SILICON MODIFICATION OF IRON BASE HARDFACING ALLOYS

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ABSTRACT

Iron base alloys of typical composition Fe-34Cr-4.5C wt.% are used extensively in industry as wear resistant coatings, deposited by arc welding. The alloys are relatively expensive because they use large concentrations of chromium, an alloying element necessary to generate a large volume fraction of hard carbides, and to provide oxidation and corrosion resistance. This work deals with the application of thermodynamic modelling to these materials, so that the role of alloying elements in general, and silicon specifically can be assessed. The theoretical analysis indicates that silicon can be utilised in high concentrations, since it beneficially modifies morphology of the normally elongated and rather brittle carbides, and to provide an oxidation resistant matrix phase. Experimental results on simulated welds containing large concentrations of silicon are presented and rationalised with respect to microstructure and wear properties.

INTRODUCTION

Iron base hardfacing alloys containing large concentrations of chromium and carbon are used widely for their good abrasive wear properties, and their intrinsic ability to resist corrosion and oxidation during service [1,2]. The alloys are usually deposited using consumable electrodes and one of a variety of arc welding processes. The final deposit may typically have a chemical composition Fe-34Cr-4.5C wt.%, and a microstructure consisting of a large volume fraction ($\cong 0.6$) of coarse M_7C_3 carbides in a matrix which is a eutectic mixture of austenite and more M_7C_3 particles [1,2]. The coarse M_7C_3 carbides represent the first phase to precipitate from the liquid (and hence are called the *primary* carbides), in the form of elongated, crystallographically facetted particles, typically many hundreds of micrometers in length and about $50\mu m$ wide. They are very hard ($\sim 1200 - 1600HV$), and when supported by a tough matrix, are responsible for imparting good wear resistance to the alloys.

The equilibrium microstructure of such alloys at ambient temperature should not contain any of the eutectic austenite, which ought to decompose during cooling below $\sim 800^{\circ}C$ to a mixture of ferrite (α) and M_7C_3 carbides [3]. However, the rather high cooling rates associated with welding mean that equilibrium is not achieved, the alloy becoming configurationally frozen at a temperature of $\sim 1150^{\circ}C$ [2]. The term configurational freezing implies that microstructural changes become sluggish and essentially cease to happen below that temperature. The austenite is thus retained to ambient temperatures, as a metastable phase with a rather high chromium concentration of about 16 wt.%. If, however, the the alloy is then subjected to service at temperatures around $700^{\circ}C$, the austenite decomposes quite rapidly into $\alpha+ M_7C_3$ [3]. The ferrite that forms is in equilibrium with M_7C_3 so that its chromium concentration is expected to be very low [3,4], possibly making if susceptible to oxidation and corrosion. Research has indicated that it is not feasible to significantly enhance the stability of the austenite by alloying with elements such as manganese or nickel [3].

The present work is a continuation of a new approach to the problem of making Fe-Cr-C hardfacing alloys both thermodynamically stable and yet oxidation resistant [5]. The approach is one in which silicon plays a major role as an alloying addition. Silicon has two major effects: it is known to have a very low solubility in many carbide phases [6], including M_7C_3 carbides [2,5], so that by analogy with high strength steels [7], it could lead to a refinement of the primary carbide size. High concentrations of silicon are also known to enhance the oxidation resistance of iron based alloys [8,9]. An additional bonus is that the partitioning of Si from the carbides leads to a large increase in its concentration in the matrix, thereby exaggerating its influence on matrix properties. Silicon is also a cheap alloying element, and since it is a very strong deoxidiser, its use in electrode coatings should enhance the recovery of the more expensive elements such as chromium during transfer across the arc.

EXPERIMENTAL PROCEDURE

The investigations were carried out using high purity experimental alloys cast in an argon arc furnace with a water cooled copper mould. It has been verified that this technique adequately simulates the microstructure and phase chemistry expected when the corresponding alloy is deposited by manual metal arc welding [5]. The chemical compositions of the alloys are given in Table 1.

Microanalysis experiments were conducted using energy dispersive X-ray analysis on scanning and transmission electron microscopes. The data were analysed using the *LINK RTS 2FLS* program for thin foil microanalysis; this corrects the raw data for atomic number and absorption, and also accounts for overlapping peaks by fitting standard profiles. Thin foil preparation and microanalysis techniques have been discussed elsewhere in more detail [2,5].

Thermodynamic analysis of phase equilibria was carried out using the *MTDATA* software of the National Physical Laboratory, Thermochemistry Division. This software allowed the determination of stable phases as a function of chemistry and temperature, using a carefully assessed thermodynamic database [10].
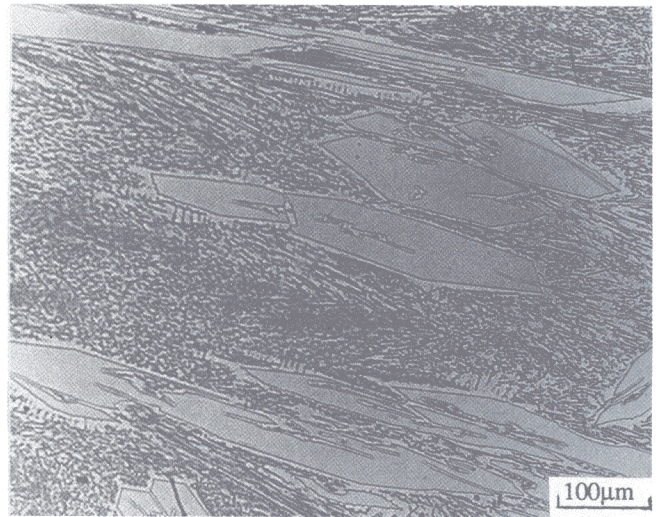
EXPERIMENTAL ALLOYS

Micrographs of the experimental alloys S1-S3 are presented in Fig. 1 [5]. While the size of the M_7C_3 primary carbides does not appear to be influenced substantially, it is evident that an increase in silicon concentration their shape more isotropic, and a similar effect is also apparent on the eutectic M_7C_3 carbides. It has been suggested that this change in morphology is probably caused by the silicon reducing the orientation dependence of the liquid/M_7C_3 interface energy [5]. The identification of ferrite or austenite in the presence of M_7C_3 is rather difficult using X-ray analysis, due to overlapping of diffraction peaks. Even though it has previously been reported that S2 and S3 have an austenitic matrix, further X-ray diffractometry suggests that the results are ambiguous between ferrite and austenite, especially since there always seems to be the possiblity of ferrite or austenite peaks at similar positions as M_7C_3 peaks. As will be seen later, microanalysis and thermodynamic calculations indicate that the matrix phase in S2 and S3 should in fact be ferrite. The results from microanalysis experiments are presented in Table 2 [5].
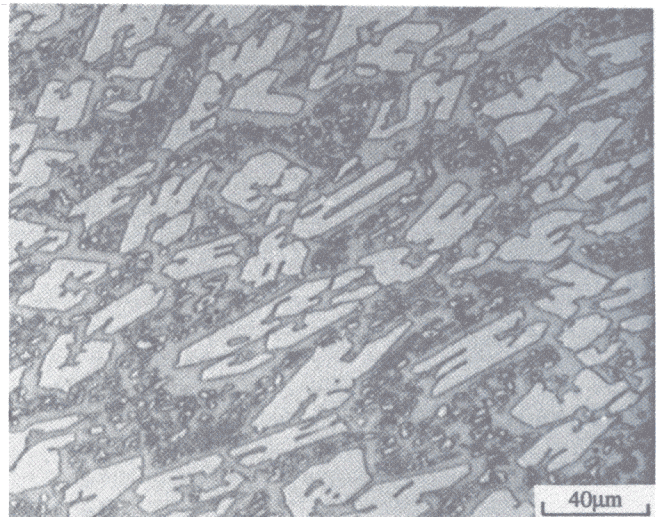
Table 1 Chemical Compositions, (wt.%).

Alloy	C	Cr	Si	Fe
S1	4.59	30.4	0.1	64.9
S2	4.48	33.6	3.6	58.3
S3	3.6	31.2	6.9	58.3

Table 2 Mean concentrations (at.%) of substitutional alloying elements in the M_7C_3 carbides and the matrix phase concerned.
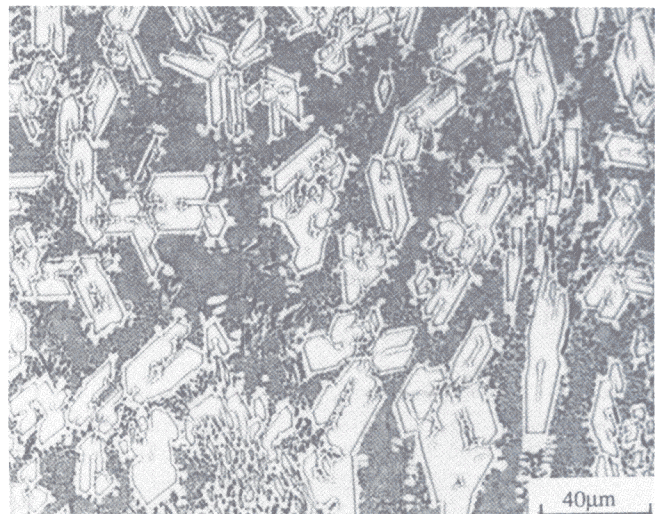
	S1 M_7C_3	γ	S2 M_7C_3	α	S3 M_7C_3	α
Cr	45.8	16.5	48.9	11.5	50.5	14.3
Si	0.01	0.2	0.2	12.4	0.1	17.2

S1

S2

S3

Fig. 1 - Light micrographs showing the as-cast microstructures of alloys S1-S3.

THERMODYNAMIC ANALYSIS
EXPERIMENTAL ALLOYS

The purpose of the thermodynamic analysis (*i.e.* multicomponent phase diagram calculation) was to assess whether the observed phases and phase chemistries are consistent with available thermodynamic data. If the computations can be demonstrated to predict the behaviour of the Fe-Si-Cr-C alloys, then the method can be used to theoretically design and optimise such alloys. However, caution must be exercised in applying thermodynamics to any discussion of welding or casting involving rather rapid cooling conditions; as indicated below, kinetic factors can then lead to deviations from equilibrium.

The analysis predicted the most stable mixture of phases, out of a set of possible phases consisting of Sigma, M_7C_3, $M_{23}C_6$, M_3C, M_6C, Cr_6C_4, SiC, TiC, Cr_3Si, Cr_5Si_3, Fe_5Si_3, $FeSi$, austenite and ferrite, for quaternary alloys containing the elements Fe, Si, Cr and C. The calculations do not allow for any solubility of Si in the carbide phases, consistent with experimental evidence that its solubility is negligible. The concentrations of the alloying elements were set to be identical to those in the experimental alloys S1-S3.

The calculated chromium concentrations in the matrix are illustrated in Fig. 2, as a function of temperature. The curve for alloy S1 shows the effect of the transformation of austenite to a mixture of ferrite and M_7C_3 at a temperature of about $800^{\circ}C$, with a concomitant reduction in the Cr concentration of the matrix phase. Austenite is not found to be stable in alloys S2 and S3 at any of the temperatures tested. Given that the alloys become configurationally frozen at around $1150^{\circ}C$, the calculations indicate that the matrix chromium content should decrease in the order S1$\rightarrow$ S2 $\rightarrow$ S3, and that the concentration should range from about 5-7 at.%.
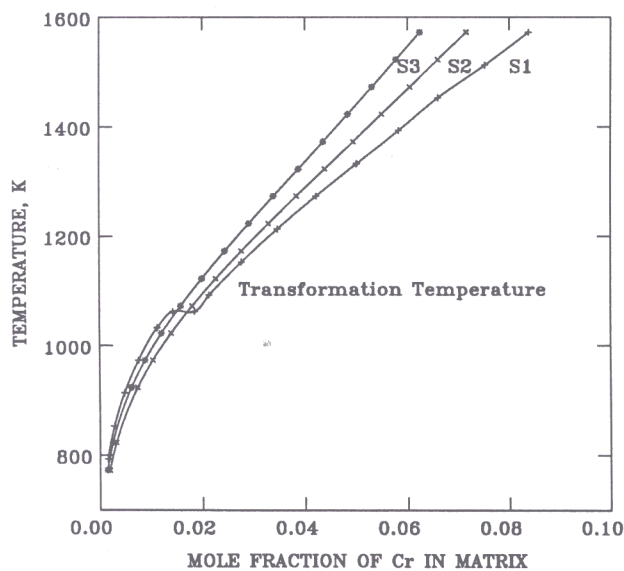
These results are not consistent with the data of Table 2, which show higher matrix Cr concentrations. The austenite or ferrite are thus found to be supersaturated with Cr, indicating that the M_7C_3 carbides *trap* iron as they grow during the nonequilibrium solidification or the cast alloys. Note that trapping implies an increase in the chemical potential of iron on transfer across the carbide/matrix interface [11]. It is likely therefore, that prolonged ageing at high temperatures should lead to a redistribution of Cr towards the equilibrium concentrations. To test this hypothesis, a sample of alloy S3 was sealed in a quartz tube containing argon, and annealed at $850^{\circ}C$ for one year. Subsequent microanalysis experiments in three regions of the ferrite matrix indicated a decrease in the chromium concentration from the original mean value of 14.3 at.% to 7.96 at.%. This confirms the trapping hypothesis, although it is evident (Fig. 2) that the chromium concentration of the ferrite is still above that expected at equilibrium.

Fig. 3 shows how the carbon concentration of the matrix phase may be expected to vary with temperature; this could not be checked experimentally since the microanalysis techniques used are incapable of estimating the concentrations of light elements. The silicon concentrations of the ferrite in S2 and S3 are fairly accurately predicted (Fig. 4, Table 2), and are found to be virtually independent of temperature. This is not surprising since Si has negligible solubility in the M_7C_3 carbide, whose volume fraction does not vary much below 1600K in S2 and S3 (Fig. 5). Since alloy S2 is expected to have the largest volume fraction of M_7C_3, followed by S1 and S3 (given that they become configurationally frozen at $\sim$ 1150$^{\circ}C$, the resistance to abrasive wear would be expected to increase in the order S2, S1 and S3, assuming that the wear rate decreases as the carbide volume fraction increases. The experimental data on the other hand show that the abrasive wear resistance increases in the order S1, S2 and S3 [5]. This emphasises the hypothesis that the more isotropic shape of the carbides in the higher silicon alloys reduces their wear rates, since elongated carbides are known to be susceptible to cracking Fig. 6, [5,12-15].

Fig. 2 - Calculated chromium concentration in the matrix phase of alloys S1-S3.
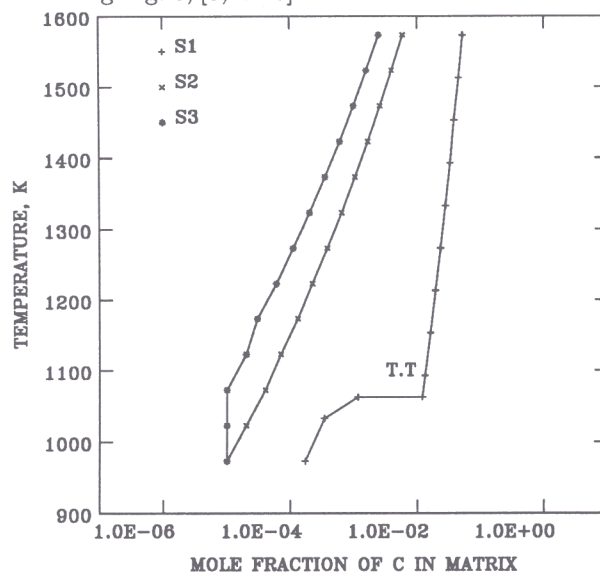

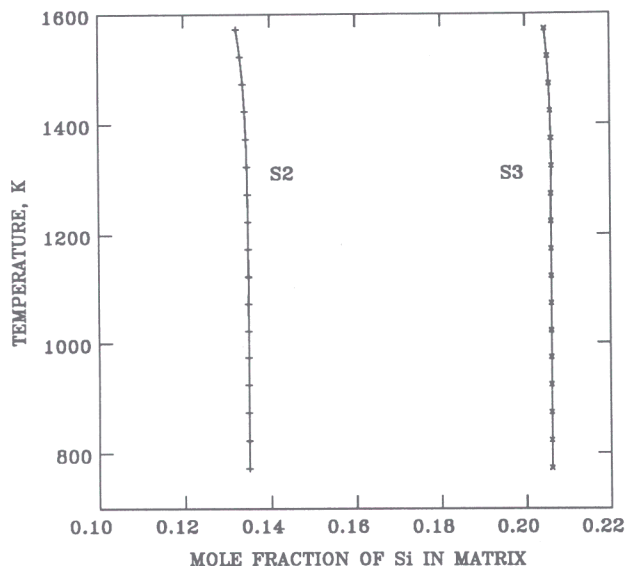Fig. 3 - Calculated carbon concentration in the matrix phase of alloys S1-S3.

Fig. 4 - Calculated silicon concentration in the ferrite of alloys S2 and S3.
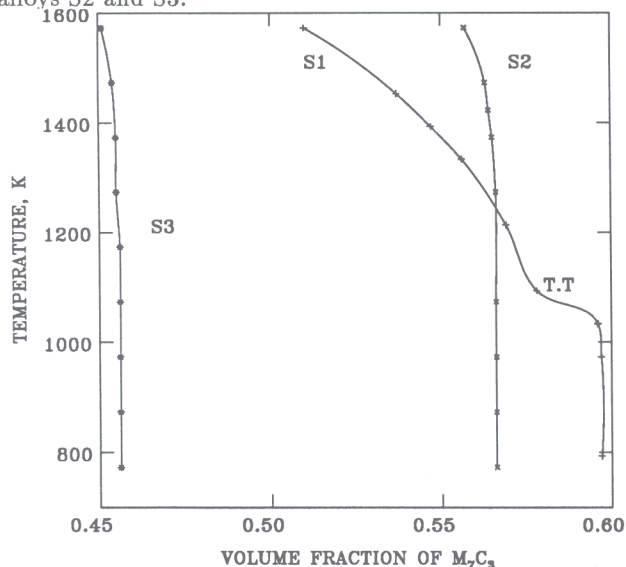

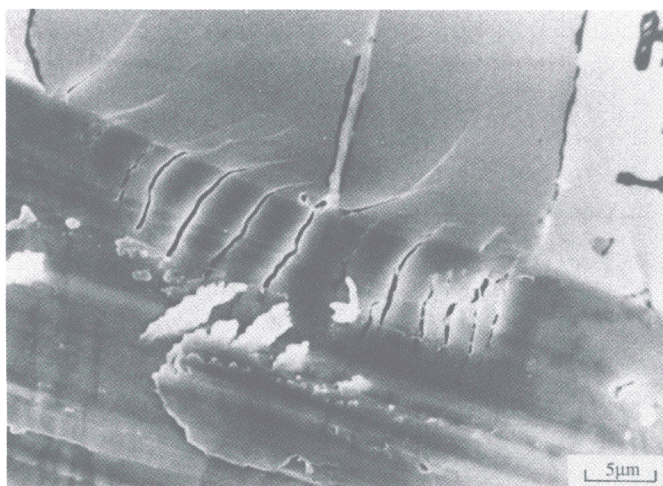Fig. 5 - Calculated volume fraction of M_7C_3 in alloys S1-S3.

Fig. 6 - Surface of alloy S1 after a scratch test using a Vicker's diamond indenter.

To summarise, it is clear that thermodynamic analysis alone does not give a complete interpretation of the experimental data, but the predicted trends provide a useful basis for alloy design. The existence of ferrite instead of austenite as the matrix phase is correctly predicted, as is the matrix silicon concentration. M_7C_3 is also correctly predicted to be the only stable carbide out of the selection of carbide phases included in the analysis. The ability to predict variations with temperature should also be of use as more experimental data become available. A further advantage is that (unlike alloys S1, S2 & S3) specific alloying element effects can be studied theoretically while keeping the other variables such as the carbon content constant. The calculations presented below thus consider a series of hypothetical model alloys chosen to emphasise the role of Si at constant carbon and chromium concentrations.

THERMODYNAMIC ANALYSIS
MODEL ALLOYS

The results for alloys M1-M4 (Table 3) are presented in Figs. 7-11. They confirm the general trends that the addition of silicon beyond about 0.5wt.% makes ferrite the stable phase at temperatures as high as 1600K, so that the austenite to ferrite phase change is missing in alloys M2-M4. The chromium concentration of the matrix phase decreases with temperarture (Fig. 7), and as the average silicon concentration is increased. Due to the rejection of silicon from the carbide phase, its concentration in the matrix reaches very high levels ($\sim 25at.\%$ in M4); this should enhance the oxidation resistance of the alloys (Fig. 8). Most of the carbon in the alloys is tied up as carbides, with very little in solution in the matrix phase (Fig. 9).

Table 3 Chemical Compositions, model alloys (wt.%).

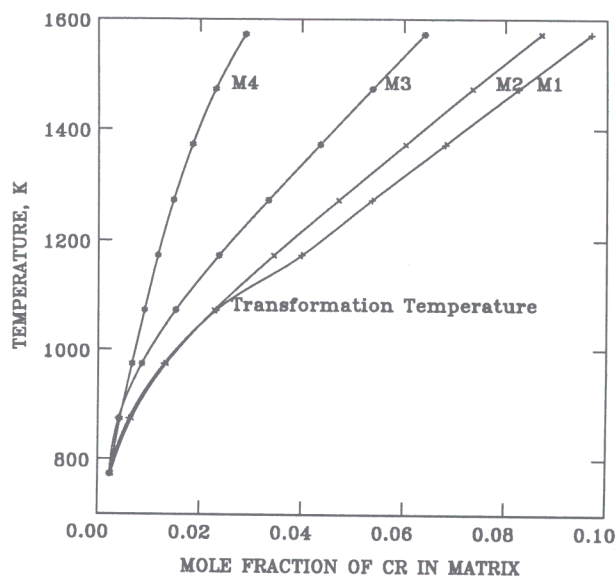| Alloy	C	Cr	Si	Fe
M1	4.5	34.0	0.5	balance
M2	4.5	34.0	2.0	balance
M3	4.5	34.0	4.0	balance
M4	4.5	34.0	8.0	balance

Fig. 7 - Calculated chromium concentration in the matrix phase of alloys M1-M4.
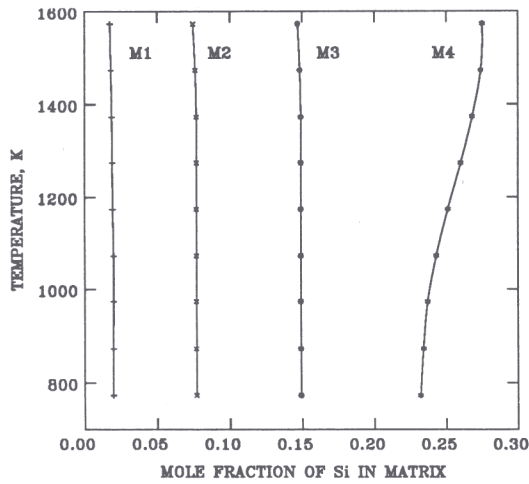
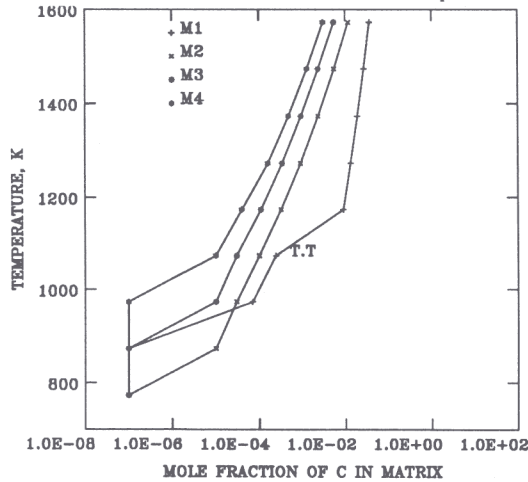Fig. 8 - Calculated silicon concentration in the matrix phase of alloys M1-M4.

Fig. 9 - Calculated carbon concentration in the matrix phase of alloys M1-M4.

The alloys are predicted to contain ∼ 0.5 volume fraction of M_7C_3 carbides at elevated temperatures (Fig. 10), but in alloy M4, the M_7C_3 carbides should partially transform to Cr_6C_4 during cooling to ambient temperature (Fig. 11). This could be a very interesting result since the transformation occurs in the solid state, so that the morphology of Cr_6C_4 might be expected to be different from that of the parent M_7C_3 carbides. This work provides a basis for the design of further hardfacing alloys, although the properties to be expected are not clear.
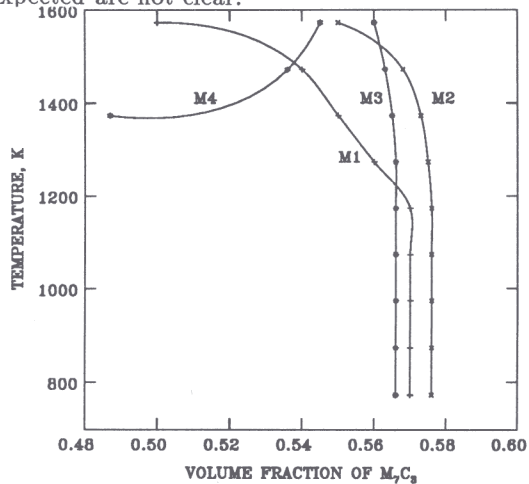

Fig. 10 - Calculated volume fraction of M_7C_3 in alloys M1-M4.
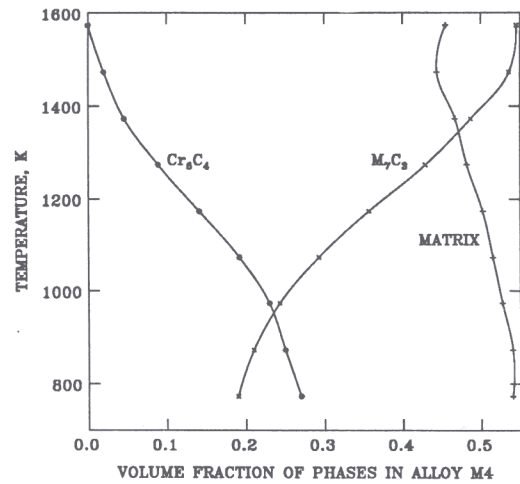

Fig. 11 - The transformation of M_7C_3 to Cr_6C_4 in alloy M4.

CONCLUSIONS

The modification of rich Fe-Cr-C hardfacing alloys with silicon has been investigated theoretically and the results predict some of the main features observed in the microstructure of some experimental alloys. It also supports the conclusion that it is the modification in the shape of the M_7C_3 carbides, to a more equiaxed morphology, that leads to enhanced wear resistance in silicon-rich alloys of the type considered in the study.

It appears that during continuous cooling under conditions appropriate to manual metal welding, excess iron is trapped in the M_7C_3 carbides. This in turn causes the chromium concentration of the matrix phase to be higher than equilibrium (as estimated using phase diagram calculations).

Additions of Si beyond about $2wt.\%$ eliminate the austenite, the matrix in such alloys being ferritic. Due to the its negligibly low solubility in the carbide phases present, most of the added silicon is partitioned into the ferrite, resulting in concentrations which should be high enough to enhance the oxidation resistance of the ferrite.

The theoretical analysis also predicts that in one of the high silicon alloys studied, the M_7C_3 carbides should undergo partial, solid-state transformation to Cr_6C_4 during cooling to ambient temperature.

REFERENCES

1. Metals Handbook, 9th edition, vol. 6, ASM, Ohio, USA, p.771 (1983).
2. L.-E. Svensson, B. Gretoft, B. Ulander and H. K. D. H. Bhadeshia, J. Materials Science 21 1015 (1986).
3. S. Atamert, Ph.D. Thesis, Department of Materials Science and Metallurgy, University of Cambridge, (1988).
4. Metals Handbook, 7th edition, vol. 8, ASM, Metals Park, Ohio, USA, p.402 (1973).
5. S. Atamert and H. K. D. H. Bhadeshia, Proc. of Heat Treatment '87, Institute of Metals, London, pp. 39-43 (1988).
6. W. S. Owen, Trans. ASM 46 812 (1954).
7. F. B. Pickering, Physical Metallurgy and the Design of Steels, Applied Science Publishers, London, (1978).
8. N. Birks and G. H. Meier, Introduction to High Temperature Oxidation of Metals, Arnold, London, p.85 (1983).
9. J. C. Rawers and E. M. Mattlin, Metall. Trans. A 18A 1805 (1987).
10. Computed in July 1988, by means of MTDATA, the National Physical Laboratory metallurgical and thermochemical databank, Teddington, Middlesex.
11. J. C. Baker and J. W. Cahn, Acta Metall. 17 575 (1969).
12. H. H. Zum Gahr, Z. Metallkunde 71 103 (1980).
13. J. S. Sun, Wear of Materials 1983, Am. Soc. Mech. Eng., New York, 79 (1983).
14. S. Junyi and J. Yuding, Wear of Materials 1987, Am. Soc. Mech. Eng. New York, 661 (1987).
15. H. H. Zum Gahr and D. V. Doane, Metall. Trans. A 11A 613 (1980).