

## Stability, wear resistance and microstructure of Fe-Cr-C and Fe-Cr-Si-C hardfacing alloys

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### ABSTRACT

Fe-34Cr-4.5C wt-% hardfacing alloys deposited by manual metal arc welding have a metastable microstructure consisting of large, primary  $M_7C_3$  carbides in a matrix which is a eutectic mixture of austenite and more  $M_7C_3$  carbides. Given thermal activation and time, the austenite in the microstructure tends to decompose into a Cr depleted ferrite and  $M_7C_3$  carbides.

In an effort to improve the high-temperature stability, oxidation, and corrosion resistance of such hardfacing alloys, a systematic study has been carried out on the role of Si in the microstructure, phase chemistry, and abrasive wear resistance of Fe-Cr-C base alloys. The investigations have been carried out on model alloys cast by an argon arc melting technique, which is in general found to simulate adequately the corresponding structures obtained by manual metal arc welding.

In all cases, Si is found to partition strongly into the austenite during solidification; Si concentrations of up to 18 at-% have been found in the matrix austenite, even though the average Si concentration used was far less.

Si is found to influence significantly the morphology of  $M_7C_3$  carbides, possibly through reducing the orientation dependence of interface energy. This is believed to be beneficial in enhancing the toughness and hence impact wear resistance of the alloys. A further effect of Si is to reduce the Cr concentration of the austenite in the as-cast alloys. This is advantageous because the Cr is used better in the formation of  $M_7C_3$  carbides. The carbon concentration of the austenite is found to increase with Si level, although the reasons for this await detailed thermodynamic analysis. Preliminary work indicates that the high-Si alloys have a better abrasion wear resistance.

### INTRODUCTION

Conventional hardfacing alloys can be classified into five main classes: hard steels, hard cast irons, highly alloyed iron base alloys, cobalt base alloys, and nickel base alloys.<sup>1</sup> These

alloys are in general very effective and have been established after many years of steady development work. They do however contain relatively large amounts of expensive and sometimes strategically important alloying additions. It is still the case that the detailed role of some of these additions is not understood. This work is part of a systematic re-examination of iron, nickel, and cobalt base hardfacing alloys<sup>2</sup> with a view to establishing a quantitative alloy design procedure to enable the optimisation properties (corrosion, oxidation, and wear resistance), alloy content, cost, and microstructural stability. The alloy design methods involve the use of thermodynamic calculations and will be reported elsewhere.

For reasons which will become apparent later, this work deals specifically with a microstructural characterisation of the influence of silicon additions to iron base hardfacing alloys of nominal base composition Fe-4.5C-34Cr wt-%. These alloys, when deposited by arc welding techniques, have a microstructure consisting of very hard ( $\approx 1400$  HV, volume fraction  $\approx 0.6$ ) primary  $M_7C_3$  carbides in a matrix which is a eutectic mixture of austenite ( $\gamma$ ) and  $M_7C_3$  carbides, when the alloy is not diluted by the metal on which it is deposited.<sup>3</sup> Although after solidification the ambient temperature microstructure is a mixture of austenite and  $M_7C_3$ , the equilibrium microstructure should consist of ferrite and  $M_7C_3$ , because at sufficiently slow cooling rates the austenite should undergo a diffusional transformation to ferrite and more  $M_7C_3$ .<sup>4</sup> However, during welding the structure becomes configurationally frozen<sup>†3</sup> at a temperature of around 1150°C, because such diffusional transformations require considerable time to accomplish both the redistribution of substitu-

\* The term  $M_7C_3$  refers to the fact that the carbide is not a pure chromium carbide, but also contains iron and other substitutional alloying additions. 'M' therefore stands for some combination of metal atoms.

† A configurationally frozen microstructure is one which does not change during cooling from the temperature at which it becomes configurationally frozen.<sup>5</sup> The term frozen is not to be confused with the freezing of liquid. In the present context, the alloy solidifies and then becomes configurationally frozen at some lower temperature where the mobility of atoms becomes inadequate, for the given cooling rate, to support diffusional transformation. It should be noted that a higher cooling rate should increase the temperature at which a microstructure becomes configurationally frozen.

tional alloying additions and to rearrange the atoms as required for the lattice changes accompanying transformation (the diffusion necessary for the latter is called reconstructive diffusion<sup>6</sup>). It follows that the microstructures obtained are thermodynamically unstable and the  $\gamma$  should tend to decompose if the hardfacing deposit is in service at high temperatures ( $\approx 700^\circ\text{C}$ ). The diffusional transformation may not influence significantly the wear resistance, but it might alter the corrosion and oxidation resistance of the alloy; the metastable austenite obtained after deposition has a relatively high Cr concentration ( $\approx 16 \text{ wt-}\%$ )<sup>3</sup> but that of the ferrite is much lower. Of course, as far as the  $\text{M}_7\text{C}_3$  is concerned, its Cr concentration ( $\approx 40 \text{ wt-}\%$ ) is more than adequate for corrosion and oxidation resistance.<sup>3</sup> A major aim of the present work was to design a Fe-Cr-C base alloy which has a better matrix corrosion and oxidation resistance at all service temperatures even following inevitable diffusional transformations. It was proposed to achieve this by adding high levels of silicon, which is known to have a very low solubility in carbides<sup>7</sup> (and specifically also in  $\text{M}_7\text{C}_3$ <sup>3</sup>). Hence, most of the silicon in the alloy should during solidification be partitioned into the liquid phase, and subsequently (during the eutectic transformation) into the austenite, giving a much enhanced level of Si. There are several advantages in this; Si is known to enhance the oxidation and corrosion resistance of iron<sup>8</sup> and it is a very cheap alloy addition. Furthermore, if the austenite subsequently transforms to ferrite and  $\text{M}_7\text{C}_3$ , then the Si concentration of the ferrite should be even higher, so that oxidation resistance should be enhanced. It was also anticipated that Si may refine the carbides in the microstructure; such an effect is well established for high strength steels.<sup>9</sup> At the same time, any influence of further alloy additions on the partitioning of Cr between the  $\text{M}_7\text{C}_3$  and matrix also needed to be investigated; any change may influence the volume fraction of hard phase and therefore wear properties.

The relationship between microstructure and wear is known to be complex and ill understood.<sup>2,10,11</sup> For example, the behaviour of an alloy under abrasive conditions may be quite different under impact conditions.<sup>12</sup> A working hypothesis is nevertheless necessary during alloy development and in the present work the rather simple and probably crude hypothesis is adopted that good abrasion resistance is obtained when the volume fraction of the hard phase is high, and when the hard phase is well supported by a relatively tough matrix. For impact wear resistance, the hard phase is prone to cracking, so that a more equiaxed hard phase should give better wear resistance in these circumstances.

#### EXPERIMENTAL PROCEDURE

The experiments utilised both welds deposited by a manual metal arc welding technique and experimental casts (weight  $\approx 65 \text{ g}$ ) made from high purity elements in an argon arc furnace with a water cooled copper mould.

The welds were deposited in three layers so that the top layer could be examined in an essentially undiluted condition. Electrodes 4 mm in diameter were used, the welding conditions being 160 A, 23 V a.c., with a welding speed of about 0.004 m/s and an interpass temperature of about  $350^\circ\text{C}$ . The electrical energy input is

therefore  $\approx 920 \text{ J/mm}$ . These conditions are the same as used by Svensson *et al.*<sup>3</sup>

Thin-foil specimens for transmission electron microscopy were prepared from 0.25 mm thick discs spark machined from the weld deposits. The discs were subsequently thinned and electropolished in a twin-jet polishing unit using a 5% perchloric acid, 25% glycerol, and 70% ethanol mixture at ambient temperature and 55 V. The foils were examined in a Philips EM400T transmission electron microscope operated at 120 kV. Microanalysis experiments were also carried out on this microscope, using an energy dispersive X-ray analysis facility. The specimens, which were about 100 nm thick, were held in a beryllium holder tilted  $35^\circ$  from the normal which is equal to the take-off angle. The X-ray count rate was optimised at about 200 counts/s, over a count period of 100 s, giving a typical statistical accuracy of  $\approx 1\%$ . The data were analysed using the LINK RTS 2 FLS program for thin foil microanalysis; this corrects the data for atomic number and absorption and accounts for overlapping peaks by fitting standard profiles. Even though the probe diameter used was about 3 nm, beam spreading due to scattering of electrons within the thin foil gave an estimated broadened beam diameter of  $\approx 20 \text{ nm}$ . The elements analysed were iron, silicon, chromium, and manganese; at typical levels found in the present alloys, it has been established that none of these elements cause significant fluorescence effects in thin foils.<sup>3</sup>

The microanalysis results reported for the primary carbides and for the regions near primary carbides were obtained using an EDAX system on a scanning electron microscope, and the data are fully corrected for atomic number, absorption, and fluorescence.

The beryllium window on the detector used in the microanalysis system absorbs X-rays from light elements; the concentration of carbon in the  $\text{M}_7\text{C}_3$  is therefore determined by assuming stoichiometry, and of austenite from lattice parameter measurements. However, the raw data obtained prior to any corrections are also presented later in the text. The raw data excludes carbon; the term  $y_i$  refers to the concentration of element  $i$  in atomic percent when the presence of carbon is ignored. The corresponding true concentration (at-%, obtained after correcting for carbon) is denoted  $x_i$ .

The carbon concentration of the austenite was determined from lattice parameter measurements carried out on an X-ray diffractometer with step-scanning at  $0.02^\circ$   $2\theta$  intervals for the range  $2\theta = 10\text{--}120^\circ$ .

Abrasion wear tests were performed on 5 mm diameter cylindrical specimens under a 0.43 kg load (P), the flat face of the specimen being in contact with a rotating (sliding velocity 0.63 m/s) 75 mesh SiC coated disc. The disc was renewed after every 10 min interval. At least three experiments were carried out for each alloy, the wear rate being deduced from the weight loss (w) as a function of time. The specific wear resistance (R) is given by  $R = w/(\rho PL)$ , where  $\rho$  is the specimen density and L is the travel distance in metres for each 10 min interval. The chemical compositions of the alloys used are presented in Table 1.

#### RESULTS AND DISCUSSION

##### Comparison between weld and experimental alloy

Much of the initial work has been carried out on experimental 65 g melts discussed earlier, because the design of suitable welding electrodes

is a more complex problem. It was therefore felt necessary to check that the essential microstructures of experimental welds compared well with those obtained by manual metal arc welding.

Alloy S1 is essentially of the same composition as alloy M1; the slightly lower carbon and chromium concentrations of S1 should not significantly influence the nature of the  $\gamma$  or  $M_7C_3$ , although the volume fraction of  $M_7C_3$  should be lower in S1. Optical microscopy (Fig. 1) demonstrated that the alloys have identical microstructures; microanalysis results (Fig. 2, Table 2) show that the austenite in S1 has a higher Cr content, and this is consistent with the fact that the casting technique involves a somewhat higher cooling rate than that associated with arc welding. This would mean that the alloy becomes configurationally frozen at a higher temperature, where the Cr concentration in  $\gamma$  in equilibrium with  $M_7C_3$  is expected to be higher. With this exception, the results show that argon arc melts can be used in simulating manual metal arc weld deposits, especially for revealing trends in microstructure and phase composition. A comparison of the compositions of M1 and S1 is presented in Table 2.

#### Higher silicon alloys

Optical micrographs of alloys S2 and S3 are presented in Fig. 3. A major effect of silicon is to change the morphology of the primary carbides. At very low silicon concentrations, the primary carbides are elongated (Fig. 1) and tend to become more equiaxed with increasing silicon concentration (considerable microscopy confirms that this is not just a sectioning effect). The changes imply that the orientation dependence of the liquid/ $M_7C_3$  interface energy becomes less orientation dependent with increasing Si. A similar effect is also evident for the eutectic  $M_7C_3$  carbides which also appear more globular in alloy S3. These morphological changes should be beneficial to the toughness of the alloy, perhaps imparting better impact abrasion wear resistance, and experiments to confirm this are in progress.

The microanalysis data (Fig. 4, Table 2) show that the silicon partitions strongly to the matrix austenite. This should considerably enhance the oxidation and corrosion resistance of the alloys.

The effect of Si is also to reduce the level of Cr in the austenite during the eutectic decomposition of liquid. This may at first sight seem detrimental, but the austenite should in any case eventually decompose to low-chromium ferrite. The decrease in the Cr level of  $\gamma$  formed during solidification should in fact be beneficial since the Cr is best used in forming the hard  $M_7C_3$  carbides during solidification.

The carbon concentration of the austenite seems to increase significantly as the silicon concentration increases. The reason for this is not clear and will have to await detailed thermodynamic analysis.

Results from the abrasion wear tests are presented in Table 3. They show that a generally improved wear resistance is obtained with the addition of Si, consistent with the interpretation of the microstructural and microanalytical data.

#### CONCLUSIONS

An attempt has been made to rationalise the influence of silicon on the detailed microstructure and phase composition of Fe-34Cr-4.5C alloys. The

investigation has been carried out on model alloys cast by an argon arc melting technique, which is in general found to simulate adequately the corresponding structures obtained by deposition during manual metal arc welding.

In all cases, Si is found to partition strongly into the austenite during solidification; Si concentrations of up to 18 at-% have been found in the matrix austenite, even though the average Si concentration used was much lower.

It is found that Si causes significant changes in the morphology of  $M_7C_3$  carbides. Both primary and eutectic  $M_7C_3$  carbides tend to adopt more equiaxed morphologies and this has been attributed tentatively to Si causing a decrease in the orientation dependence of the liquid/ $M_7C_3$  interfacial energy. In any case, the effect may be advantageous in enhancing the toughness and hence impact wear resistance of the high-Si alloys.

A further effect of Si is to reduce the Cr concentration of the austenite in the as-cast alloys. This is regarded as beneficial since the Cr is used better in the formation of  $M_7C_3$  carbides whose volume fraction should therefore increase with Si level. It is pointed out that if the austenite eventually decomposes to low-Cr ferrite, as required by equilibrium, then there is little point in having a high Cr content in the  $\gamma$  in any case.

The carbon concentration of austenite significantly increases with Si; the reasons for this are not clear and an explanation must await detailed thermodynamic analysis of the equilibrium between austenite and  $M_7C_3$  carbide. This effect can be compensated for by increasing the general carbon level of the alloys.

Preliminary abrasion wear tests indicate that the high silicon alloys have a better wear resistance, and welding electrodes are currently being prepared for further investigations in which the effect of dilution on the first two layers of the usual manual metal arc deposits will also need to be studied.

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Table 1 Chemical compositions of Fe-C-Cr-Si alloys, in wt-%. Alloy numbers beginning with the letter 'S' are experimental casts while the others have been deposited using manual metal arc welding

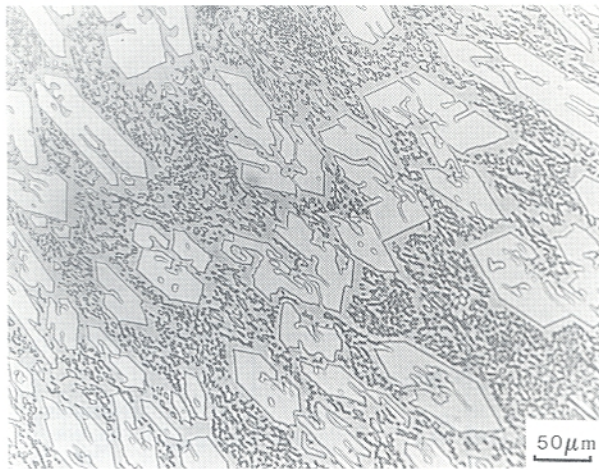
No.	C	Cr	Mn	Si
M1	4.50	37.9	1.41	0.86
S1	3.90	33.6	0.00	0.20
S2	4.48	34.4	0.00	3.60
S3	3.60	31.2	0.00	6.90

Table 2 Mean concentrations (at-%) of phases found in various alloys. The concentrations reported for regions near primary  $M_7C_3$  are probably unreliable due to some overlap of information from both primary  $M_7C_3$  and  $\gamma$

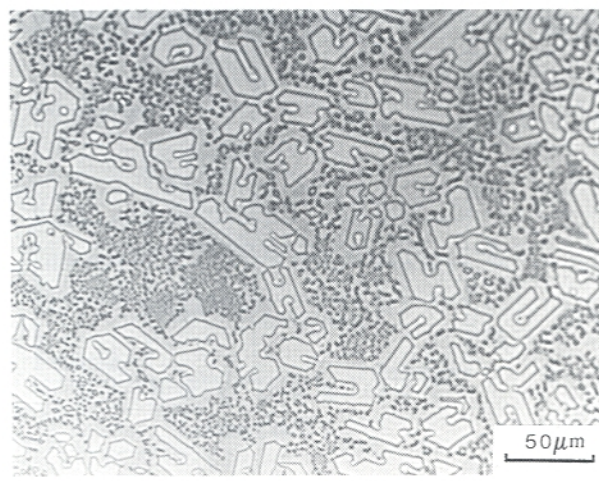
	Primary $M_7C_3$	Near Primary $M_7C_3$	$\gamma$	Eutectic $M_7C_3$
M1				
Cr	44.9	14.7	15.0	42.8
Mn	0.9	1.9	1.7	0.1
Si	0.1	1.9	1.7	0.1
C	30	5.8	5.8	30
S1				
Cr	50.8	22.9	20.9	
Si	0.1	0.2	0.2	
C	30	2.4	2.4	
S2				
Cr	48.9	11.5	11.5	
Si	0.2	12.2	12.4	
C	30	3.7	3.7	
S3				
Cr	50.5	10.9	14.3	
Si	0.1	19.2	17.2	
C	30	6.3	6.3	

Table 3 Specific wear resistance data

Alloy	R, $m^2/(kg \ 10^{-11})$
S1	0.860
S2	0.014
S3	0.004

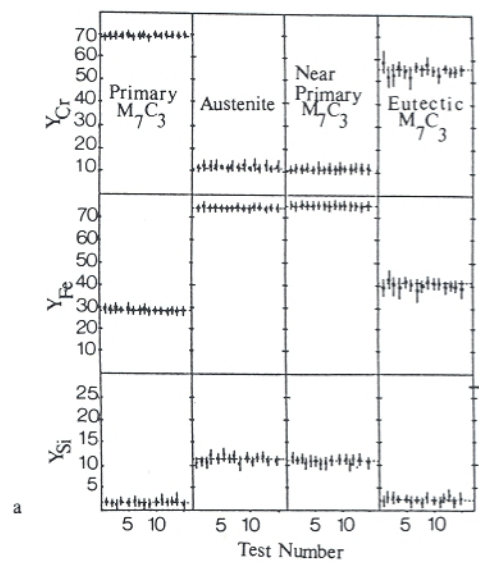


a

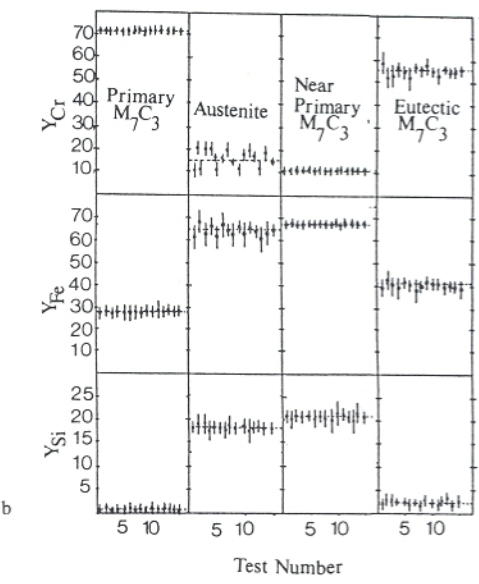


b

Fig. 3 Optical micrographs of high-silicon cast alloys: (a) S2, (b) S3



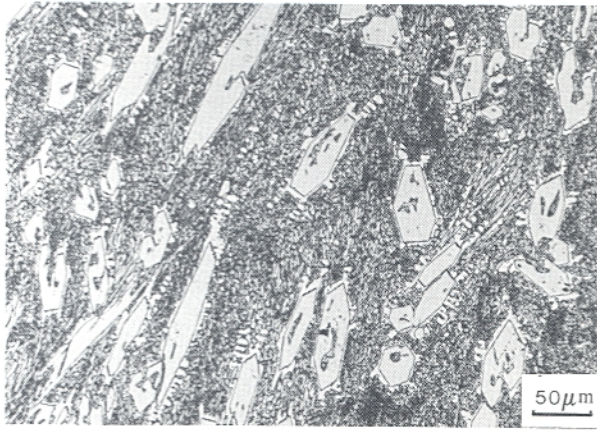
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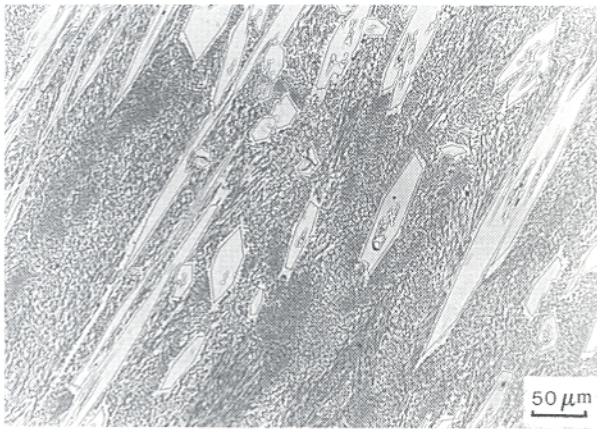
b

Fig. 4 Microanalytical data obtained using transmission and scanning electron microscopy: (a) alloy S2, (b) alloy S3



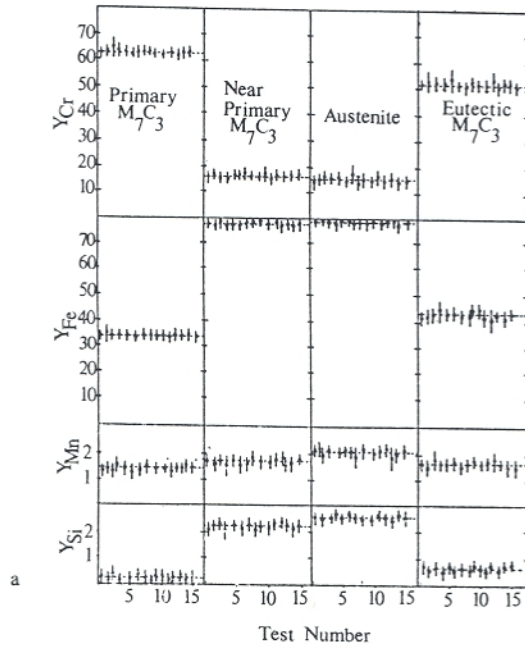


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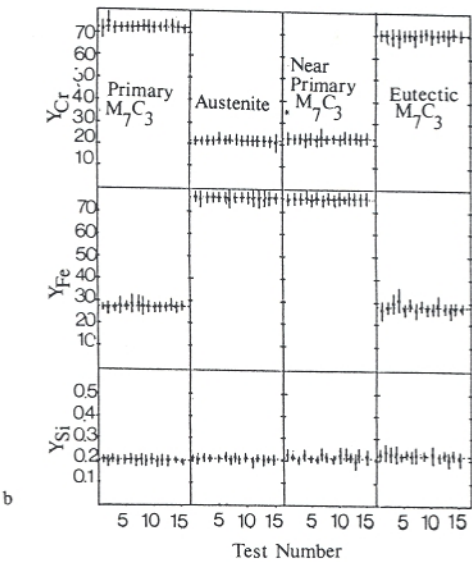


b

Fig. 1 Optical micrographs showing large primary  $M_7C_3$  carbides in a eutectic mixture of  $\gamma + M_7C_3$ : (a) top, undiluted layer of alloy M1 deposited by manual metal arc welding, (b) alloy S1 argon arc melted in a water-cooled copper mould



a



b

Fig. 2 Results of microanalysis experiments carried out in a transmission electron microscope. Continuous lines refer to average composition; concentrations  $y_i$  are in at-% and ignore the presence of carbon: (a) alloy M1, (b) alloy S1