during actual wear tests indicate that an adhered layer of 17-4 PH forms at an early stage on the wear-pin surface. It is the continual breakaway and renewed build-up of this layer that produces the wear debris. The 17-4 PH readily shears from the counterface due to the plastic softening resulting from localized heating during sliding and impact. When, however, a sufficiently thick layer has been transferred to the wear-pin the adhered zone exhibits a hardness of about 800 DPN. The increase in hardness arises from a combination of precipitation hardening, mechanical mixing of alloy phases and oxides, and the presence of untempered martensite formed as a result of wear test induced heat treatments. In addition to being hard, microstructural observation of severe cracking shows Zone A structures to be rather brittle. Interestingly, the cracks in the adhered 17-4 PH layer do not propagate into the cemented carbide material. Presumably this is because the matrix phase readily accommodates the intensified stress field at the crack tip by plastic deformation. Although there are no detectable cracks within the near-surface region of the SK material, a small amount of SK nevertheless is removed. Presumably, this arises from the small amount of near-surface material, which is firmly bonded to the fragments of adhered 17-4 PH, detaching itself during the wear process.

From the experimental observations, and the preceding considerations, it is evident that glazing is advantageous in improving wear resistance provided that appreciably thick, brittle and tenaciously adherent layer does not form. Such a conclusion is well supported by the wear experiments using a hardened M42 steel counterface. Little or no detectable adhered layer is formed, presumably because the good hot hardness prevents plastic shearing. In this case, the material degradation process appears to be surface abrasion involving the continued removal of fine particles. The creation of such particles must involve surface microcracking, but such cracks are highly localized since they do not penetrate the glazed surface layer. This type of wear process occurs on both the SK wear pin and the M42 counterface. In the glazed condition the fine particle fragmentation is reduced, thus showing the beneficial effect of electron beam glazing in reducing wear.

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New Titanium Carbide Grades for Metal Cutting

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ABSTRACT

Hardmetals based on titanium carbide are shown to be considerably more economical than conventional tungsten-based materials; and their major restrictions to market penetration have been poor performance because of relatively low edge strengths and occasional failure by plastic deformation.

A new group of TiC hardmetal with important additions of vanadium carbide and titanium nitride has shown consistently high strength and improved resistance to plastic deformation.

This paper discusses the development of such grades and illustrates their performance with examples from applications in major industrial concerns.

KEYWORDS

Metal cutting; titanium carbide; tungsten-free cemented carbide; vanadium carbide; titanium nitride; plastic deformation; grain refinement.

INTRODUCTION

The first titanium carbide cutting tools became commercially available as far back as 1930, when they consisted of a mixed TiC-Mo₂C crystal in a nickel matrix. Though nickel rather than cobalt (conventionally used with tungsten carbide grades) is used to improve wettability (Hollox, 1968) and grain growth (Landau, 1976) during liquid phase sintering, these early TiC based cutting tools failed because their strengths were just not high enough. In the 1960s a successful development of a finishing grade of TiC put the material on the commercial map (Meredith, 1976); this was essentially connected with the addition of molybdenum carbide.

In recent years an alternative to tungsten carbide based alloys has been sought because of the market instability of its constituent raw materials, in particular cobalt and tantalum carbide. TiC-based alloys could thus become very attractive since nickel replaces cobalt as the binder, and titanium nitride replaces tantalum carbide as grain refiner -- provided, of course, the mechanical properties are sufficiently good.

However, when compared to WC based tools, low transverse rupture strength, poor edge strength and plastic deformation still limit the application of TiC based materials in heavier duty, interrupted cutting (e.g., milling). Recent developments at ISCAR in association with the Ford Motor Company were made to overcome this limitation. These developments involve the additions of titanium nitride and vanadium carbide (Moskowitz, 1981). Such was the success of these additions that this family of TiC grades is commonly used in P01-P25 applications.

EXPERIMENTS

Table 1 illustrates six principal experimental alloys which comprise the following changes in composition:

The nickel content was increased in Alloy 6.

The vanadium carbide was absent in Alloy 2.

The titanium nitride content was varied.

These alloys were prepared by conventional mixing, wet-ball milling and vacuum drying in 5 kg quantities.

TABLE 1 Summary of Mechanical Properties

Alloy No	TiC	Composition Wt. %				TRS psi	Hardness HRA
		TiN	VC	Mo ₂ C	Ni		
1	57.5	-	10.0	10.0	22.5	278,000	90.6
2	57.5	10.0	-	10.0	22.5	233,000	90.7
3	49.5	10.0	10.0	10.0	22.5	262,000	91.0
4	53.5	4.0	10.0	10.0	22.5	273,000	90.4
5	50.0	7.5	10.0	10.0	22.5	340,000	90.7
6	47.5	7.5	10.0	10.0	25.0	295,000	90.5

RESULTS

This new family of TiC-based alloys is compared with conventional TiC alloys in Table 2, and the improvements are clearly seen.

TABLE 2 Summary of Properties of 'Old' and 'New' Grades

TiC + Ni + Mo ₂ C (Old)				TiC + Ni + Mo ₂ C + TiN + VC (New)			
Alloy No	%Ni	TRS psi	Hardness HRA	Alloy No	%Ni	TRS psi	Hardness HRA
7	7.5	165,000	93.8				
8	12.5	210,000	92.8	12	12.5	225,000	93.0
				13	15.0	255,000	92.5
9	17.5	255,000	91.8	14	17.5	285,000	92.1
10	22.5	270,000	90.5	5	22.5	340,000	90.7
11	25.0	275,000	89.8	6	25.0	295,000	90.5

A typical structure is illustrated by the scanning electron micrograph in Fig. 1 below.

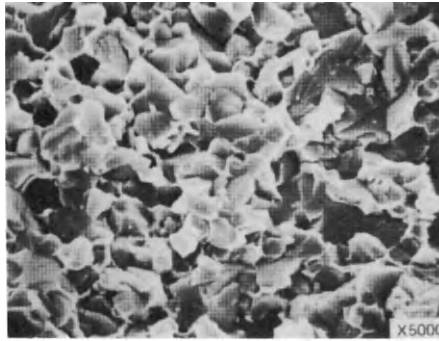


Fig. 1 SEM micrograph of Alloy 5

The results can be explained by studying the effect of each variant:

Effect of titanium nitride (TiN): Increasing the TiN content causes an initial small drop, after which the hardness steadily increases, as shown in Fig. 2. This is explained by a solid solution softening effect as nitride replaces carbon in the mixed crystal of titanium, until an excess of finely distributed TiN acts as a grain refiner, increasing the overall hardness.

A sinusoidal graph is obtained for transverse rupture strength with increasing TiN (Fig. 3). An initial decrease in TRS is attributed to a mechanical problem of satisfactorily distributing small amounts of material, so that the TiN tends to agglomerate, and thus reduce the strength.

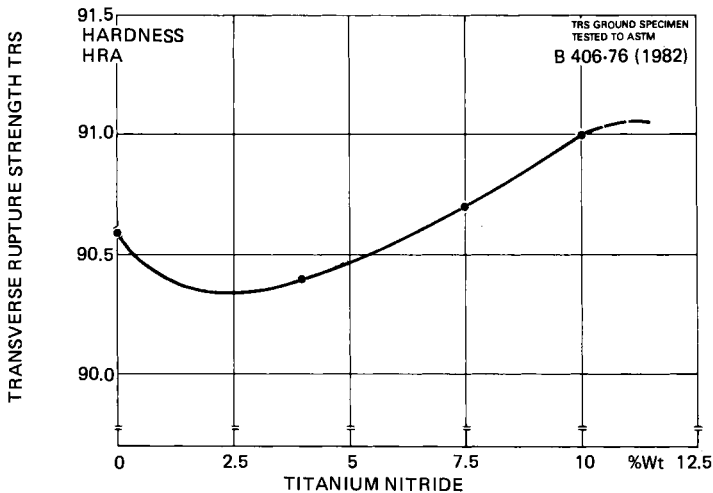


Fig. 2 Effect of TiN Additions on Hardness of TiC-based Hardmetal

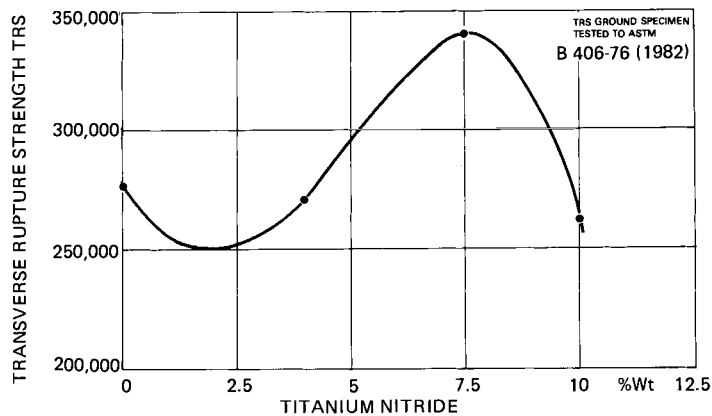


Fig. 3 Effect of TiN Additions on TRS of TiC-based Hardmetal

Maximum TRS was found at 7.5% TiN and is believed to be associated with the optimum grain size of TiC -- too strong a grain refining action will produce too fine a TiC grain. Figures 4 and 5 illustrate the effect of TiN on TiC grain size, comparing the microstructures of an alloy without TiN (Alloy 1) and of one containing 10% TiN (Alloy 3).

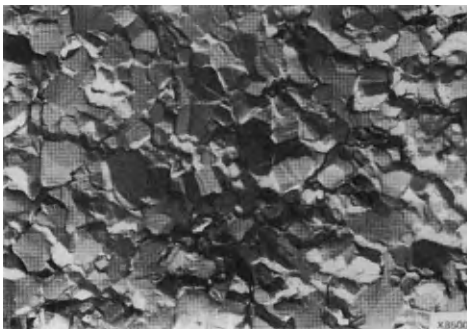


Fig. 4 SEM Micrograph of Fracture Surface of TiC with 0% TiN

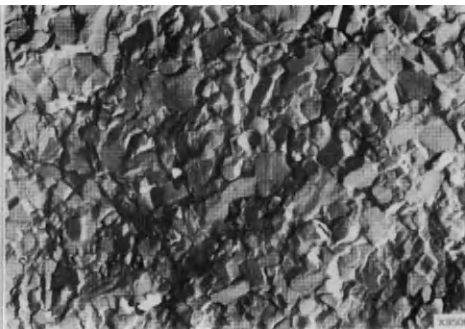


Fig. 5 SEM Micrograph of Fracture Surface of TiC with 10% TiN

Effect of vanadium carbide: Vanadium carbide will form a mixed crystal with TiC, and it has been shown that the compressive strength increases up to 25% VC (Meredith, 1976). Viswanadham (1979) indicates that a maximum in strength in the TiC-VC-Ni-Mo₂C system is reached at 11% VC and a maximum hardness at 16% VC. It is believed that VC increases the plastic deformation resistance of TiC and this has been confirmed in our work from results of Alloys 1 and 2 shown in Table 1; for this reason a fixed VC content has been used in this work.

Effect of molybdenum: Increasing molybdenum content produced a small increase in hardness, but virtually no difference in strength. The higher molybdenum alloy showed improved properties at faster cutting rates during milling.

Effect of nickel: The results are reviewed with reference to the two principal cutting operations: Turning -- Comparing Alloy 5 (22.5% Ni) with Alloy 6 (25% Ni) in turning tests (SNG432 at 200mm/min, 2.5mm depth of cut and 0.25mm/rev feed on AISI 1045), there was a decrease in wearland and crater wear that resulted in an increase in tool life of approximately 15%.

Milling -- In this edge strength test of the same two alloys, the 22.5% Ni performed better at all cutting speeds: at 88m/min, material reached 0.7mm/tooth before fracture; at 176m/min, 0.5mm/tooth.

Figures 6 and 7 illustrate the effect of additions of VC and TiN on the performance of Alloy 5 in the milling of 181 front wheel spindles (courtesy of the Ford Motor Company).

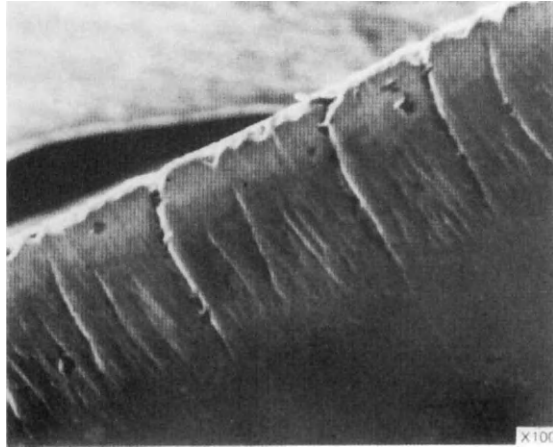


Fig. 6 SEM Micrograph of TiC With No Addition of VC and TiN After Milling 181 Front Wheel Spindles

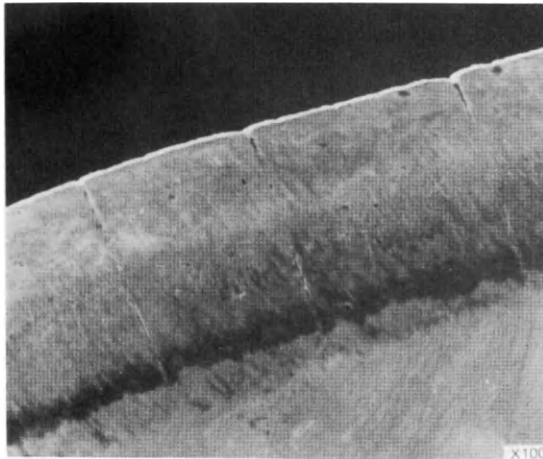


Fig. 7 SEM Micrograph of TiC With Addition of VC+TiN After Milling 181 Front Wheel Spindles

Another justification for TiC based cutting tools is the ability to cut at very high speeds. Below is listed an example of milling an engine block requiring a very high surface finish. This was done at 297m/min, at which speed no other hardmetal can work and which saves an additional grinding operation.

Type of Steel	: SAE 4140
Type of Cutting Tip	: SPK42EDTR
TiC Carbide Grade	: IC55T
Mill Diameter	: $\phi 315\text{mm}$
Milling Head Speed	: 300 rpm
Table Speed	: 80mm/min
Tooth Load	: 0.017 mm/tooth
Depth of Cut	: 1mm
Workpiece Dimensions	: 2 x 35 x 200mm (2 parts milled simultaneously)

Results:

Cutting Edges	: 60 - 70 pairs
Cutting Time	: $200/80 = 2.5\text{min}$
Tool Life	: $2.5 \times 60 = 150\text{min}$ (for 60 pairs)

ECONOMICS

The results show that TiC alloys containing VC and TiN not only have a wider range of fine turning applications than do the conventional TiC grades, but that they can now be used as alternatives to WC based alloys for rough turning and even milling (U.S. Patent, 1965; Wertheim, 1976).

Conversion costs for TiC alloys are only marginally greater than their WC equivalents, and the raw material costs are lower. In this respect, the TiC based alloys including those containing VC and TiC are not only free of strategic materials (cobalt) but are much less costly. For example, if we compare Alloy 5 with a P25 alloy used for milling steel, combining both the lower raw material cost and the difference in specific gravity, Alloy 5 represents an advantage of more than 50 per cent on real raw material costs.

CONCLUSIONS

1. Turning ranges are greatly increased for the new TiC-TiN-VC alloys described here, as a result of increased resistance to plastic deformation and rupture strength.
2. Interrupted cutting (or milling) is now feasible in some applications, as a result of improved edge strength.
3. On a technical basis these new TiC grades are challenging traditional WC alloys and have a distinct economic advantage.

ACKNOWLEDGEMENT

We wish to thank Messrs. M. Humenik and D. Moskowitz and the Ford Motor Company for their cooperation and permission to publish several photographs on these materials.

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Thermodynamic Calculations and the Chemical Vapour Deposition of Hard Materials

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ABSTRACT

The importance of thermodynamic calculations for the CVD of hard materials is emphasized. Examples are given for the SiC and Si_3N_4 systems by the use of calculated CVD phase diagrams.

KEY WORDS

CVD, thermodynamic calculations, hard materials, SiC, Si_3N_4 , silicon carbide, silicon nitride.

INTRODUCTION

Chemical Vapour Deposition (CVD) is an important technique for the fabrication of hard materials and hard material coatings. The procedure involves the high temperature reaction of selected chemical precursors and the deposition of the required product material on a heated substrate. The technique is used for the fabrication of the following groups of materials: (1) Solid state devices, typically based on Si and SiO_2 ; (2) monolithic hard materials which are primarily intended for structural and wear-resistant applications, typically SiC or Si_3N_4 (see for example, Gebhardt, Tanzilli and Harris, 1976, and Fitzer, Hegen and Strohmeir, 1979); (3) hard material coatings, including TiC, TiN, TiB_2 , BN, B_4C , Si_3N_4 , SiC and MoSi_2 on a variety of substrates including carbon, Al_2O_3 , tool steels, stainless steels, cemented carbides, SiC and Si_3N_4 (see for example, Fitzer and Kehr, 1976; Motojima, Tamura and Sugiyama, 1982, and Lee, Chun and Oh, 1981); (4) precursor powders, e.g. Si_3N_4 and WC, used for sintering into a monolithic material (Hojo, Oono and Kato, 1980).

The CVD technique is of value for the following reasons:

- (i) The high purity and quality of the deposits attainable.
- (ii) Absence of impurities on the grain boundaries. This factor can significantly improve high temperature strength and creep resistance (Gebhardt, Tanzilli and Harris, 1976), as well as oxidation resistance (McDonough, Wu and Morgan, 1981).
- (iii) The deposition of homogeneous materials of complex compositions, for example titanium carbonitrides (Pierson, 1977), and also multiple coatings.

(iv) Controllable crystallinity and morphology of the deposits. This includes the deposition of coatings with very small grain size, which can show a marked increase in strength (Dutta, Rice, Graham and Mendiratta, 1980).

(v) The deposition temperature. This can be low in comparison with sintering temperatures.

Thermodynamic calculations can play a number of roles in assisting the CVD processor. These include:

(i) Evaluation of the feasibility of utilizing a particular CVD system.

(ii) The prediction of condensed phases deposited at equilibrium in complex systems.

(iii) Provision of the necessary data for modelling of simple CVD processes (Spear, 1982).

The calculations are therefore useful for the setup, optimization and understanding of CVD systems. This paper provides examples of the manner in which this may be done.

PROCEDURES

The computer program used in this work is a modification of SOLGASMIX (Eriksson, 1975), which has been described for use in CVD systems by Spear (1979). The program calculates the equilibrium composition of the system given the input gas concentrations, temperature and total pressure. The equilibrium composition corresponds to that unique composition which results in the minimum system free energy and is calculated using a free energy minimization subroutine (White, Johnson and Dantzig, 1958). Output data is typically presented as "CVD phase diagrams", which yield the phases deposited as a function of the input gas concentration, at given temperature and total pressure. Enthalpy changes for the system and theoretical deposition efficiencies can also be calculated, as discussed below.

The procedure requires thermodynamic data for all possible gaseous and condensed species as program input. The effect of low concentration species is therefore also included.

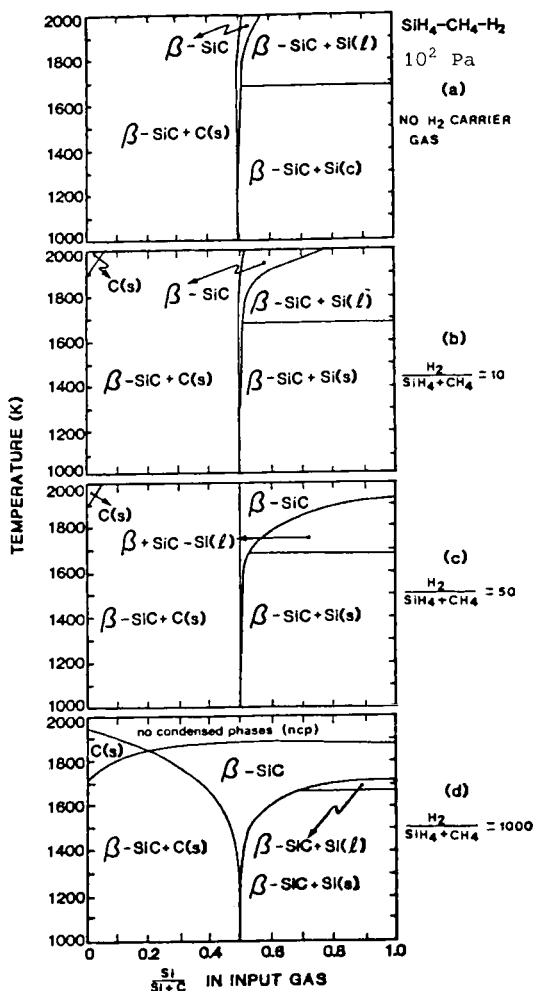


Fig. 1. Condensed phase in the SiH_4 - CH_4 - H_2 system showing the effect of pressure.

THE SiC SYSTEM

One of the problems in the deposition of SiC, for both monolithic and coating applications, is the occurrence of mixed phases (Kington, Lutz, Liaw and Davis, submitted). These are typically SiC + Si or SiC + C. This occurrence has usually been ascribed to kinetic effects. The substantial influence of thermodynamic factors such as system pressure, temperature and input gas concentrations, are shown below.

Fig. 1 shows the influence of system pressure on the deposition of phases in the Si-C-H system. The precursor gases are SiH₄, CH₄ and H₂. Note the fairly limited range of equilibrium conditions under which single phase SiC can be produced, and in particular the sensitivity to the SiH₄ and CH₄ input gas concentrations. Fig. 2 shows the influence of the H₂ carrier gas concentration on the conditions for single phase SiC deposition. The partial pressures of SiH₄ and CH₄ decrease with increasing H₂ concentration. The sensitivity of the single phase deposition field to the thermodynamic parameters is in line with the numerous literature reports of SiC + C or SiC + Si deposition.

Thermodynamic calculations have also been performed for the Si-C-H-Cl system, using the precursor gases SiCl₄, CCl₄ and H₂. Fig. 3 shows the influence of system pressure on the deposition of various phases. Once again, pressure has a marked effect.

The above figures have shown predicted equilibrium compositions for the condensed phases. Equilibrium gaseous species are also calculated. On the basis of these calculated compositions it is possible to deduce which are the major equilibria controlling the deposition process (Kington, Lutz, Liaw and Davis - submitted).

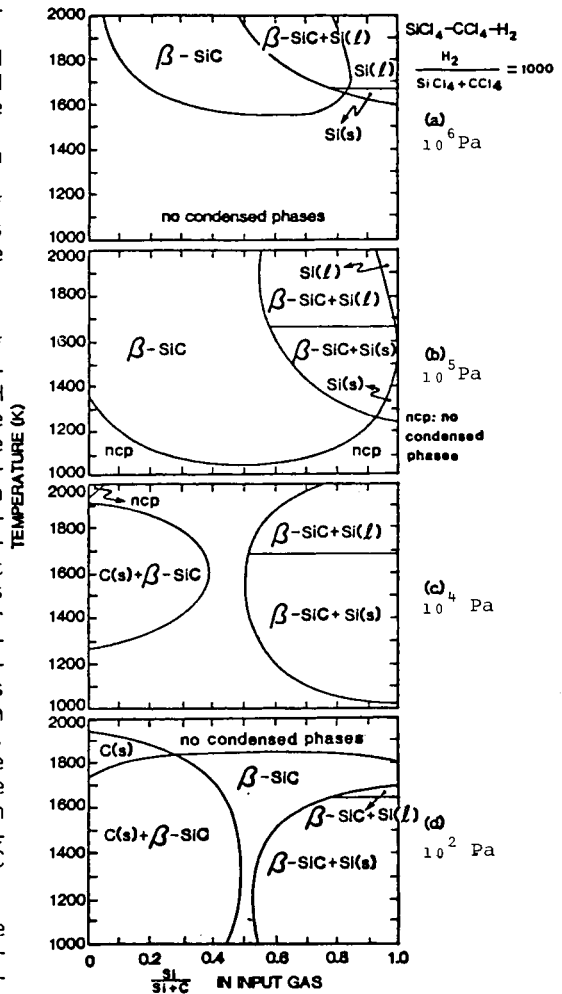


Fig. 2. Condensed phases in the SiH₄-CH₄-H₂ system showing the effect of H₂ carrier gas concentration.

THE Si_3N_4 SYSTEM

There have been a number of reports on the chemical vapour deposition of Si_3N_4 (Kington, Lutz and Davis, submitted). A reported problem is the co-deposition of Si under certain conditions. Fig. 4 shows CVD phase diagrams for the SiH_4/NH_3 system at two different pressures. Si is codeposited with Si_3N_4 at values of $(\text{Si}/\text{Si}+\text{N}) > 0.43$ for the input gas. Relatively low SiH_4 concentrations should therefore be used. Fig. 4(b) reveals an important problem in the CVD of Si_3N_4 , viz the relatively low maximum temperature at which Si_3N_4 may be deposited when the system pressure is lowered. A similar effect is observed at high carrier gas concentrations (Kington, Lutz and Davis, submitted). The effect is due to high stability of N_2 in the gaseous phase at higher temperatures.

In Fig. 4, "theoretical deposition efficiencies" are included in the phase diagrams. This "efficiency" expresses the amount of Si_3N_4 deposited at thermodynamic equilibrium as a percentage of the total amount of Si_3N_4 which could be deposited if all the input gases could react without any kinetic or thermodynamic constraints. The deposition efficiency for Si_3N_4 in the SiH_4/NH_3 system is high for the conditions shown in Fig. 4.

Fig. 5 shows a CVD phase diagram for Si_3N_4 deposited from SiCl_4 and NH_3 input gases. Deposition efficiencies are high at low SiCl_4 concentrations. There is no region of Si deposition. A region appears where no condensed phases are formed. This is a result of the high stability of chlorosilanes as well as N_2 in the gas phase.

Fig. 6 shows a CVD phase diagram for Si_3N_4 deposition from SiF_4 and NH_3 . Of note are the low theoretical deposition efficiencies, as well as the implication that one must utilize low SiF_4 input gas concentrations if one wishes to deposit at relatively high temperatures.

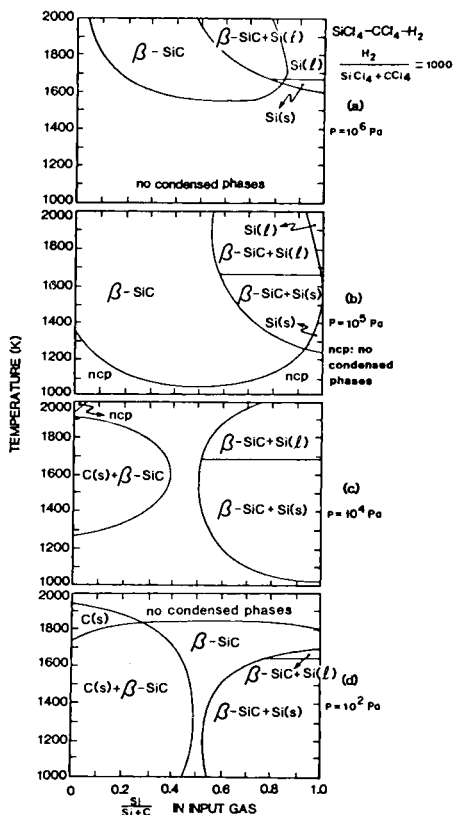


Fig. 3. Condensed phases in the $\text{SiCl}_4 - \text{CCl}_4 - \text{H}_2$ system showing the effect of pressure.

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The Adhesion of Hard and Wear Resistant Coatings

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ABSTRACT

The scratch test is applied to determine the adhesive or cohesive strength of hard coatings deposited on steel and cemented carbide. A Rockwell diamond cone is used to scratch the surface of the coated specimen at a constant speed and under a stepwise or continuously increasing load. The "critical load", at which the coating flakes off or spalls off, is determined by optical or electron microscopy and/or by acoustic emission detection.

KEYWORDS

Coatings; adherence; adhesion; flaking; friction, wear, tribology; CVD; PVD.

INTRODUCTION

CVD and PVD low friction, wear and abrasion resistant coatings such as TiC, TiN, Ti(C,N), Al₂O₃, Cr₇C₃, TiB₂, SiC, Si₃N₄ etc. alone or in combination are increasingly used in industrial applications, especially on cutting and forming tools, machine elements and general wear parts (see e.g. Hintermann, 1980, 1981). During cutting operations with coated cemented carbide inserts or high speed steel tools, failure by flaking is sometimes observed. A similar phenomenon can occur with hard coated deep drawing tools, punch and die assemblies and knife edges made of high carbon/high chromium steel. Furthermore, roller bearing elements can deteriorate due to minute local flaking within the coating caused by cohesion loss. Coatings on gears, on wedge pieces of reverse locking clutches, less often on pistons, slip rings and sealing rings might spall after prolonged periods of operation due to fatigue or improper adherence.

No appropriate means seem to be available to characterize the mechanical properties of the substrate/coating interface, in particular the adhesion strength, and to correlate it with an industrially meaningful property such as flaking, spalling, or chipping - neither on a laboratory scale nor - even

less so - for quality control in production. Thus, a device has been developed: the scratch test. It is based on a principle first advanced by Heavens (1950), Heavens and Collins (1952) and subsequently further developed mainly by Benjamin and Weaver (1960a, 1960b), Weaver (1975), and by other workers (see compendium of authors referred to by Perry, Laeng and Hintermann, 1981) to its present state.

PRINCIPLE AND REALISATION

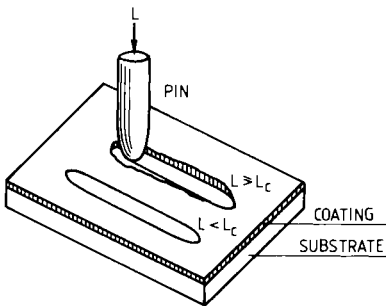
Definition

In the following, adhesion means the property and capability of a coating to remain intact over all of the substrate surface when the composite is subjected to tensile or shear stresses. The adhesion therefore characterizes the rupture strength of the interface or of the transition zone between the coating and the substrate.

Model

The test consists of scratching the surface of the coated specimen at constant speed with a loaded diamond point of defined curvature. The load applied on the diamond can be increased either stepwise or continuously, depending on the equipment (LSRH, 1981). The smallest load at which the coating chips off or flakes off and loses its load-bearing capacity, is defined as the "critical load L_c " taken as a measure of the adhesive or cohesive strength of the coating depending on the locus of failure. In the case of hard coatings this value is reasonably well defined and reproducible.

The surface of the tested sample deforms plastically under the action of the diamond point and shear stresses are generated in the coating/substrate interface. On the basis of these considerations Benjamin and Weaver (1960a, 1960b) have developed a model, and obtained a relation between the adhesion shear strength, the hardness of the substrate, and the measured critical load.



CHARACTERISTIC QUANTITY: LOAD L_c

Fig. 1. Principle of scratch test

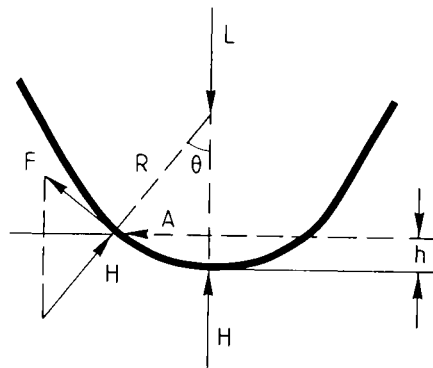


Fig. 2. Benjamin and Weaver's model (1960a, 1960b)

According to Fig. 2, one derives:

$$F = H \cdot \tan \theta \quad (1)$$

$$H = \frac{L}{\pi A^2} \approx \frac{L}{2\pi Rh} \quad (2)$$

$$\tan \theta = \frac{A}{\sqrt{R^2 - A^2}} \quad (3)$$

$$\therefore F = \frac{L}{\pi A^2} \cdot \frac{A}{\sqrt{R^2 - A^2}} \quad (4)$$

where:

F : shear stress at the interface of contact

H : substrate hardness

L : applied load

A : radius of contact circle

b ≈ 2A: width of scratch

R : radius of diamond point

h : depth of the scratch

At the critical load, L_c , and with parameters at which $R \gg A$, and after introducing a correction factor K, with $0.2 < K < 1$, depending on the particularities of the model (Benjamin and Weaver, 1960; Weaver 1975), it follows that the adhesion strength, F_c , can be calculated according to equation (5), or with a good approximation by equation (6) if the hardness is not known.

$$F_c = K \sqrt{\frac{H \cdot L_c}{\pi R^2}} \quad (5);$$

$$F_c \approx K \cdot \frac{2L_c}{\pi Rb} \quad (6)$$

Equipment

On the basis of the model presented LSRH (cf. author's address) has developed and tested two scratch test instruments, with a stepwise and with a continuously increasing applied load respectively. Both instruments have been successfully used in laboratory studies and for quality control in production. From the experience obtained as a result of numerous experiments and in correlation with the model, the following characteristics of the diamond cone have been chosen: radius 0.2 mm, cone angle 120° (Rockwell point). The scratches are examined under the optical or in the scanning electron microscope, SEM.

Criteria for determining the critical load are the microscopical inspection as well as the detection of an acoustic emission (AE). Emission occurs when brittle rupture takes place in a plane parallel or nearly parallel to the surface and is more pronounced the more brittle the coating is.

The acoustic emission is detected by a piezoelectric detector fixed next to the diamond point. The amplified and rectified signal is recorded or transmitted by earphone. The signal amplitude is small and relatively steady until the critical load is reached; at the critical load it increases rapidly and approaches a threshold value which does not increase any further even at higher load. In order to obtain a better insight into the nature of the rupture and possibly into the failure mechanism of adhesion, efforts have to be made to interpret the rise and oscillations of these curves.

MEASUREMENTS AND RESULTS

The following figures illustrate the application of the scratch test on some typical coating/substrate combinations, produced by Chemical or Physical Vapour Deposition (CVD or PVD).

Acoustic emission as a function of load

Figure 3 shows three repeats of the acoustic emission as a function of the load applied on the diamond when scratching a cemented carbide (cc) cutting tool insert which had been coated with $6\text{ }\mu\text{m}$ TiC by CVD. The critical load, L_c , is indicated by the threshold at which the acoustic emission suddenly increases. The scattering is less than 10 %.

Experience has shown that the acoustic emission detected when the coating cracks perpendicularly to the plane of the surface is negligible compared to that produced when the coating flakes off. The exact cause of the acoustic emission is not yet clear, but it is probably due to (i) either the elastic energy release during the rupture of the coating or the interface or (ii) the irregular friction of the diamond tip on the surface just damaged in front of the diamond due to coating failure. Whatever the exact cause may be, there is a good correlation between the microscopical observation and the acoustic detection of the failure.

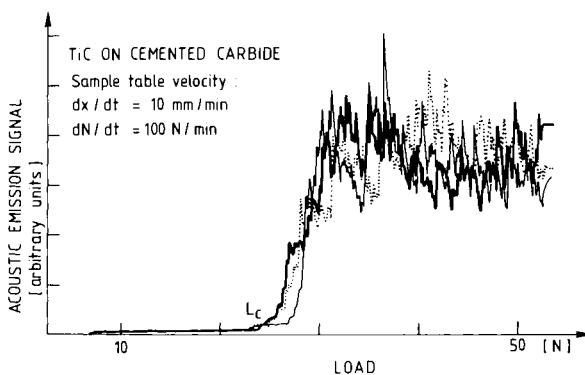


Fig. 3. Acoustic emission (AE) vs. applied load L :
 $6\text{ }\mu\text{m}$ TiC (CVD) on cemented carbide (cc)

Selectivity of scratch test

Figure 4 shows characteristic "acoustic emission (AE) - load (L)" diagrams for TiC and TiC/TiN CVD-coated cemented carbide inserts from production of six different manufacturers (a)-(f). The scratch test is selective in the sense that each of the industrial products is characterized by a different "AE-L" diagram. Hence the "AE-L" curve is so to speak a finger-print of the composite and should allow its identification. This property of the "AE-L" characteristics is presently applied in the production control for tools with

CVD and PVD hard coatings on steel and cemented carbide. An adhesion or cohesion failure would manifest itself by a different curve and a displacement of the threshold of the acoustic emission onset, i.e. of the critical load.

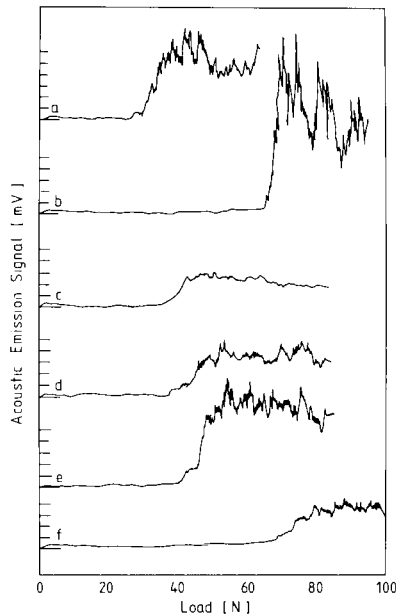


Fig. 4. Characteristic "AE-L" diagrams for TiC(CVD) coated cc cutting tips of different origin: (a) $6\text{ }\mu\text{m}$ TiC, (b) $10\text{ }\mu\text{m}$ Ti(C,N), (c) $\approx 6\text{ }\mu\text{m}$ TiC, (d) $6\text{ }\mu\text{m}$ TiC, (e) $8\text{ }\mu\text{m}$ TiC, (f) $12\text{ }\mu\text{m}$ TiC+Ti(C,N)+TiN

Pure adhesive flaking

Figure 5 represents a scanning electron micrograph (SEM) of scratches made on a RF-sputtered $2.4\text{ }\mu\text{m}$ thick TiC coating on a steel substrate. The applied load was increased stepwise from scratch to scratch. On this coated specimen no failure could be observed along the scratches up to loads of 9 N. At loads above 10 N, however, characteristic flaking could be seen on either side of the scratch, particularly in the rim zone, i.e. the zone of highest tension. The fracture surface exposed obviously coincides with the steel surface and in this case pure adhesive flaking occurred.

Mixed cohesive adhesive flaking or chipping

The failures shown in Fig. 6 are of a completely different nature. The tested composite is a steel substrate coated by CVD with $8\text{ }\mu\text{m}$ TiC. The first signs of failure occurred at a load of 16 N in the form of lateral vents. A chemical analysis of the fractured surface indicates that elements which are typical of the substrate are to be found only at the rim in the immediate transition zone between the untouched surface and the scratch, i.e. where the stresses are largest and where the damage across the coating is deepest. In

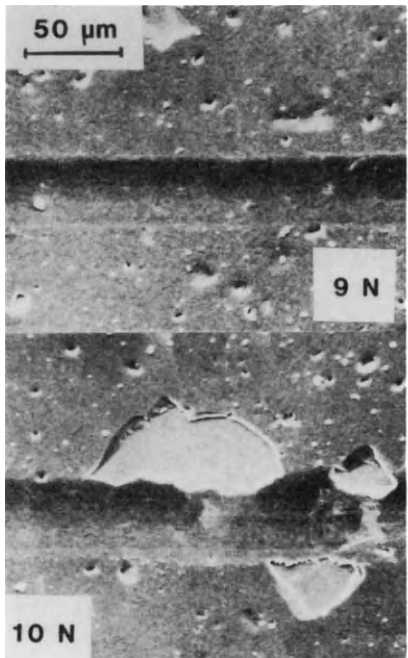


Fig. 5. Adhesive failure; scratch in 2.4 μm TiC (PVD) coating on steel ($\text{HV}=710 \text{ daN/mm}^2$); $9 \text{ N} < L_c < 10 \text{ N}$

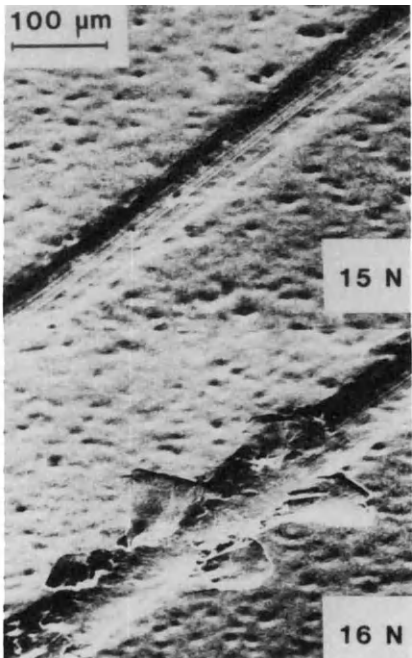


Fig. 6. Cohesive-adhesive failures; scratch in 8 μm TiC (CVD) coating on steel ($\text{HV}=280 \text{ daN/mm}^2$); $15 \text{ N} < L_c < 16 \text{ N}$

other words, fracture has most probably originated at the coating/substrate interface and propagated to the coating surface in an oblique rupture. This results in a characteristic "sea-shell" fracture surface. In this case a mixed cohesive-adhesive flaking or chipping is the failure mode.

Multi-layer coating

As an example, a cemented carbide (WC-Co) cutting tip coated with TiC (5 μm) and Al_2O_3 (1-2 μm) by CVD is shown in Figs 7 and 8. The first failures due to

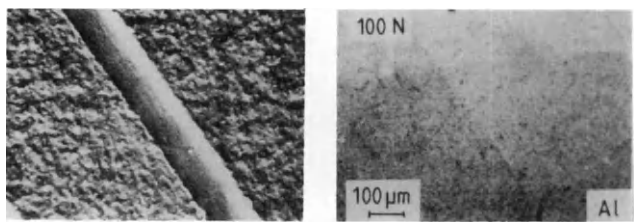


Fig. 7. TiC (5 μm) Al_2O_3 (1-2 μm) CVD double coating on cc insert: $L = 100 \text{ N} < L_c$, X-ray image shows that the Al_2O_3 coating is present everywhere

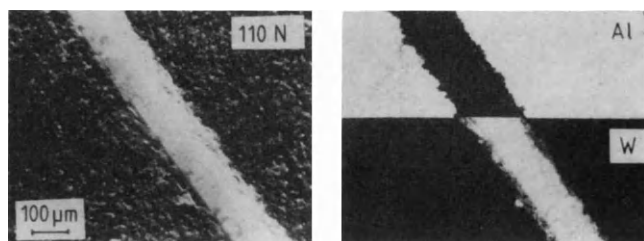


Fig. 8. As in Fig. 7, $L = 110 \text{ N} > L_C$, X-ray image reveals complete removal of the double coating and exposure of the substrate (W-signal)

scratching occur at a load of 110 N. At 100 N X-ray imaging does not indicate any damage of the Al_2O_3 top layer (Fig. 7), whereas at 110 N the trace of the diamond pin is very visible due to flaking of the $\text{TiC}/\text{Al}_2\text{O}_3$ coating (Fig. 8). The flaking occurs at the cemented carbide/ TiC interface.

Influence of specimen preparation

Figure 9 shows the adhesion behaviour of a TiN coating, $5 \mu\text{m}$ in thickness, deposited by CVD onto a Co-Cr-Mo-Ni alloy with a high Co-content. In an oxidizing atmosphere the surface of this alloy is readily transformed into chromium oxide, which is difficult to reduce. This oxide coating is probably the cause for the poor adhesion of the TiN coating on the substrate when a special surface treatment prior to deposition is not applied (left and middle photographs, $28 \text{ N} < L_C < 32 \text{ N}$).

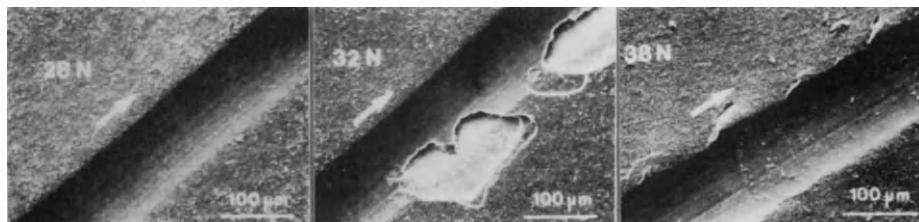


Fig. 9. Influence of the specimen preparation: $5 \mu\text{m}$ TiN (CVD) on a Co-Cr-Mo-Ni alloy. Left and middle photographs: without any preliminary treatment ($28 \text{ N} < L_C < 32 \text{ N}$), right photograph: chemically etched before coating ($L_2 \approx 38 \text{ N}$).

However, if the substrate surface is suitably chemically etched prior to coating with TiN , a distinctly better adhesion is obtained. This is indicated by a higher critical load observed (right photograph, $L_C \approx 38 \text{ N}$). In this case the failure mechanism is dissimilar to the former, and the pattern of the damaged coating area is different. In the first case the observed failure is purely adhesive flaking, while in the second case the failure of the coating is caused by fissures, probably due to separation at the grain boundaries along the columnar grains.

DISCUSSION AND CONCLUSION

The cited examples have shown that by means of the scratch test it is possible to assign a value to a quantity designed as the critical load which can be correlated with the occurrence of an adhesive or cohesive coating failure. The determination of the locus of failure and the examination of the shape and extension of the damages caused to the coating can provide additional information on the mechanism of failure and on the origin of the weakness of a given coating/substrate combination. However it is obvious that the measured critical load depends not only on the strength of the interface but also on the mechanical properties of the coating and of the substrate. Recent works by Laeng and Steinmann (1981) and Perry (1981a,b) have shown how the critical load can vary with the hardness of the substrate and with the thickness of the coating for samples having presumably similar interfaces. In particular the observed relation between the critical load and the hardness of the substrate is in disagreement with the predictions of Benjamin and Weaver's model. Thus more work is needed both on the theoretical and on the experimental side in order to establish the correct relation between the stress distribution generated by the scratching action, the critical load and the mechanical properties of the substrate and of the coating. Nevertheless it appears that the adhesion (or cohesion) strength of similar coatings deposited on similar substrates can be directly compared by measuring simply the critical load. In the case of hard and brittle coatings this quantity is relatively well defined and the measurements are satisfactorily reproducible.

ACKNOWLEDGEMENT

The authors express their gratitude to the Swiss National Science Foundation for supporting this project within a five-year research programme at LSRH. Recognition is due to Mr. P.A. Steinmann for his collaboration, Dr. L. Chollet and Mr. J. Béguin for the SEM work, Miss M. Rüegg, Messrs. Ph. Guinand and Ch. Jeanneret for assistance in the preparation of this paper.

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Erosion Behaviour of CVD TiB₂ Coatings on TiB₂-based Ceramic Substrates in High-velocity Coal-oil Slurries*

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ABSTRACT

The erosion behaviour of CVD TiB₂ coatings deposited on TiB₂ ceramic substrates was studied via impingement of a liquid stream containing 8 wt % of coal-derived (SRC-1) solids in anthracene oil upon the CVD surface and compared with erosion of a high-density uncoated TiB₂ ceramic specimen.

Erosive exposure of all specimens was conducted at ~350°C for 1 h at a liquid flow velocity of 100 m/s and an incidence angle of 20° between the liquid jet and the specimen surfaces. These conditions simulate those present in pressure let-down valves in direct coal liquefaction processes. The principal materials variables included the microstructure and composition of the TiB₂ ceramic substrates, while the CVD coatings were all deposited under identical conditions at 900°C from TiCl₄ and BCl₃. The deposited CVD coatings, which were ~50 µm thick, exhibited strong preferred orientation as determined by X-ray diffraction. Relative erosion resistance was assessed by determining the maximum depth of the erosion crater formed in the TiB₂ surface at the point of jet impingement. For the four CVD coatings exposed, the maximum crater depth values were 0, 1.5, 5.5, and 5.5 µm, while the uncoated specimen had a depth of ~22 µm. Prior work had shown that only consolidated or single-crystal diamond provided zero crater depths under these conditions. The outstanding erosion resistance of the CVD coatings was apparently related to the crystallographic texture produced in them when they were deposited on the TiB₂ ceramic substrates.

KEYWORDS

CVD, TiB₂, coal-oil slurry erosion

INTRODUCTION

Chemical vapour deposited (CVD) TiB₂ coatings have been proposed for use under highly erosive conditions in coal conversion plants, as well as for other uses such as parts in fusion reactors and cutting tools for metal machining (Pierson and Randich, 1978). In spite of the high hardness of the material (VHN-3333), experience to date reveals variable erosion behaviour during exposure under simulated coal liquefaction let-down valve conditions

(Mueller and Wright, 1978), possibly due to a thermal expansion substrate/coating mismatch with non-TiB₂ substrates or due to chemical incompatibilities. The object of this study was to determine the erosion behaviour under coal liquefaction process conditions of CVD TiB₂ coatings deposited on TiB₂ ceramic substrates whereby the thermal expansion mismatch between the coating and substrate would be minimized. The erosion behaviour of a high-density TiB₂ ceramic without a CVD TiB₂ coating was used for comparison with the coated specimens. Erosion studies on a wide variety of materials in the special facility at the Battelle Columbus Laboratories (BCL) used in this study have provided data for direct comparison with the present results. The four CVD TiB₂ coatings on TiB₂ ceramic substrates and an uncoated TiB₂ ceramic were exposed to impingement of a jet of 8% SRC-I solids in anthracene oil at ~350°C, a velocity of 100 m/s, and an incidence angle of 20° for 1 h.

Both the substrate production technique and the coating method have been previously described (Tennery and colleagues, 1981; Pierson, Randich, and Mattox, 1979; Curlee and Hawn, 1978). This paper reports the results obtained for four different TiB₂-Ni substrates coated under identical conditions, plus one uncoated TiB₂ ceramic. The substrates were fabricated to include a range of TiB₂ grain size, Ni content, O content, and Young's modulus. Exposed coatings were evaluated by X-ray diffraction, ion microprobe analysis, profilometry, and scanning electron microscopy.

The relative erosion resistance of a variety of materials has been determined at BCL using the maximum crater depth formed in the specimen surface as a measure of material stability. Under the exposure conditions employed in this study, one of the most erosion resistant commercially available materials reported is a WC-Co composition identified as K701,¹ which exhibits a crater depth of 6 to 7 µm. The best materials reported prior to the present study are single crystal and consolidated diamond, neither having measurable craters.

PREPARATION OF TiB₂ SPECIMENS

TiB₂-Ni Ceramic Substrate

Production of high-density TiB₂-Ni ceramics has been previously described (Tennery and colleagues, 1981). Briefly, the fabrication process includes the vacuum hot pressing of prescribed amounts of TiB₂ and Ni powders in graphite die assemblies at 1425°C, resulting in compacts of above 99% theoretical density.

The as-pressed, 4-cm-diameter disk-shaped compacts were cut into specimens of ~7 × 7 × 7 mm size. Prior to CVD coating, one 7 × 7 mm face of each specimen was polished metallographically and photographed under polarized light to reveal the microstructure, including grain boundaries of the TiB₂. The polished surface in each case was oriented perpendicular to the original hot-pressing direction. The average boride grain size was then determined by analytical microscopy procedures. Specimens were also analyzed by X-ray fluorescence, neutron activation, and sonic velocity — techniques to obtain the Ni content, O content, and Young's modulus, respectively. Table 1 presents these values. Specimens NT 90J, NT 80"O", NT 90AC, and NT 90AD were subsequently coated on the polished 7 × 7 mm surface with CVD TiB₂.

¹Product of Kennametal, Inc., Latrobe, Pennsylvania.

TABLE 1 Properties of TiB₂-Ni Ceramics

Property	Substrate Type				
	NT 90J	NT 80"0"	NT 90AC	NT 90AD	NT 85R
Density ^a (g/cm ³)	4.59	4.18	4.50	4.63	4.52
Ni (wt %) ^b	1.9	0.9	0.8	1.3	0.25
C (wt %) ^c	0.3	0.2	0.2	0.2	0.2
O (wt %) ^d	0.8	9.0	1.0	0.6	1.2
Young's modulus ^e (GPa)	536	381	571	577	559
Grain size (μm) ^f	9.1	4.1	5.3	7.4	6.5

^aBy immersion: theoretical density of TiB₂ = 4.52 g/cm³.

^bX-ray fluorescence determination.

^cInfrared detection of CO₂ from ignited sample.

^dNeutron activation determination.

^eFrom sonic velocity.

^fQuantimet determination of polarized-light photograph.

TiB₂ CVD Coating of TiB₂-Ni Ceramic Substrates

The TiB₂ coatings were deposited on polished, ultrasonically cleaned specimen surfaces using CVD reactions generated by the reaction of BCl₃ and TiCl₄ at 900°C and 8×10^4 Pa (0.8 atm) total pressure. All four samples were exposed simultaneously. Pierson and Randich (1978) give details of the apparatus and procedure. The flow rates used were: TiCl₄ (liq), 0.004 ml/s; BCl₃ (g) 4 ml/s; H₂ (g) 33 ml/s; and Ar (g) 1.2 ml/s. As a preliminary step, the liquid TiCl₄ was vaporized at 300°C and transported at elevated temperatures by the Ar. Under these conditions, the TiB₂ deposition rate on the specimens was ~0.004 μm/s with the deposition time 8200 s. The samples were heated on an inductively coupled graphite susceptor monitored by a thermocouple, while sample and susceptor surface temperatures were checked with an optical pyrometer through the fused quartz reactor chamber. In spite of simultaneous coating deposition, subsequent coating studies suggested variations in local deposition conditions within the apparatus which are not fully understood, and whose effect on coal oil slurry erosion will be the subject of a later paper.

EXPERIMENTAL RESULTS

Characterization of TiB₂-Coated Substrates

Before erosion exposure, the area normal to the as-deposited CVD surface was examined by scanning electron microscopy and by oil-immersion optical microscopy. X-ray diffraction patterns of the CVD coated specimens obtained using CuKα radiation were compared with those obtained for the surface of the uncoated erosion specimen (NT 85R), for the surface of a high-density hot-pressed TiB₂ specimen, and with the X-ray diffraction data on file for this compound. The following conclusions can be made at this time. The four CVD TiB₂ coatings all exhibit pronounced preferred orientation, with the (002) reflections being undetectable. The (101) and (110) diffraction line intensities of the TiB₂ were also much reduced compared to randomly

oriented TiB_2 . These results indicate that, on the average, the crystallographic c-axes of the TiB_2 crystallites in the coatings are oriented parallel to the substrate surfaces. In addition, strong extra diffraction lines were observed at ~ 2.326 , 1.743 , and 1.353 Å which do not belong to hexagonal TiB_2 . In all of the coatings, the line at ~ 1.743 Å was either the first or second most intense line in the diffraction patterns. An explanation for these "extra" lines is not yet available. They are probably either due to the presence of a substantial amount of a phase other than TiB_2 in the coatings, or the deposition resulted in some modification to the TiB_2 structure which has not been previously reported in the literature. If these lines are due to a second phase, it must have relatively high symmetry and/or have high preferred orientation to explain the low number of lines observed.

To characterize the composition of the CVD TiB_2 coating versus that of the TiB_2 -Ni substrate, polished profile sections were made perpendicular to the as-deposited surface. The coating thickness was estimated to be between 40 and 50 μm for the four coated specimens. Ion microprobe analyses were made across the substrate/coating boundary on the polished sections, and elemental compositions were determined, including Ti, B, C, O, Cl, and Ni. These analyses indicated that the B/Ti ratios in the coatings were essentially identical to those in the ceramic substrates and that no Ni or O diffused from the substrate to the coating during deposition. Since the B/Ti ratios in the coating is substantially the same as in the substrate, with the 2- μm beam diameter of the ion microprobe, certain conclusions are possible. The B/Ti ratio in the ceramic substrates is known to be ~ 2 from previous direct measurements including determination of TiB_2 lattice parameters, etc. Since X-ray diffraction results clearly show that TiB_2 is at least a major phase in the coatings, the average ratio of B/Ti ≈ 2 can only be maintained in the coating if at least three phases are present, one with B/Ti < 2 such as TiB, and Ti_2B_5 or Ti_3B_4 , both of which have B/Ti > 2 . It appears unlikely that a three-phase mixture would be formed under the coating deposition conditions, since X-ray diffraction did not reveal these phases. These results therefore suggest that the "extra" diffraction lines are due to a previously unreported modification of the TiB_2 structure. Figure 1 shows the B, Ti, and Ni ion intensities measured for a second NT 90AD specimen coated under conditions identical to those employed in fabricating the erosion specimens.

Characterization of TiB_2 Surfaces Exposed to Slurry Erosion

The slurry erosion exposures were performed as described by Wright at BCL (Mueller and Wright, 1978). Profilometry and scanning electron microscopy were used to determine the effect of slurry jet impact on the surface of the TiB_2 specimens. X-ray diffraction was employed to determine if any phase changes occurred on the TiB_2 surfaces during the erosion exposure. The surface geometry at the point of slurry impact was determined using a profilometer having a 12.7 μm diamond stylus and a normal force of 5×10^{-4} N. Typically, the slurry erodes the surface of a hard material as a crater which has an elongated shape in the longitudinal direction (i.e., along the axis of the original jet). In the direction transverse to the jet axis, the crater is quite narrow in the area of jet impact, but becomes much shallower and wider beyond this region in the flow direction. Maximum crater depth, which has been employed as a measure of material erosion resistance under the conditions employed at the BCL facility, is the vertical distance measured from the average original surface to the deepest portion of the crater.

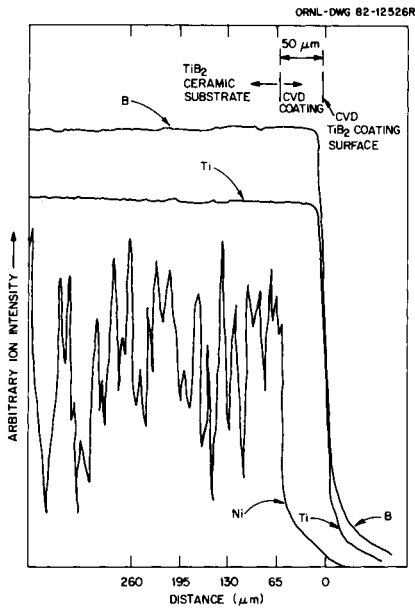


Fig. 1. Boron, titanium, and nickel concentrations as function of distance from outer CVD TiB_2 coating surface for specimen NT 90AD as determined via ion microprobe.

The four CVD-coated specimens designated NT 90AD, NT 80"0", NT 90AC, and NT 90J had maximum crater depths of 0, 1.5, 5.5, and 5.5 μm , respectively. The crater depth of zero for specimen NT 90AD (no detectable erosion) had been previously observed only for diamond by BCL workers. The high-density, uncoated TiB_2 specimen, NT 85R, had a maximum crater depth of $\sim 22 \mu\text{m}$. Longitudinal profilometry results for specimens NT 90AD and NT 85R are shown in Fig. 2. The CVD TiB_2 coated surfaces were initially quite rough, consisting of boride crystals and crystal clusters projecting perpendicular to the substrate-coating interface. Some of the TiB_2 growth features extended above the surface an average of $\sim 2 \mu\text{m}$. These surfaces became smoother in the jet impact area, but even where a measurable crater was formed, the surface still consisted of TiB_2 crystals projecting upward and oriented perpendicular to the substrate, as shown in Fig. 3.

Specimen NT 85R originally had a metallographically polished surface prior to erosion exposure. In this case, the jet eroded a substantially deeper and longer groove than produced in any of the four coated specimens. For the CVD-coated specimen NT 90AD, no obvious erosion crater could be measured, as shown in Fig. 2, but a shallow depression having a depth of $\sim 0.5 \mu\text{m}$ was produced along the axis of the jet $\sim 1 \text{ mm}$ beyond the point where the jet axis intersects the TiB_2 surface. Energy dispersive X-ray analyses indicated that no significant contamination of the TiB_2 surfaces occurred by elements heavier than Na from the slurry during the exposure.

RESUMÉ

CVD TiB_2 coatings deposited on TiB_2 ceramic substrates exhibit limited erosion crater depths ranging from zero to $\sim 5.5 \mu\text{m}$ when exposed to a slurry jet simulating conditions in a coal liquefaction let-down valve. In contrast, an uncoated TiB_2 ceramic specimen exhibits a relatively large

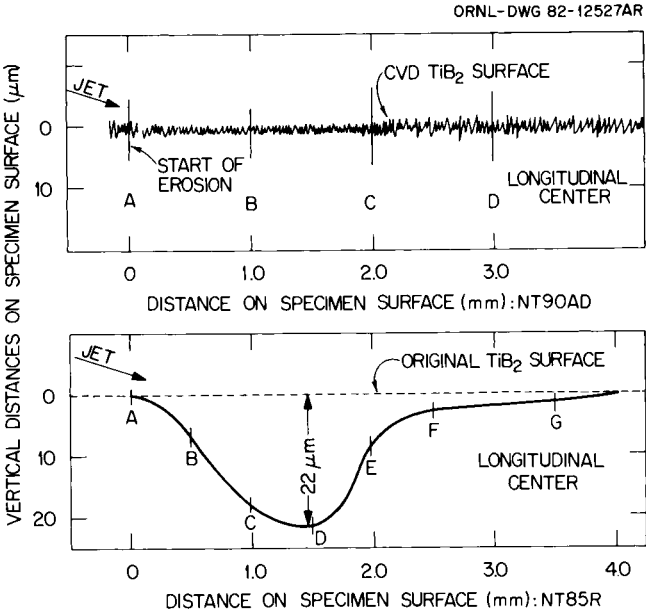


Fig. 2. Profilometry results for two TiB₂ specimens following erosive jet exposure. (a) NT 90AD specimen with CVD TiB₂ coating; (b) NT 85R specimen without CVD TiB₂ coating.

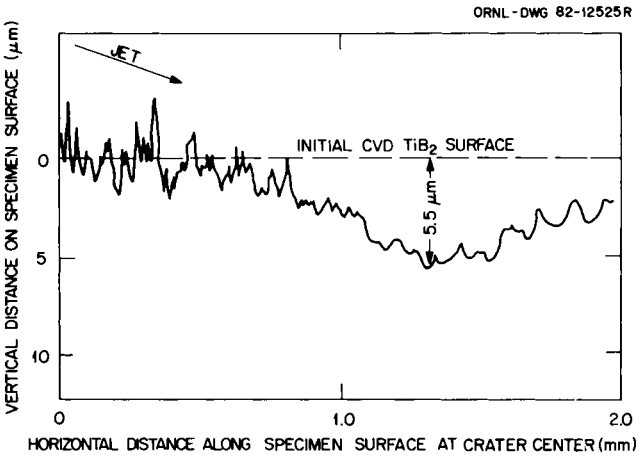


Fig. 3. Detailed longitudinal profilometry of specimen NT 90AC showing lessening of surface roughness near crater bottom. Erosive jet exposure conditions: 1 h, 343°C, 100 m/s, 20° incidence angle.

crater depth of ~22 μm . The outstanding erosion resistance of the CVD TiB₂ coatings is possibly associated with the strong preferred orientation of the TiB₂ crystallites in the coatings. Further work is in progress to analyse these textures and to explain the strong additional X-ray diffraction lines observed in the coatings. In general, the TiB₂-based substrates appear to enhance the coal-oil slurry erosion resistance of TiB₂ CVD coatings deposited on them.

ACKNOWLEDGMENT

The authors acknowledge the support of the Division of Materials Sciences, U.S. Department of Energy (contracts W-7405-eng-26 and DE-AC-04-760A00789). Special thanks are extended to S. Waters, P. Becher, W. Farmer, O. Cavin, R. Eby, W. Christie, F. Foust, and F. Stooksbury. Appreciation is also expressed to I. Wright of Battelle Columbus Laboratories and to H. O. Pierson and J. F. Smatana of Sandia National Laboratory.

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Erosion of Sintered WC-Co Alloys

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ABSTRACT

The effects of WC grain size in the range of 0.9-3.0 μm and Co contents of 4.5 to 11.3 wt % on the erosion of sintered WC-Co alloys was investigated using a sandblaster-type erosion tester employing 240 grit Al_2O_3 particles carried in an air stream at velocities of 30-100 ms^{-1} and impact angles of 20°-90°. Limited SEM studies were made of the surface damage produced by the erosion. No clear effect of WC grain size on the erosion rate $E_R^{\text{WC-Co}}$ (g/g) was established. The effects of volume fraction of Co (f_{Co}), particle velocity (v) and angle of impact (α) on $E_R^{\text{WC-Co}}$ was given by

$$E_R^{\text{WC-Co}} = a + b f_{\text{Co}} = a + b_{90} f_{\text{Co}} + (b - b_{90}) f_{\text{Co}}$$

where $a = A(v \sin \alpha)^2$, $b_{90} = B(v \sin \alpha)^{3.2}$ and $(b - b_{90}) = C(v \cos \alpha)^2$, A, B and C being constants. a was identified with E_R^{WC} . Assuming a rule of mixtures, $E_R^{\text{Co}} = [A(v \sin \alpha)^2 + B(v \sin \alpha)^{3.2}] + C(v \cos \alpha)^2$. The results are discussed in terms of existing theories of the erosion of ductile and brittle materials.

KEYWORDS

Normal component; WC grain size; Co volume fraction; microstructure; elastic Hertzian fracture; elastic-plastic fracture; cutting and deformation wear.

INTRODUCTION

The failure of components due to erosion is recognized to be an important technological problem. It is especially serious in coal conversion plants, being responsible for the failure of such components as the control and let-

down valves and slurry feed pumps.

A family of materials frequently used for components where erosion represents a problem is the cemented WC-Co alloys. However, only little is known about the erosion of such alloys, especially regarding the effects of microstructure. Although all previous work (Dan'kin, 1970; Uuémýis and coworkers, 1974; Hanson, 1974; Conrad, McCabe and Sargent, 1981) indicates that the erosion rate of WC-Co alloys increases with Co content, there is some disagreement on the effect of WC grain size and the angle of impact at which maximum erosion occurs, both of which seem to depend on the erosion conditions. The present investigation was therefore undertaken to further evaluate the erosion behaviour of sintered WC-Co alloys, giving special attention to the effects of microstructure.

EXPERIMENTAL

The cemented WC-Co alloys used in this study were provided by Multi-Metals, a Division of Vermont American Corporation. The alloys represented a range in Co content from 4.5 to 11.3 wt.% (8-21 vol.%); the WC grain size ranged from 0.9 to 3.0 μm . The erosion tests were performed using a sandblaster-type of erosion tester employing 240 grit Al_2O_3 particles (30 μm mean size).

The tests were carried out under ambient conditions at velocities of 30-100 ms^{-1} determined by the rotating disk method of Ruff and Ives (1975). The particle impingement angle was varied from 20° to 90° . The erosion tests were performed on the as-received specimen surface, which had been lightly grit blasted by Multi-Metals using 46 to 120 grit SiC. The tests were periodically interrupted to ascertain the weight loss of the specimen as a function of the amount of abrasive which had impacted it. Following a short initial transient, whose extent depended on the erosion conditions, a steady state specimen weight loss per gram of impacting particles was soon reached, which is termed the erosion rate $E_R(\text{g/g})$.

Limited scanning electron microscopy (SEM) studies were made of the surfaces of eroded specimens to determine the nature of the damage produced by the erosion.

RESULTS

The variation of E_R with the angle of particle impact α is illustrated in Fig. 1, where it is seen that maximum erosion rate occurs at $\alpha \approx 90^\circ$ for all Co contents. Similar behaviour was observed for all conditions investigated.

The effect of Co content on E_R at $\alpha = 90^\circ$ as a function of particle velocity v is depicted in Fig. 2. It is here seen that E_R increases linearly with volume fraction of Co (f_{Co}) at all velocities, the slope increasing with velocity. Similar behaviour was observed for all impact angles considered.

The effect of WC grain size d_{WC} on the erosion rate was not clearly resolved. However, it appeared that E_R goes through a maximum at $d_{\text{WC}} \approx 1.5 \mu\text{m}$. This could explain why different investigators have reported opposite effects of d_{WC} on E_R .

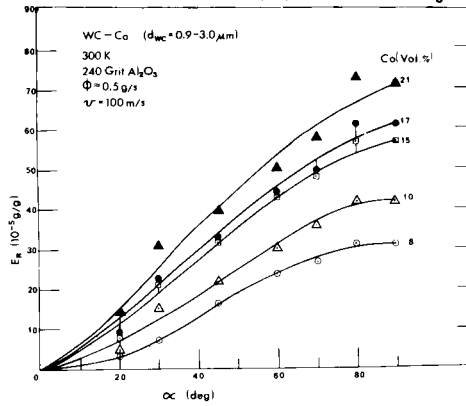


Fig. 1. Effect of angle of particle impingement on erosion rate as a function of Co content.

The form of the curves in Fig. 1 suggests that the angular dependence of E_R may be given by the normal component of the particle velocity $v_{90} (=v \sin \alpha)$. This was found to be the case for $\alpha > 45^\circ$; however, for smaller impact angles, E_R was always larger than that based on $(v \sin \alpha)$ alone. This result is

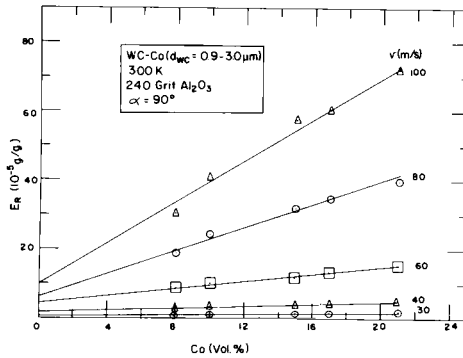


Fig. 2. Effect of Co content on erosion rate as a function of particle velocity.

illustrated in Fig. 3, where it is seen that good agreement exists for the two sets of data corresponding to $v_{90}=87 \text{ ms}^{-1}$ ($v=87 \text{ ms}^{-1}$, $\alpha=90^\circ$ and $v=100 \text{ ms}^{-1}$, $\alpha=60^\circ$), whereas this is not the case for the two sets corresponding to $v_{90}=50 \text{ ms}^{-1}$ ($v=50 \text{ ms}^{-1}$, $\alpha=90^\circ$ and $v=100 \text{ ms}^{-1}$, $\alpha=60^\circ$). In the latter case

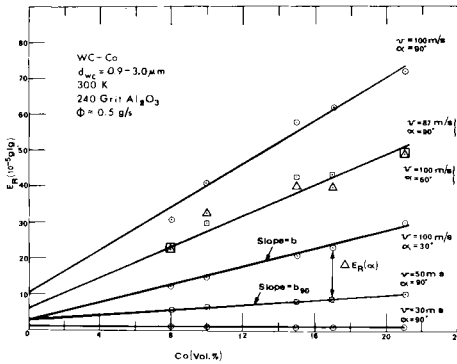


Fig. 3. Erosion rate versus Co content as a function of the normal component of the particle velocity.

there occurs an additional amount of erosion $\Delta E_R(\alpha)$ due to the glancing angle, which amount decreases with decreasing Co content becoming zero at zero Co content. The results of Fig. 3 lead to the following expressions

$$E_R^{WC-Co} = a + b f_{Co} \quad (1)$$

$$= a + b_{90} f_{Co} + (b - b_{90}) f_{Co} \quad (1a)$$

where a and b are constants which depend on particle velocity and angle of impact and f_{Co} is the Co volume fraction. a can be considered to give the erosion of pure WC, b that due to the addition of Co, b_{90} that part of b due to the normal component of the velocity and $(b - b_{90})$ that due to the glancing component. The effects of the particle impact angle α on a and $(b - b_{90})$ are shown in Fig. 4, where it is seen that the maximum of a occurs at $\sim 90^\circ$ and that for $(b - b_{90})$ at $\sim 30^\circ$. These angular dependencies of a and of $(b - b_{90})$ are in accord with those normally found for the erosion of brittle and ductile materials, respectively.

The form of the curve for the constant a in Fig. 4 suggests that the erosion of pure WC is determined principally by the normal component of the velocity. Support for this is provided in Fig. 5, where a is plotted versus $(v \sin \alpha)$ on a log-log scale, yielding a slope of $n=2.0$. Log-log plots of b_{90} versus

($v \sin \alpha$) and of ($b-b_{90}$) versus ($v \cos \alpha$) yielded $n=3.2$ and 2.0 respectively.

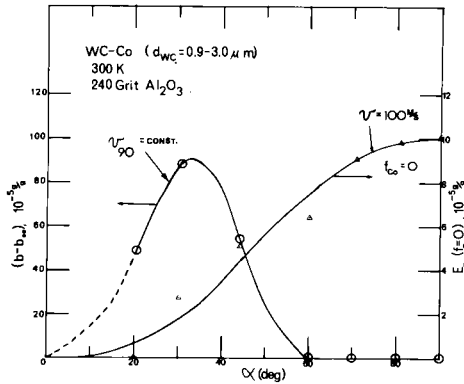


Fig. 4. Variation of the constant $a=E_R^{WC}$ and the quantity ($b-b_{90}$) with particle impact angle.

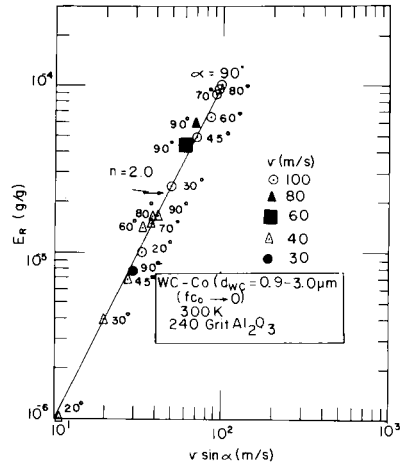


Fig. 5. Log-log plot of the constant $a=E_R^{WC}$ versus the normal component of the particle velocity. Indicated with each data point is the impact angle.

The limited SEM studies of eroded specimens indicated the following damage features: a) cracking of carbide grains, (b) protrusion of carbide grains, c) highly distorted structure near the surface, d) ridges and furrows the Co phase and e) shadowing of the Co phase by the WC grains at small impingement angles.

DISCUSSION

Of interest is the mechanism by which the erosion of the sintered WC-Co alloys occurs. It is important in this regard to characterize the present conditions, namely we are here considering the erosion of a material whose microstructure consists of the mixture of a hard brittle WC phase in a ductile Co matrix, where the hard WC phase exists in the larger amount (volume fraction) with a grain size which is an order of magnitude smaller than that of the impinging angular Al_2O_3 particles and whose hardness (VHN $\approx$ 1800) is smaller than those of the Al_2O_3 particles (VHN $\approx$ 2800).

The angular dependence of the constant a of Equation 1 indicated in Figs. 4 and 5 is in accord with that for the erosion of brittle materials (Finnie, 1980; Hockey, Wiederhorn and Johnson, 1978; Roubart, Scattergood and Turner, 1980) and it seems reasonable to assume that it represents the erosion of WC, which then according to Fig. 5 is given by

$$a = E_R^{WC} = A(v \sin \alpha)^2 \quad (2)$$

The exponent 2 over the velocity term is more in accord with an erosion mechanism based on elastic Hertzian fracture (Sargent, Mehrotra and Conrad, 1979; Mehrotra, Sargent and Conrad, 1980) than an elastic-plastic indentation fracture (Evans and Wilshaw, 1976; Evans, Gulden and Rosenblatt, 1978; Ruff and Wiederhorn, 1979).

Equation 1 suggests that the erosion of the sintered WC-Co alloys considered here may obey a rule of mixtures. If this is so, one can show that

$$E_R^{Co} = E_R^{WC} + b \quad (3)$$

$$= E_R^{WC} + b_{90} + (b - b_{90}) \quad (3a)$$

Substituting $A(v \sin \alpha)^2$ for E_R^{WC} , $B(v \sin \alpha)^{3.2}$ for b_{90} and $C(v \cos \alpha)^2$ for $(b - b_{90})$ we obtain

$$E_R^{Co} = [A(v \sin \alpha)^2 + B(v \sin \alpha)^{3.2}] + [C(v \cos \alpha)^2]; \alpha < 60^\circ \quad (4)$$

$$\text{and} \quad E_R^{Co} = A(v \sin \alpha)^2 + B(v \sin \alpha)^{3.2}; \alpha > 60^\circ \quad (5)$$

where $A = 1.0 \times 10^{-8}$ g/g, $B = 1.3 \times 10^{-9}$ g/g and $C = 1.0 \times 10^{-6}$ g/g. The terms in the first set of brackets on the right hand side of Eq. 4 represent the erosion due to the normal component of the velocity, whereas that in the second set of brackets is due to the tangential component. Equation 4 is similar in form to that proposed by Wood (1966) for the erosion of ductile metals due to the combined cutting and deformation wear mechanisms (Bitter, 1963a, 1963b).

The present results thus suggest that the erosion of the sintered WC-Co alloys follows a rule of mixtures, the erosion of the WC phase occurring by a Hertzian elastic fracture mechanism and that of the Co phase by combined cutting and deformation wear mechanisms. Although reasonable agreement exists between the experimental results and the prediction of these mechanisms, additional work is needed before one can accept these mechanisms as being more than tentative explanations. Needed are erosion data on pure WC and Co. Also, consideration needs to be given to the influence of the interfacial bonding between the WC and Co phases on the fracture of the WC grains and on the subsequent ejection of the fractured segments.

ACKNOWLEDGEMENT

The authors wish to express appreciation to Mr. J. R. Hoffman of Multi-Metals for providing the WC-Co specimens. Also, they wish to acknowledge support of this work by the University of Kentucky Institute for Mining and Minerals Research.

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Non-oxide Ceramics — A New Class of Engineering Materials

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ABSTRACT

The non-oxide ceramic materials especially those based on silicon nitride and silicon carbide belong to the latest developments in the field of material technology - a development which is expected to continue for some time yet - but are also increasingly being used in applications to solve material problems. This is due to their most interesting combination of mechanical, thermal and chemical properties.

The non-oxide ceramic materials can therefore be considered as an already established new group of materials, which can be used for energy production and energy conversion, especially in high-temperature engines, but also under severe abrasive and corrosive environmental conditions.

KEYWORDS

Non-oxide ceramics; silicon carbide; silicon nitride; engineering properties; manufacturing; application; engine components; valve components; mechanical seals.

INTRODUCTION

One of the first achievements of non-oxide ceramics was the use of reaction sintered silicon nitride in aluminium melting metallurgy (Feld, 1969), but very soon it was also used as machine components, particularly as a seal in the rotary piston engine (1972). An important stimulus was given to the development of these materials by the extensive work on the "ceramic" gas turbine and also piston engine in several countries.

The basis (Gugel and Leimer, 1973) on the one hand is the intention to operate automotive engines at higher temperatures for reasons of greater economy and on the other hand the knowledge that the metals for high-temperature applications can hardly be improved beyond their present stage.

The main applications today are in the fields of wear resistant parts in the seals and valve technology, but there seems to be almost no area in which tests are not under way to realize the interesting combination of properties. Production techniques have now been developed so far that a wide range of shapes can be provided and today existing material limits can be overcome.

MATERIAL

Non-oxide ceramics include the compounds that the light elements boron, carbon, nitrogen and silicon form together. This group includes silicon carbide SiC , silicon nitride Si_3N_4 , boron nitride BN , boron carbide B_4C , the boron silicides SiB_4 and SiB_6 and, properly seen, also carbon in the form of graphite and diamond (carbon carbide!).

These compounds share the characteristics of strongly covalent bonding with short atomic distances (which means high theoretical strength and hardness), low thermal expansion and good thermal and chemical stability (disregarding their oxidation behaviour). The mechanical properties, however, are restricted in use because of their incapability of relieving stress concentrations by local yielding. Like all ceramics, they are brittle and the designer and engineer must be acquainted with this intrinsic property.

The boron silicides have not yet been of any significance. Hot-pressed boron carbide and boron nitride are represented on a limited market for certain applications as sand-blast nozzles, abrasion tools, grinding devices and also in nuclear-reactor and high-temperature insulation technology.

For high temperature applications silicon carbide and silicon nitride are the candidate materials because of their well-known resistance to oxidation. So the interest in the application of ceramics was focussed on materials based on SiC and Si_3N_4 , which led to the development of several very interesting compositions that are listed in Table 1 with their characteristic properties.

TABLE 1 Characteristic Properties of Silicon Nitride and Silicon Carbide Ceramics

P R O D U C T N = Silicon Nitride C = Silicon Carbide	Bulk Density g/cm ³	Porosity %	Modulus of Rupture (4-point)			Young's Modulus 10 ³ MN/m ²	Thermal Expansion 10 ⁻⁶ K ⁻¹
			20 °C	1000 °C	1400 °C		
			MN/m ²	MN/m ²	MN/m ²		
N - Reaction Sintered (1)	1,9 - 2,2	25 - 40	150	150	150	120	3,0
N - Reaction Sintered (2)	2,4 - 2,7	15 - 25	250	250	300	150	3,0
N - Pressureless Sintered	3,3	< 2	600	550	300	310	3,3
N - Hot Pressed	3,2	0	700	650	400	320	3,2
C - Reaction Sintered	2,7	16	250	250	250	280	4,5
C - Silicon Impregnated	3,1	0	350	400	200	360	4,3
C - Recrystallized	2,6	20	100	100	100	200	4,5
C - Pressureless Sintered	3,15	< 2	400	450	400	400	4,4
C - Hot Pressed	3,2	0	550	550	450	420	4,5

(1) = Axial dry pressed; extruded - (2) = Isopressed, slip cast; injection and transfer molded

MANUFACTURING

The stability of these crystals complicates sintering by volume diffusion, the mechanism frequently operative in sintering of ceramics. In order to be able to utilize the favourable properties of a workpiece, other methods for component manufacturing had to be developed, namely reaction sintering and hot-pressing (Table 2).

TABLE 2 Production Survey of Silicon Nitride and Silicon Carbide Ceramics (Additives/Temperature)

Process \ Material	Silicon Nitride	Silicon Carbide
REACTION SINTERING	(+ Fe, Fe ₂ O ₃) 1300 - 1500 °C	(with Si-surplus) 1400 - 1700 °C
HOT PRESSING	+ MgO, Y ₂ O ₃ 1700 - 1800 °C	+ Al ₂ O ₃ , B 2000 - 2100 °C
PRESSURELESS SINTERING	+ Al ₂ O ₃ , AlN → Sialon + Y ₂ O ₃ , Al ₂ O ₃ , CeO 1700 - 1900 °C	+ B, C 2100 - 2200 °C
RECRYSTALLIZING	-	2300 - 2500 °C

In reaction sintering, the material is developed as a result of a chemical reaction of the constituents within the body, which is shaped in any possible ceramic forming method.

For silicon nitride (Fig. 1), a silicon powder compact is shaped, that is heated in a nitrogen atmosphere - if necessary after including a burning-out process to remove temporary bonding agents - a process requiring a high degree of caution because of the exothermic reaction involved. When silicon is converted to silicon nitride in the reaction-sintered material, an increase in weight and in volume will result. The latter takes place within the body into the porous area (Gugel, Hauck and Flörke, 1979) and consequently has practically no effect on total volume. This proves to be a significant advantage of this material, i. e. its dimensional accuracy referred to the raw body is below -0.5%. Thus little or no machining is required. Certain additions or impurities such as iron accelerate the nitriding process or make it possible with parts having thicker walls. The material produced by this method is porous, but because of the very fine grain structure of the silicon nitride crystals in the pores, the pore size is remarkably small and is normally below 0.2 μm.

Developments have now increased the density to 2.8 - 2.9 g/cm³ but it is doubtful whether such a material can be produced homogeneously in a component.

To produce reaction sintered silicon carbide, a mixture of carbon, silicon carbide and a plasticizer is formed by the same methods shown in Fig. 1 and is then siliconized in a special furnace with molten or gaseous silicon.

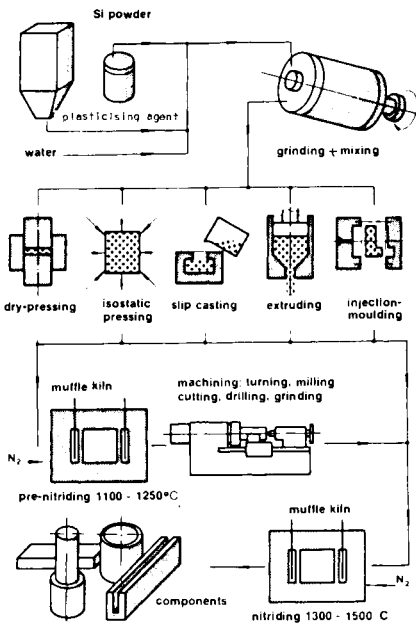


Fig. 1. Production diagram for reaction sintered silicon nitride.

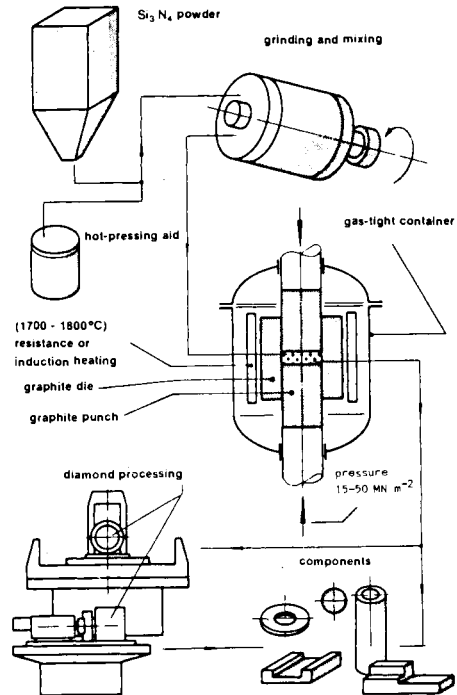


Fig. 2. Production diagram for hot-pressed silicon nitride.

This process can be controlled so that a porous, but pure silicon carbide body is obtained, or that its porous area is filled with silicon. Since the silicon-containing, dense product is more advantageous with regard to low temperature strength, it is the most fabricated product. Here, too, the outer change of volume of the component is negligible.

The hot-pressing process starts from silicon nitride or silicon carbide powder with special additives allowing densification until practically theoretical density is reached. For silicon nitride the α -modification is necessary to obtain the needle-like linked microstructure by transformation to β -Si₃N₄, which creates the extraordinary high strength. The additive - normally MgO or Y₂O₃ - reacts with the SiO₂ in the α -Si₃N₄ - lattice and also at the surface to form a liquid silicate glass, in which the α -Si₃N₄ dissolves and from which it reprecipitates as elongated β -Si₃N₄-grains. The secondary silicate phase, however, limits the strength and creeping resistance at temperatures beyond 1000 °C.

Fig. 2 shows the method for hot-pressing of silicon nitride. The limited flowing capability of the material explains why only relatively simply shaped bodies can be manufactured. Nevertheless in the last years this method could be developed to a remarkably high level (Kessel, 1981). For the future isostatic hot pressing appears to be a promising tool for more complex parts, when the sealing problem can be solved with satisfaction.

Machining by means of diamond tools to the final shape is normally necessary. The significance of grinding, however, also lies in forming the surface in such a way that optimum mechanical properties are achieved. Loss of strength of as much as 40 % can result in case of unfavourable machining (Kessel and Gugel, 1978).

Hot-pressed silicon carbide finds little application, since hot-pressed silicon nitride has proved to be more suitable in most cases, which is due to its thermal expansion and its lower Young's modulus, which makes it somewhat tougher.

Pressureless sintering of covalent compounds to full density is extremely difficult, even with the use of additives, especially when they dissociate rather than melt at normal pressures, such as SiC and Si_3N_4 . At temperatures, where the atomic mobility is high enough, decomposition is already a severe problem. So it was not before 1973 that silicon carbide could be pressureless sintered for the first time, using sub-micrometric powder with simultaneous addition of boron and carbon (Prochazka, 1973). The result is a fine homogeneous microstructure, which seems to have not reached its final strength level yet (Gugel and Leimer, 1979).

For the pressureless densification of silicon nitride, a higher amount of oxide additions, 10% and more, is necessary. The result is a more composite material, but still with interesting properties that offers basically the chance to replace the more sophisticated hot-pressed silicon nitride, as far as the high temperature strength is satisfactory. The sintering itself causes more difficulties than with SiC, since at the temperature required silicon nitride already shows some decomposition.

Further investigations are therefore of extreme importance. The shaping again can be done by any ceramic forming method, using temporary binders, so the shaping capability is not limited as with hot-pressing. A disadvantage is certainly the high shrinkage - linearly up to 20 % - which decreases the accuracy of net shaped components by warping, especially in comparison with the reaction-sintered products.

For the sake of completeness recrystallized silicon carbide has to be mentioned. Here a silicon carbide compact is fired at temperatures so high that even a certain evaporizing-condensation process takes place that leads to a recrystallization and hence to a porous product with a moderate strength level (Table 1).

To complete the survey of material processing, the sialons have to be mentioned. This is a special class of material comprising solid solutions of metal oxides - originally Al_2O_3 and later also MgO , Y_2O_3 , BeO a. o. had been developed - in the $\beta\text{-Si}_3\text{N}_4$ crystal structure (Jack, 1973). They can be hot-pressed or pressureless sintered. Although known for ten years they have no importance in application up to now, with only recently some success reported in their use as cutting tool tips.

PROPERTIES

The strength of the porous types falls off sharply above 1400°C. The dense, hot-pressed materials, however, have the highest strength values ever found with ceramics, but because of the

use of hot-pressing additives, strength is reduced more or less rapidly at temperatures above 1000 °C. For economic reasons, hot-pressed material will only be selected if this is absolutely necessary because of strength or abrasion resistance. The composite material silicon carbide/silicon takes its place between the above-mentioned types with regard to its strength, which is not maintained beyond the 1400 °C melting point of silicon.

The Young's modulus of materials based on silicon nitride is comparatively low. Together with their high strength, they are characterized by a fairly high elastic strain. Consequently, silicon nitride proves to be relatively tough for a ceramic.

For high temperature applications the creep behaviour and long term strength are of specific interest. These properties were thoroughly investigated by Thuemmler (1976) and it is shown that the amount of a second (oxide) phase is all-important.

Also, the unusually low thermal expansion, especially of silicon nitride should be pointed out. This is a great advantage with regard to resistance to thermal shocks, but proves to be problematic, as far as designs are concerned that are connected with metals with higher thermal expansion. Silicon carbide, however, is characterized by its very high thermal conductivity, which is also advantageous for thermal shock behaviour. For isolation applications silicon nitride is to be preferred. Finally, the low specific weight should be mentioned that offers considerable advantages for some applications, as well as the excellent abrasion resistance that is a result of hardness and mechanical strength.

The significance of non-oxide ceramics lies in the combination of their favourable properties. Together with their manufacturing potential, they present a most important factor in the materials sector.

APPLICATION

Several properties are usually involved in a single application and therefore any effort to classify applications will be difficult. From the large variety of possibilities already tested in order to demonstrate the capability of silicon nitride and silicon carbide materials, some essential matters will be mentioned to stimulate further reflection.

Hot pressed silicon nitride as drawing tool has been already introduced (Haarscheidt, 1982), but needs further application development. The same material has also been successfully tested for ball bearings (Lorösch and coworker, 1980). At high speed and load they show superior performance, and they can be used at elevated temperatures, or in aggressive liquids without lubrication. The life time of valves, e. g. for pressure release in coal liquification plants, could be extremely elongated by using components made of non-oxide ceramics (Fig. 3). A new increasingly used material for mechanical seal rings is reaction or pressureless sintered silicon carbide (Fig. 4), which competes successfully with hard metals and alumina ceramics (Mayer, 1981).

For reaction sintered silicon nitride the very wide-spread application as supports or fixtures for brazing, welding and other heating processes, and for high temperature testing should be mentioned. An interesting



Fig. 3. Valve components made of hot-pressed silicon nitride - CERANOX NH - and reaction-sintered silicon carbide - CERANOX CS. Fig. 4. Mechanical seal rings made of reaction-sintered silicon carbide - CERANOX CS.

very new field is that of cutting tools made out of silicon nitride based ceramics. First very promising results have been reported in machining grey iron and super-alloys.

The most spectacular potential application of these materials is in the field of energy conversion, mainly in automotive engines (Fig. 5). For more than forty years designers were looking for ceramic materials, but only after the development of the non-oxide class of ceramic material in the last decade is there a realistic chance to reach this goal.

A large number of technical demonstration programmes are conducted, which should encourage the use of ceramics as engineering materials. The results are very promising. The basic applicability in heat engines has been demonstrated at operating temperatures that were about 300°C higher than were possible with uncooled super-alloys. This development is a major step for decreasing fuel consumption and saving critical raw materials necessary for super-alloys.

CONCLUSION

The state of the art of production and use of non-oxide ceramic materials has reached an advanced level, in solving material problems that up to now could hardly be overcome. Problems, which ought to be observed very carefully are the improvement of reliable and affordable mass production techniques and on the application side the proper attachment of the ceramic components to the metallic system. Non-destructive testing has seriously to be taken into consideration.

In all these areas a considerable amount of basic knowledge already exists. So ceramic engineering components are set to penetrate

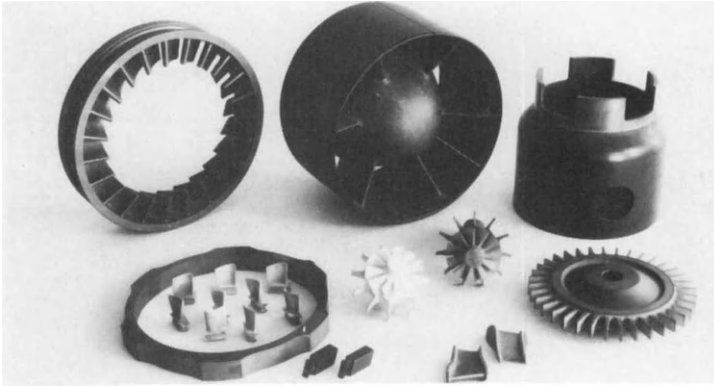


Fig. 5. CERANOX components for automotive engines: Gas-turbine nozzle ring, nose cone, combustion chamber, shroud, rotor, single vanes and others; turbocharger rotor.

almost every area of technology where resistance to severe environmental conditions is required. Such a statement could not be made until recently.

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The Growth of Twins and Twin Lamellae in Synthetic Diamond Crystals

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ABSTRACT

The growth histories of a number of synthetic diamond crystals have been studied by cathodoluminescence imaging of crystal sections. It is found that twins and twin lamellae, when formed, nucleate during the early stages of the growth process and the development of the {100} and {111} growth sectors on either side of such boundaries proceeds independently. These effects can have a marked influence on the final morphology of the diamond crystals.

KEYWORDS

Synthetic diamond, crystal growth, twinning, twin lamellae, cathodoluminescence.

INTRODUCTION

In general, synthetic diamonds grow with a simple cubo-octahedral habit in which the {100} and {111} faces are produced by the development of discrete {100} and {111} growth sectors. Under electron bombardment the {100} and {111} sectors both cathodoluminesce, but emit different wavelengths in the visible spectrum. Woods and Lang (1975) reported that the cube sectors appear lime green, whereas the octahedral sectors glow a deep red colour, and used this to observe the growth history for polished crystal sections. In a scanning electron microscope, fitted with a suitable detector, the same features can be observed, since the {100} sectors cathodoluminesce more strongly than {111} sectors and therefore appear brighter.

The subject of this paper is an SEM cathodoluminescence study of diamond crystals which show deviations from the normal cubo-octahedral growth morphology.

RESULTS AND DISCUSSION

Complex crystal shapes can result when twinning produces either macles or cyclic twins (Pipkin and Davies, 1979). The former may result in the

formation of a flat symmetrical crystal with a morphology which reflects the mirror symmetry of the twin boundary, *t* (Fig. 1a), or of a less symmetrical crystal arising from differences in the number and development of the {100} and {111} growth sectors on either side of the twin boundary, *t* (Fig. 1b).

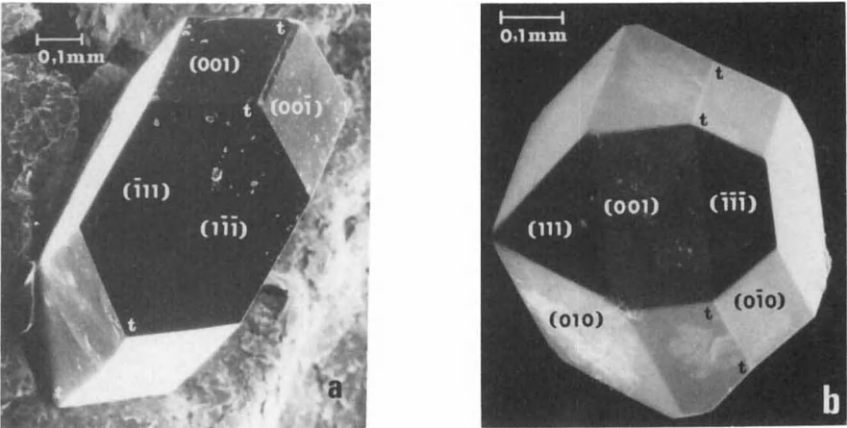


Fig. 1 Diamond crystals showing the two common macule twin morphologies found in synthetic diamonds. (The twin boundary in each case is the boundary *t*, *t*, *t*, *t*.)

Other crystals have been found with surface discontinuities, and at first sight could be mistaken for twins but are, in fact, single crystals with re-entrants (Fig. 2a). A re-entrant is defined here simply as a step in a crystal face where no change in the orientation of the crystal on either side of the step is apparent from the external crystal morphology. For example the two (001) faces designated *a* and *a'* in Fig. 2a are in exactly the same crystallographic orientation but are separated by the development of a {111} facet, *b*, producing a step ABCD. Combinations of twin boundaries and re-entrants have also been observed in some crystals (Fig. 2b).

Whenever an {001} re-entrant has been observed the dividing face has always been of the form {111}. Conversely re-entrants in {111} faces have always been associated with the development of additional {100} facets.

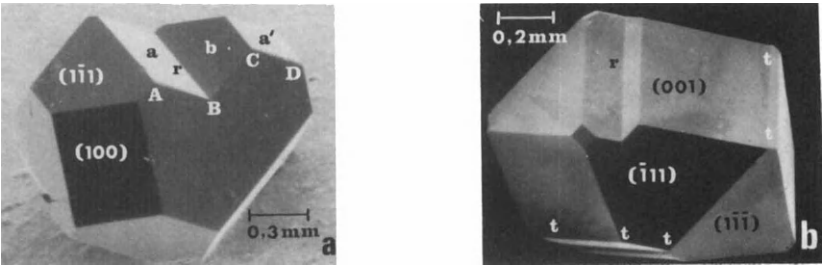


Fig. 2 Typical examples of crystals showing a re-entrant, (a) and a re-entrant, *r*, twin boundary, *t*, combination (b).

The lines of intersection of a re-entrant with either $\{100\}$ or $\{111\}$ crystal faces always follow $\langle 110 \rangle$ crystal directions and, where two or more re-entrants are present on a single particle, their lines of intersection with the crystal faces are continuous and trace the intersection of a single $\{111\}$ plane with the crystal surface. The boundary AEF in Fig. 3b is a typical example of this. Finally, "ghost-lines" of the type shown in Fig. 3a, and which also trace the line of intersection of a $\{111\}$ plane with the crystal surface, have been observed. Sometimes crystals are found which show up to three sets of "ghost-lines" and sometimes they occur in combination with a re-entrant (Fig. 3b).

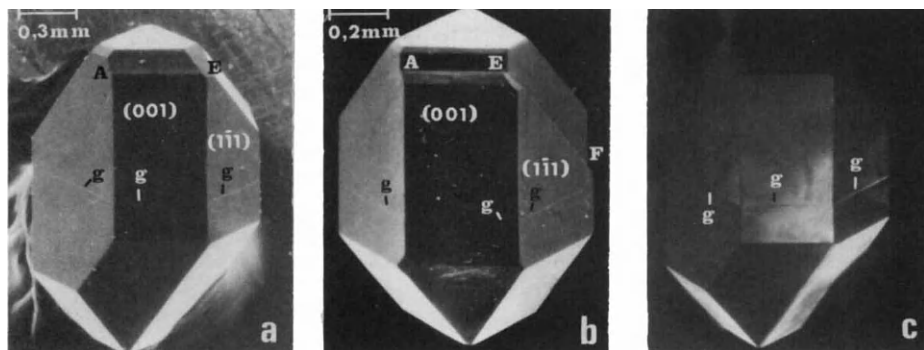


Fig. 3 Example of diamonds with "ghost-lines", g, in a single crystal (a) and in a re-entrant crystal (b). The cathodoluminescence image (c) corresponds to the crystal (a).

To study the origin of all these features, selected crystals were polished, parallel to one of the crystal faces, to a section as near as possible to a plane containing the nucleation centre, and examined by cathodoluminescence imaging. The nucleation point is easily located since metal inclusions are trapped in the growing diamond in the boundaries between adjacent growth sectors and the rows of metal particles radiate out from the nucleation centre.

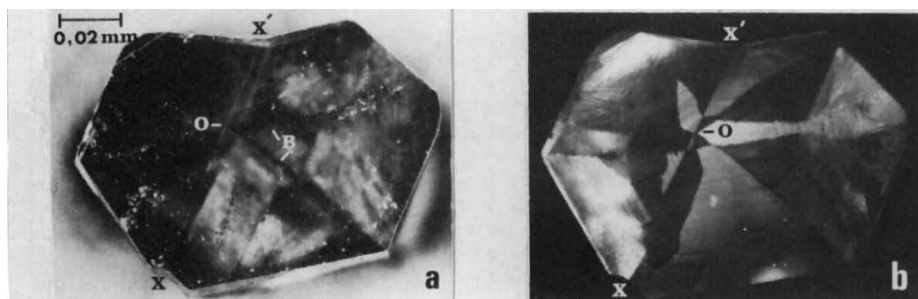


Fig. 4 Optical (a) and cathodoluminescence (b) images of a sectioned macule twin.

A typical macle twin section is shown in Fig. 4a from which it can be seen that the nucleation point, 0, as defined by the intersection of the inclusion bands, B, lies close to the twin boundary, X-X'. Similarly, the cathodoluminescence image (Fig. 4b) shows how the growth sectors radiate from the same point.

Many additional crystals were examined and in every case the same observations were made. It seems reasonable, therefore, to conclude that twinning, in synthetic diamond, occurs early in the growth process and most probably during the nucleation stage.

Similar examinations of re-entrant crystals showed that these are also nucleation phenomena. Figure 5a shows a macle twin with a re-entrant, E F. After sectioning and cathodoluminescence imaging, a narrow linear feature, t, is highlighted and radiates from a point, 0', near the nucleation centre, 0, (which lies on the twin boundary, X-X'), and extends up to the line of the re-entrant, r (Figs. 5b and c). The points 0 and 0' are not coincident because the nucleation centre lies very slightly below the polished surface of the crystal.

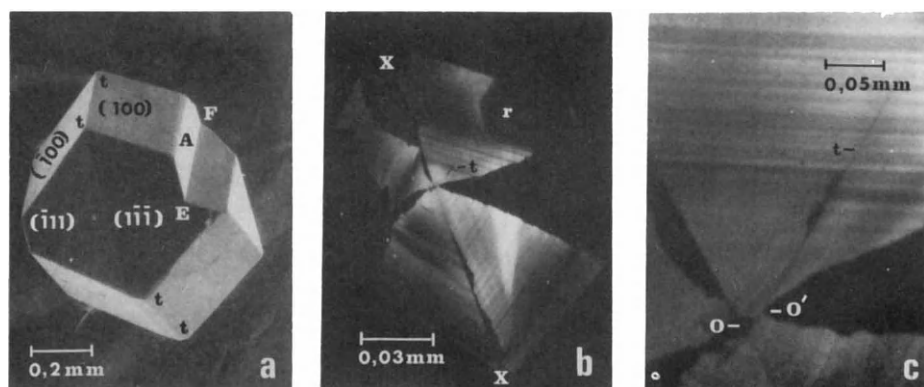


Fig. 5 Macle twin with a re-entrant (a) and cathodoluminescence images of a polished section (b and c).

Similar observations were made when examining "ghost-lines" (Fig. 6) and the difference between the formation of a re-entrant and of a "ghost-line" appears to be a function only of the relative rates of growth of the growth sectors on either side of the linear feature associated with them.

It is interesting to note that the (111) face, A, in Fig. 5a is produced, not from the development of a (111) growth sector, but by the differential growth of the (100) sector on either side of the re-entrant. However, some re-entrant crystals are found where the re-entrant is defined by the boundary between a (100) and a (111) growth sector. For example, the (111) face, F, in Figs. 7a and b, is clearly a (111) face developed from a (111) growth sector and results in a deep red colouration in cathodoluminescence imaging. Similarly the (100) face, G, is formed by the development of a (100) growth sector.

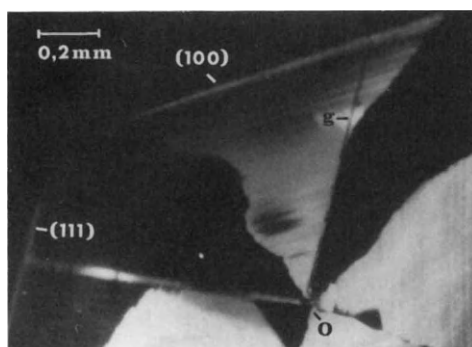


Fig. 6 Cathodoluminescence image of a sectioned crystal containing a "ghost-line".

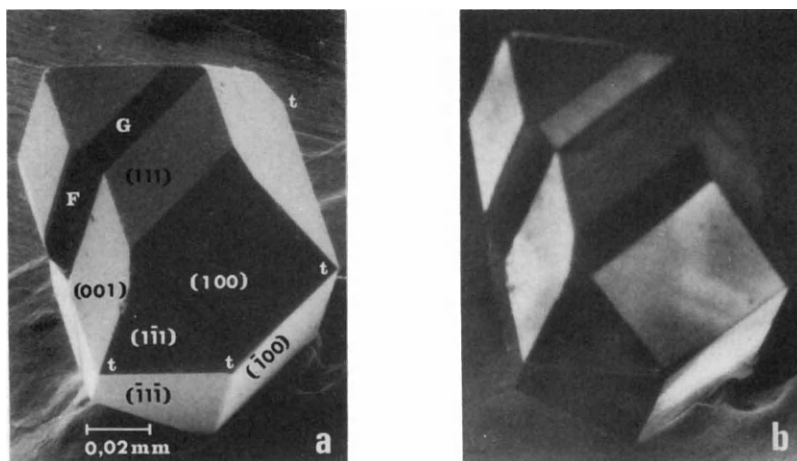


Fig. 7 Secondary electron (a) and cathodoluminescence (b) images of a twinned crystal with a re-entrant.

The nature of the linear features associated with re-entrants and "ghost-lines" is not certain, but it has always been found that where such a feature crosses a light {100} growth sector it appears dark and when it crosses a {111} sector it appears bright. This corresponds to deep red and lime green colouration respectively when viewed optically.

Figure 3c is the cathodoluminescence image of the crystal shown in Fig. 3b and this again demonstrates how the "ghost-line" changes as it crosses the {100} and {111} faces.

These observations are all consistent with the linear defects being twin lamellae which contain their own individual {100} and {111} growth sectors.

They lie on {111} planes and their cathodoluminescence responses reflect the operation of a 180° rotation of the crystal lattice about a $\langle 111 \rangle$ direction which occurs at a twin boundary.

In all cases the twin lamellae, like the twin boundaries, are nucleated in the early stages of crystal growth and were found to radiate from the nucleation centres.

CONCLUSIONS

Twins and what appear to be twin lamellae are frequently found in samples of synthetic diamond crystals and are always formed in the early stages of growth and almost certainly during the crystal nucleation period.

The nucleation and growth rates of the {100} and {111} growth sectors on either side of a twin or a lamella boundary are not necessarily interdependent. As a result, the presence of one or more of these twin features within a single diamond particle can give rise to the development of complex crystal morphologies based on the normal cubo-octahedral growth of synthetic diamonds.

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Diamond Polishing — Diamond's Affinity for Scaife Materials in the Polishing Process of Diamond

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ABSTRACT

The impact of the diamond's chemical affinity for the scaife material when polishing is reviewed. A theory which explains the effect of pearlitic scaife on the polishing of diamonds is proposed by the author. The role of the various metal components of scaives in the polishing operation is described. Many experiments have been conducted with respect to the affinity between various metals in order to minimise wear of cutting tools. In the polishing of diamonds there is an interest to use materials which will "destroy" the diamond chemically as well as by other means. Additional experience gained during practical work in polishing of diamonds further indicates that the affinity of the diamond for the scaife material is a very important factor in the polishing operation. Especially metals forming carbides are of value as scaife ingredients.

KEYWORDS

Diamond, graphite, scaife, chemical affinity, metals, grinding, polishing.

For centuries, diamonds have been polished on cast iron scaives. The question arises whether it is due to inertia that the old system, namely scaives made from cast iron, remained in use to this day, or whether it is because of some special property of cast iron which is necessary for the polishing of diamonds. In the last few years, two new types of scaives were introduced. One is made of tool steel and the other of sintered metals containing diamond powder.

Polishing and grinding are two different methods for getting fine surfaces. By grinding we reduce the material to a desired shape with some prescribed accuracy mainly by an abrasive action. The operation is mechanical: hard grains of SiC, Al₂O₃, BN or diamond powder (natural or synthetic) are used on the material and chip off smaller or bigger particles, according to the grain size of the abrasive. Polishing, on the other hand, often involves thermal and chemical reactions between the polishing wheel (the matrix as well as the polishing agent) and the machined material. The polishing material may be either hard or soft at room temperature. In polishing diamonds the polishing agent is diamond powder, which is laid freely on the scaife and can then rotate or move on the scaife, whereas in grinding the

hard grains are rigidly embedded in the matrix. Polished facets of diamonds show hardly any traces of machining lines.

The three types of scaives act on different principles. The good old fashioned pearlitic cast iron scaife consists of grains of lamellar cementite and ferrite layers alternatively. The cementite lamellae are very hard in comparison with the ferritic ones. The distance between two well-arranged cementite lamellae is approximately $1-3\mu\text{m}$ which matches the size of the most common diamond powder. Diamond grains embed themselves between the hard lamellae and act as if they were in a grinding wheel with the advantage that when they are blunted or when large forces are exerted on them, they rotate or tear out. Thus through the rotation new sharp edges (also of the same one-edge-worn grain) appear and polishing carries on. The ferritic lamellae tend to wet the diamond at the hot spots of contact and at this temperature they "chemically" absorb carbon atoms from the diamond. Other grains in the cast iron are phosphides which are hard and brittle. Diamond powder is not embedded in them, but can rotate in them under the pressure of the polished diamond.

The scaives are scratched by hand with the aid of a grinding stone or are surface-marked by shot blasting with SiC grains. The grooves are at least ten times deeper than the biggest diamond powder grain. These scratches or marks do not contribute directly to the polishing operation as holding posts for grinding grains of the diamond powder, but rather as stores for diamond paste. When the scaife gets hot through the polishing operation, the grooves supply, as a result of heat expansion, fresh paste to the "working tables", which are the surfaces in contact with the polished diamond (Fig.1, Fig.2).

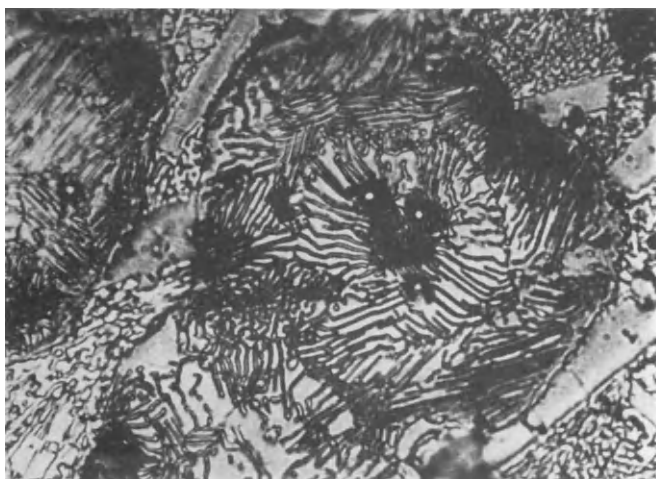


Fig.1 Pearlitic structure of scaife with some diamond grains embedded (surface electro-chemically polished). (X1000)



Fig.2 Model demonstration of surface texture of scaife in enlarged scale (X1000) the board represents a 2.5mm diamond and the gravel the diamond powder 2-3 μm .

The tool steel scaife is new and was introduced only a few years ago. These scaives are also scratched. The metallurgical structure of this material is homogeneous.

Throughout decades of diamond polishing research, various metals for scaives were tested but none of them was as good and as cheap as the cast iron scaives. Research on metal cutting and on relations between the materials to be cut and the tool materials under varied pressure and temperature conditions pointed to the fact that a chemical reaction can take place between the two materials. For instance, cutting Al with ceramic tools, which consist of Al_2O_3 , has disadvantages. The Al sticks to the tool and the machined surface obtained is very rough. Cutting ferrous materials with diamond tools spoils the diamond tool very quickly. The face of the chip formed in the cutting process touching the diamond tool is enriched in carbon that has been extracted from the diamond. Experiments performed many years ago with various metals (cutting and being cut) pressed together and heated to adequate temperature for a fixed period of time, showed that there are combinations of materials which undergo chemical reactions and should thus be avoided when used as cutter and cutting material, especially when the tool's lifetime is the decisive factor. Two articles, one by Tanaka, Ikawa and Tsuwa (1981), on the "Affinity of Diamonds for Metals", and the other by Miyoshi and Buckley (1980) under the name "Adhesion and Friction of Single Crystal Diamond in Contact with Transition Metals" show that:

- 1) Graphitization of diamond was observed when heated in a powder of Fe and Mn.
- 2) Numerous small dents were observed on the surface of diamond when heated in a powder of Al, Ca, Ti, Cr, Co or Ni.

- 3) Unexpected thermal erosion was observed on the surface of diamonds heated in powders of Pb or Bi.
- 4) Coefficient of friction for diamonds in contact with various metals is related to the relative chemical activities (of d valence bond character) of these metals. The more active the metals the higher the coefficient of friction.

The following metals showed chemical reactions with diamond: Y, Ti, Zr, Co, Ni, Fe, W, Pd. In these transition metals the d valence bonds are not completely filled and therefore they are reactive. Generally speaking, we can say that all metals which are able to form carbides have the potential to spoil the diamond. The less saturated the d valence bond is, the more active will they be.

These negative spoiling properties of diamond tools become most helpful whenever one is interested in the polishing of diamonds. The stronger the chemical reaction with the diamond, the quicker will be the polishing process.

The sintered metal with diamond powder scaife acts as a grinding stone and is mainly used for grinding - polishing of hard-to-polish diamonds like knotted (naats) diamonds. The grain size of the diamond powder is responsible for the grinding operation whereas the metallic matrix contributes to the chemical and thermal wear of the diamond.

In conclusion, the three types of scaives for polishing diamonds act by slightly different mechanisms. The cast iron scaife graphitizes and abrades. The bad heat conduction of cast iron helps the graphitization process. The tool steel scaife causes wear of diamonds by abrasion and chemical reaction. Carbides of the ingredient metals of the scaife are produced by absorbing carbon from the diamond surface. Here the chemical affinity of the ingredients for the diamond is of major importance. The sintered scaife causes the wear of the polished diamond mainly by mechanical abrasion. The contribution of the matrix is mainly to get a polished surface. The chemical affinity of the matrix ingredients for the diamond is once more the reason for the good-looking surface of polished diamond in this case.

The transition metals especially as well as all the metals that form carbides and those which cause graphitization or serve as catalysts to chemical reactions with diamonds can be used as active components in scaives for polishing diamonds.

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TEM Observation of Microstructures of Sintered Diamond Compacts

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ABSTRACT

The microstructures of high-pressure sintered diamond compacts were observed by transmission electron microscopy. Slip bands extending along $\{111\}$ planes and dislocation forests were found within diamond grains. In very fine-grained (below $1\mu\text{m}$) sintered compacts, these defects in grains were rarely seen. The matrix phases of the compacts were also investigated, and stacking faults in the Co phases were found.

KEYWORDS

Sintered diamond compacts; high-pressure and high-temperature sintering; TEM study; slip bands; stacking faults

INTRODUCTION

High-pressure sintered diamonds with Co or other iron group metals as a bonding medium are now widely used for cutting tools, wire-drawing dies, rock-drilling bits, etc. The sintering conditions are usually 5 GPa and 1350°C , or more, at which diamond is stable and the bonding metal melts. These extreme conditions are quite different from those of usual liquid-phase sintering of cemented carbides or other powder materials, and are expected to cause unique microstructural features of sintered diamonds. The purpose of the present investigation was to study the microstructural features of some different kinds of sintered diamonds, especially defect structures in the diamond grains, through transmission electron microscopy (TEM).

EXPERIMENTAL

Preparation of Sintered Diamond Compacts

Four kinds of sintered diamond compacts (samples A,B,C and D in Table 1) were prepared in our laboratory. The diamond grain size, composi-

tions, and high-pressure sintering conditions are shown in the table. The maximum grain size is listed because of the wide grain size distribution, except for sample C.

Samples A,B, and D were prepared as follows. A starting synthetic diamond powder was packed into a Ta cup and a thin Co, WC-Co cemented carbide, or Ni-Cr plate was laid over the packed diamond powder. The sample was charged in a girdle-type high-pressure apparatus for sintering. Under the applied pressure and temperature (given in the table), the melted binding medium infiltrated into the compacted diamond grains, and liquid-phase sintering occurred. As for sample C, the starting materials, i.e., very fine synthetic diamond powder and very fine WC-Co cemented carbide powder, were mixed, then the mixed powder was packed into a Ta cup and sintered by the high-pressure apparatus. The sintering time of all samples was 20 min. A commercially available sintered compact (sample E) was used for comparison.

TABLE 1 Samples Used For Experiment

	Diamond grain size (μm)	Diamond content (vol.%)	Bonding medium	Sintering pressure	Sintering temperature
A	6	90	Co infil.	5 GPa	1400°C
B	6	90	WC-Co infil.	5 GPa	1400°C
C	av.0.3	80	WC-Co mixed.	5 GPa	1350°C
D	7	88	Ni-Cr infil.	5 GPa	1350°C
E	6	90	Commercially available compact		

Procedures for Microstructure Observation

The sintered compacts were ground by a diamond wheel and polished by a lapping machine using a plated diamond disk for optical microscope observation. Thin foils for TEM observation were prepared from the sintered compacts. The specimens were ground by a diamond wheel to obtain wafers 0.2mm thick. To obtain electron-transparent thin foils, an ion-beam milling technique was used. Using a dipole parallel-beam apparatus, the wafers were thinned to 20 μm by argon ion sputtering. The final thinning was carried out by an ion-gun sputtering apparatus. At the first stage, the angle between the ion beam and the rotating specimen surface was set at 60° and then inclined to an angle of 15° or less to obtain a flat surface. The ion beam energy was also decreased from 8-10kV at the first sputtering stage to 4kV or less. These procedures avoided sputtering damages in foil specimens. Transmission electron microscopy was carried out using a TEM 200CX operating at 200kV.

RESULTS AND DISCUSSION

Optical Microscope Observation

Typical optical micrographs of samples A and C are shown in Figs. 1 and 2, respectively. Sample A consists of rather coarse (3-6 μm) diamond grains and fine ones. The diamond grains are in very close contact with each other. In sample C, very fine (below 1 μm) grains are uniformly distributed.

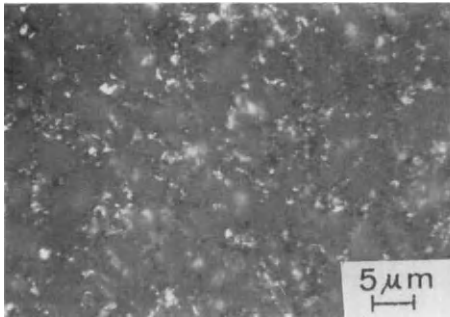


Fig. 1. Optical micrograph of sample A.

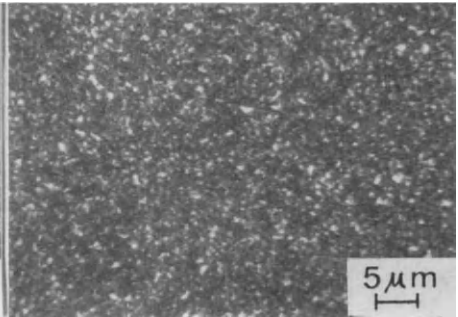


Fig. 2. Optical micrograph of sample C.

TEM Observation

Microstructures of diamond grains. Typical electron micrographs of sample A are shown in Fig.3. There are several diamond grains contacting each other, and Co binder phases (black areas) are observed. As to diamond grains, the micrographs indicate that there are three characteristic features within the grains. Firstly, parallel and intersecting slip bands are observed (indicated as ① in Fig.3 (b),(c)). Secondly, highly deformed "mosaic" structures are shown in diamond-diamond bridging regions (indicated as ② in Fig. 3 (a)). Thirdly, strain fringes are observed in the grains. When the electron beam entrance angle is slightly tilted, the fringe patterns within a grain disappear or move (indicated as ③ in Fig. 3

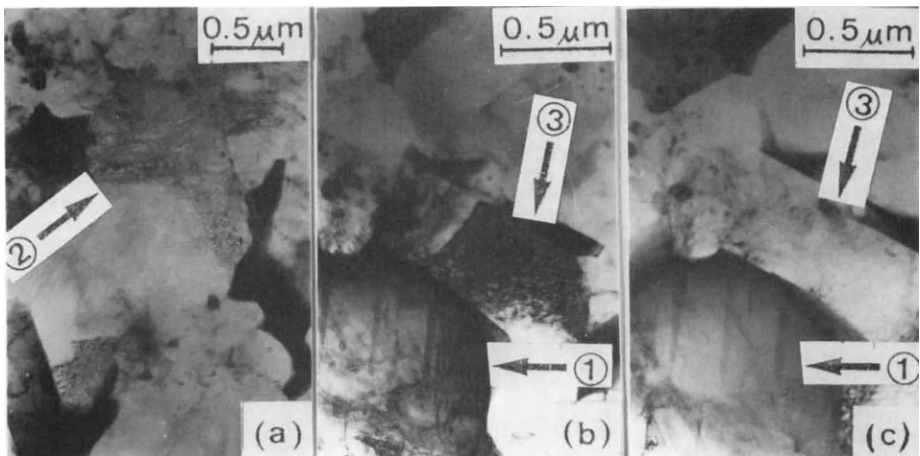


Fig. 3. Typical TEM micrographs of sample A. Mosaic structure (②) is seen in (a). Slip bands (①) and strain fringes (③) are seen in both photos (b) and (c), which were obtained by slightly tilting the beam angle.

(b),(c)). In samples B,D,and E the same characteristic structures are observed. This observation established that diamond grains in high-pressure sintered compacts have been highly deformed elastically and plastically.

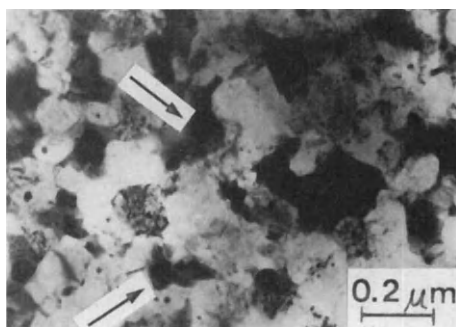


Fig. 4. Typical TEM micrograph of sample C.

Figure 4 is a typical TEM micrograph of sample C. This very fine-grained compact consists of 80 vol% diamond, fine WC (arrows), and a Co matrix. As can be seen in the photo, the diamond grains are not as highly strained as in the other coarser grained samples.

Slip bands within diamond grains. Parallel striations have been found within diamond grains in polished sections of framesite, a naturally occurring polycrystalline diamond, by DeVries (1973). The striations have been interpreted as representing oriented deformation bands on $\{111\}$ slip planes within the diamond grains. Wentorf, DeVries and Bundy (1980) found similar structures in some high-pressure sintered diamond compacts. In the reported works, relief structures of the polished specimen surfaces were observed optically. The diamond grains in the framesite and those sintered compacts that included striations were coarse ones, probably more than several tens of micrometres. The orientation of traces was not directly confirmed, but estimated using stereographic analysis. In the present work, using smaller grained (less than $7\mu\text{m}$, as indicated

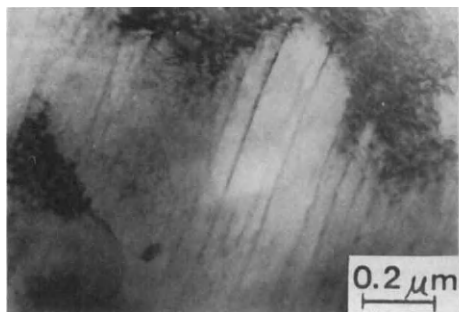


Fig. 5. Slip bands observed in sample D.

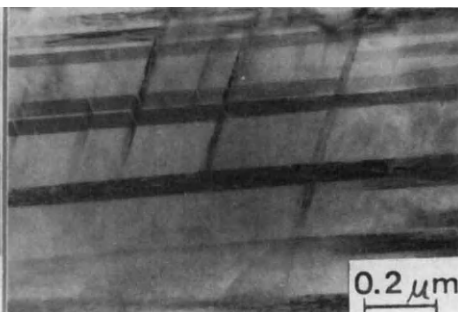


Fig. 6. Intersecting slip bands observed in sample A.

in Table 1) sintered samples, TEM observation of the slip patterns within the grains was carried out.

Figures 5 and 6 show parallel slip bands and intersecting sets of parallel slip bands in samples D and A, respectively. The intersecting angle between the two sets of slip bands coincides with that of $\{111\}$ planes. To obtain direct experimental confirmation of the slip-band orientation, selected area diffraction (SAD) patterns, and dark-field image techniques were used. Figure 7 (a) is a bright-field image of slip bands within a grain of

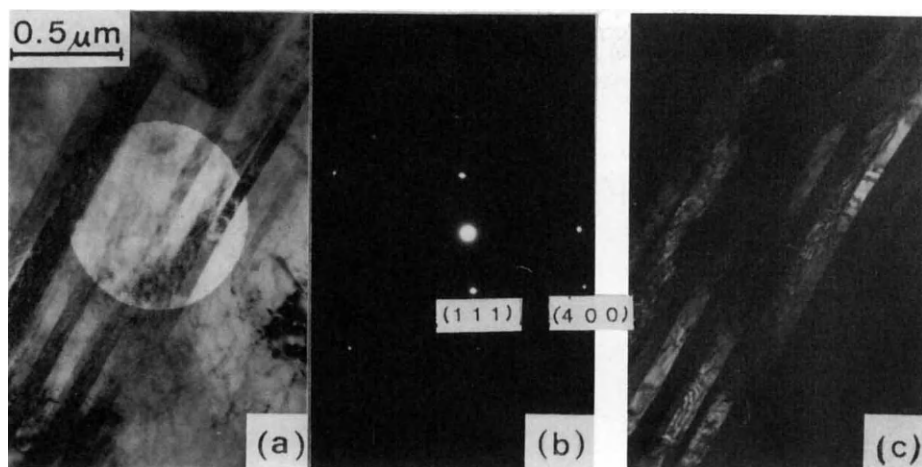


Fig. 7. Slip bands observed in sample D. (a): bright-field image (b): SAD pattern (c): dark-field image obtained from (111) diffraction spot.

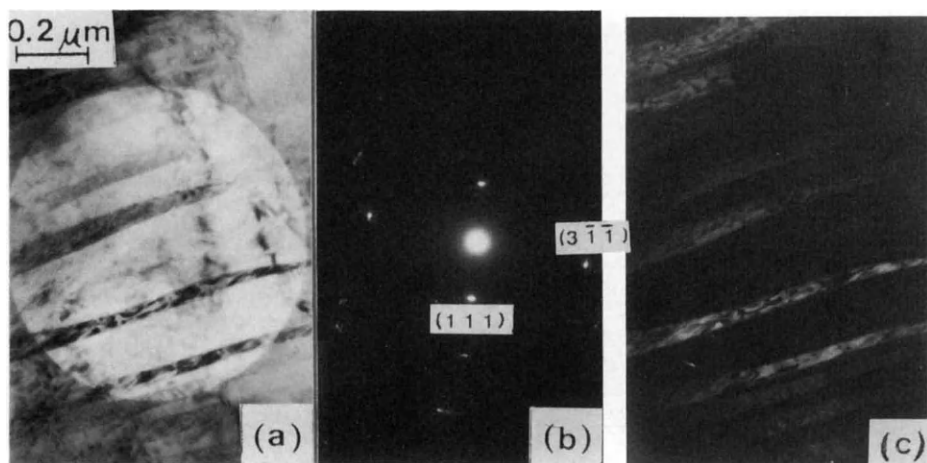


Fig. 8. Slip bands observed in sample D. (a): bright-field image (b): SAD pattern (c): dark-field image obtained from (111) diffraction spot.

sample D. The SAD pattern (Fig. 7 (b)) indicates that the crystal direction parallel to the incident beam is $[011]$. Figure 7 (c) is a dark-field image obtained from the (111) spot in the SAD pattern. This confirms that the slip bands belong to $\{111\}$ planes.

Figures 8 (a), (b), and (c) are other examples, obtained from a grain of sample D. In this case, slip bands show slight curvature, indicating strain in the crystal. The elongated spots in the SAD pattern (Fig. 8 (b)) also reflect the orientational variation of the crystal.

The TEM observation revealed that many diamond grains of specimens A,B,D, and E, especially coarser grains more than about $2\mu\text{m}$ in size, contained slip bands. On the other hand, slip bands were rarely observed in the grains of sample C, which was composed of very fine grains (av. $0.3\mu\text{m}$). Figure 9 is a very rare example of a grain containing slip bands observed in sample C.

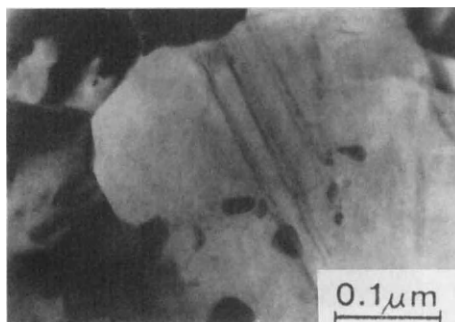


Fig. 9. TEM micrograph of a grain containing slip bands observed in sample C.

Dislocations in diamond grains. Highly deformed "mosaic" structures within grains were observed in diamond-diamond bridging regions. It is supposed that the regions are heavily stressed during sintering at high pressure. Figure 10 (a) shows a contact region of two diamond grains, which have different crystal orientations, observed in sample A. Figure 10 (b) was obtained by slightly tilting the specimen from the state of Fig.10 (a). The "mosaic" structure of the right-hand crystal disappears and dislocations are observed in the left-hand crystal, indicating that the structure is dependent on the crystal orientation. Figure 10 (c) is a dark-field image obtained from the (220) spot in the (111) reciprocal lattice plane of the left-hand crystal. Figure 10 (d) is another example of a dislocation forest in a grain of sample A. Bex and Wilson (1977), from X-ray diffraction analysis of diamond compacts, deduced a mosaic structure in the diamond grains. Estimated crystallite sizes, i.e., $0.040\text{--}0.090\mu\text{m}$, by the X-ray study are comparable to block sizes surrounded by dislocations observed in this study as shown in Fig.10 (d).

Observation of matrix phase. The thin foils prepared for TEM observation in this study were also used to examine matrix phases of sintered compacts. Using the STEM technique, compositions of the matrices of the samples were examined. In the matrices of samples B and E, both composed predominantly of Co and a small amount of W, no precipitation of tungsten carbide was observed. As for sample D, which was infiltrated with Ni-Cr alloy during high-pressure sintering, chromium carbide precipitated in a Ni matrix.

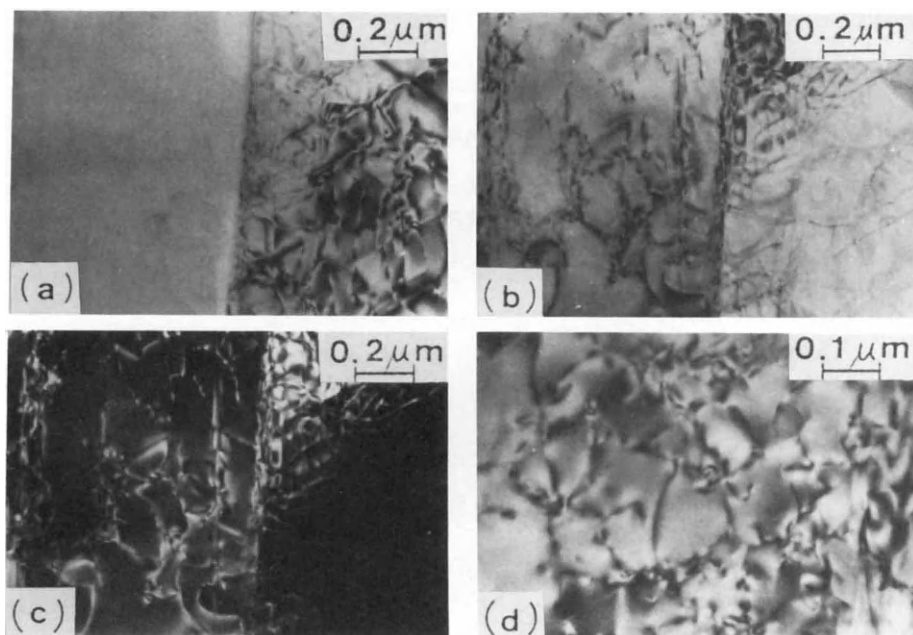


Fig. 10. Mosaic structure and dislocation forest within diamond grains in sample A. (a): mosaic structure in contact region between grains (b): same region from different angle (c): dark-field image obtained from (220) diffraction spot. (d): another example of dislocation forest.

Figure 11 (a) is a TEM micrograph of a Co matrix phase of sample B. Figure 11 (b) is a SAD pattern obtained from the center area of Fig. 11 (a). It is clear that the Co matrix in the region is composed of one fcc Co crystal. Our investigation has revealed that crystalline size of matrices of sintered compacts is larger than diamond grain size, which

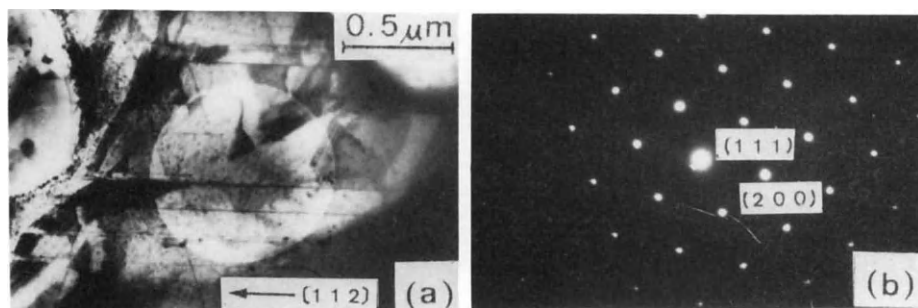


Fig. 11. TEM micrograph of Co matrix phase of sample B
(a): bright-field image (b): SAD pattern

is similar to the situation in WC-Co cemented carbide.

In Fig.11 (a), two sets of lines are shown intersecting at an angle of 70.5° . Crystallographic inspection revealed that the sets of lines belong to $\{111\}$ planes and are perpendicular to the film surface. These lines are stacking faults in the Co matrix, which is clearly confirmed by Fig. 12 obtained by tilting the specimen towards incident beam angle.

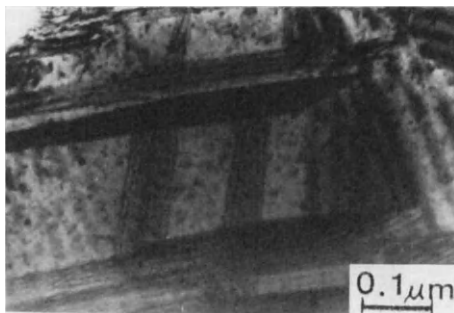


Fig. 12. Stacking faults in Co matrix.

CONCLUSION

The microstructures of four kinds of high-pressure sintered diamond compacts were examined using TEM. Three types of characteristic features were observed within diamond grains, i.e., slip bands, "mosaic" dislocation forests, and strain fringes. These deformed structures depend on the grain size of the compacts and probably affect the wear resistance and strength of the compacts.

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Applications of Hardmetal in the Zambian Mining Industry

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ABSTRACT

This paper presents field results of rotary percussive drill bits and attempts to correlate these failures with production and service problems.

KEY WORDS

Applications hardmetal, percussive drilling ; properties.

INTRODUCTION

Hardmetal is used in Zambian mines in fabricated rock cutting bits. These bits are used to drill blast holes or take core samples for geological and mineralogical analysis.

Blast holes are produced using a rotary-percussive action and the bit consists of sintered hardmetal inserts brazed into a steel body. Core samples are obtained by rotary drilling using diamond cutting elements retained by an infiltrated hardmetal matrix. This paper presents field results obtained from two mines and attempts to correlate the failures with production defects and service conditions.

FIELD RESULTS

Tables 1 and 2 give the historical data available from two mines for detachable bits and integral steels.

TABLE 1 - DETACHABLE BIT DISCARD ANALYSIS

Product Type	Sharpenings Per Discard	Carbide ¹ Failure %	Steel Failure %	Good Wear %	Lost/ Blasted %
Taper Bits					
1975	15	30	21	46	3
1976	11	34	20	45	1
1977	13	40	27	25	8
1978	12	34	22	23	21
1979	13	49	14	31	6
1980	15	53	17	25	5
1981	12	66	9	24	1
Average	13	45	19	29	7
57 mm Threaded					
1975	16	25	4	70	1
1976	13	30	13	56	1
1977	12	21	10	65	4
1978	9	39	21	34	6
1979	12	1	1	97	1
1980	14	19	0	79	2
1981	16	63	1	36	0
Average	13	27	9	61	3

TABLE 2 - INTEGRAL STEEL DISCARD ANALYSIS²

	1975	1978	APRIL 1982	JUNE ³ 1982
Frontal Wear%	17.2	17.0	10.3	0.0
Longitudinal Cracks %	17.1	16.8	18.4	22.5
Tungsten Out %	21.7	18.4	19.1	29.2
Cracked Corners %	17.4	23.0	22.8	21.3
Transverse Cracks %	17.6	18.0	23.5	27.0
Gauge wear %	9.0	6.8	5.9	0.0
Sharpenings Per discard	10	10	8	7

1. Total carbide failures. A breakdown into failure types not available.
2. Carbide discards only. Steel failures account for 30 to 60% of total discards.
3. Steels imported from Boart International, Springs complex.

DISCUSSION

The results given in Table 1 show a significant increase in carbide failures during 1981. Although no figures are available to quantify the various failure types, the samples returned for failure investigations have shown tungsten out and cracked corners. Virtually all samples seen, show gross overdrilling and occasionally reverse taper.

The variation in sharpenings per discard, in Table 1, are not considered significant. However it is known that there was a personnel change on the mine in 1977 and that the grinders have been deteriorating rapidly during the last two years. Poor bit sharpening and shortages of bits could account for the high carbide failures.

Table 2 shows a substantial decrease in the percentage of steels discarded for wear, and a general increase in carbide failures. These failures could be attributed to the breakdown of this mine's electrolytic grinders, as conventional grinding can lead to higher stresses. Further, the underground sharpening shops now have problems maintaining the required throughput, resulting in steel being overdrilled in order to maintain production. Recently, this problem has been aggravated by a general shortage of foreign exchange for raw materials. Hence, the importation of finished steels to ease the situation.

The high incidence of longitudinal cracks was initially thought to be a result of high brazing stresses caused by uneven braze gaps during manufacture. However, the higher incidence of this failure in imported steels suggests another cause, such as high grinding or service stresses. This is partly substantiated, in the imported steels, as no failure occurred before the third sharpening.

It is difficult to determine the cause of the tungsten out failures without a physical examination, as these could be caused by braze or carbide fracture. Braze failure can result from a manufacturing defect such as poor wetting or oxidation or may result from overheating during grinding. Alternatively, a crushed carbide type failure resulting from overdrilling or poor grinding may have been classed as a tungsten out failure.

The generally high carbide failure rate may indicate that the carbide presently used has insufficient fracture toughness to withstand the current abuse. Further, as the mines are generally encountering harder granites at the lower levels, the 9% cobalt grade currently used may no longer be suitable. Therefore, Diacarb intends testing four alternative grades, to determine if a tougher grade can be utilised, without a serious reduction in life as a result of abrasive wear.

The alternative to grade changes, is to persuade the mining industry to adopt a thorough training programme for its drilling and sharpening personnel in order to reduce the abuse that it currently being experienced. However, unless the foreign exchange situation improves and sufficient bits are available to allow sharpening to be carried out at the correct intervals, the failures will continue.

FUTURE DEVELOPMENTS

Diacarb will shortly be producing button bits which utilise a harder 6% cobalt hardmetal in the form of hemispherical headed cylinders. These buttons are interference fitted into holes drilled in the bit body. A harder cobalt grade can be used in the absence of any brazing stresses and the shape of the inserts allow the bit to be used without sharpening, although button sharpening may improve the penetration rate. Button bits, however, perform better when used with independent rotation machines, which are not very common in Zambia at present, as the high rotational speed of fixed rotational speed machines cause rapid gauge wear.

Further developments in hardmetal technology may result in improved performance of all bit types, if these can be matched by improvements in the other materials and fabrication techniques. However, the use of hardmetal may be substituted in certain applications by diamond compact elements, which are already making significant inroads in certain rotary drilling applications, or other drilling techniques which are under investigation.

ACKNOWLEDGEMENTS

The author would like to express his gratitude to Boart International Limited for permission to publish this paper and in particular to the Management of Diacarb Division of Boart Zambia. Recognition is due to Dr. G.J. Rees and D.W. George who's efforts resulted in this paper being written.

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