DEMIR, O. and ERIC, R. H. The reduction of chromite in Fe–Cr–C–Si alloys. *INFACON 6. Proceedings of the 6th International Ferroalloys Congress, Cape Town.* Volume 1. Johannesburg, SAIMM, 1992. pp. 99–105.

The Reduction of Chromite in Fe–Cr–C–Si Alloys

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The kinetics of the reduction of LG-6 chromite spinels in iron–chromium–carbon–silicon alloys were studied at 1600 °C under an inert argon atmosphere. The rotating-cylinder technique was used, and the rotational speed of the chromite spinel cylinder ranged from 100 to 800 r/min. The melt consisted of 10 and 20 per cent chromium, the carbon content varied from 2,8 per cent to saturation, and the silicon content varied from zero to 2 per cent. The initial chromium-to-iron ratios of the melts varied between 0,11 and 0,26.

The reduction of the chromite spinel was analysed in terms of the percentage decrease in the chromium content of the spinel cylinder. The stirring rate was effective to a certain extent at carbon contents below the saturation level. At rotational speeds in excess of about 600 r/min, the reduction rate remained almost constant. When the iron–carbon alloy was saturated with carbon, the effect of rotational speed was even less on the reduction process. Having the same rotational speeds for both the cases, carbon saturation itself increased the reduction rate about 1,5 times. The addition of chromium to the carbon-saturated iron–carbon alloy had a positive effect on the reduction rate. An increase in the chromium content of the alloy from 10 to 20 per cent increased the reaction rate considerably during the initial stages, resulting in about the same amount of reduction at the end of 4 hours. The addition of silicon increased the reaction rate drastically. In the presence of silicon, the rotation was effective, and variations in the chromium content from 10 to 20 per cent and in the carbon content from 2,85 per cent to saturation level had no effect.

Further studies of the reacted samples and alloys are being undertaken in an effort to establish a mechanism for the reduction.

Introduction

During the refining of ferrochromium alloys and in the production of stainless steels, solid chromite may be added both as a source of chromium and as a decarburizing agent. Knowledge of the mechanism and kinetics of the reduction of chromite in iron–chromium–carbon alloys is therefore extremely important from a practical point of view.

In a recent study[1] of the reduction of chromite in iron–chromium–carbon alloys, some important conclusions were reached regarding this mechanism. The investigation was carried out by the rotating-cylinder technique in the temperature range 1400 to 1680 °C in an inert argon atmosphere. The chromite cylinders were immersed in liquid iron–chromium–carbon alloys, and were rotated at various speeds about their vertical axes for 4 hours. It was found that, as the stirring of the melt increases, decarburization increases. This effect was found to be more pronounced in the early stages of reduction. An increase in the rotational speed beyond 400 r/min had no appreciable effect on the decarburization. During the initial stages of reaction (approximately 30 minutes), the rate was probably determined by the liquid-phase mass transfer of oxygen at the oxide–melt interface, and stirring by boiling of carbon monoxide was effective. Thereafter the solid chromite surface was covered by a slowly growing layer of iron–chromium carbides – (mainly $(Fe, Cr)_7C_3$) – which slowed the reduction considerably. Further reduction was probably by diffusion of carbon through this solid product layer.

Sevinc and Elliot[2] used the rotating-cylinder method to study the reduction of solid chromium oxide by liquid iron–chromium–carbon alloys. They concluded that the rate of the reaction is affected strongly by the stirring rate and temperature. In the early stages of a run, because of the high degree of turbulence caused by the gas bubbles, the reaction was not influenced by the rotational speed of the solid oxide cylinders, but rotation became important at low rates of evolution of carbon monoxide. However, the carbon content was never more than 1 per cent in that study.

Fruehan[3] studied the rate of reaction of Cr_2O_3 with carbon and with carbon dissolved in liquid-iron alloys, and the decarburization of iron–chromium–carbon alloys in mixtures of argon and oxygen gas. In a few experiments, rotating chromium oxide cylinders were tested in iron–carbon melts at 1550 °C. It was observed that the reaction rate increased as the rotational speed of the cylinder increased, indicating that the rate of reaction is controlled by liquid-phase mass transfer, and not by a surface chemical reaction.

Barmin *et al.*[4] conducted a similar study on the rate of reduction of solid chromium oxide by carbon dissolved in soft iron. They found a similar effect of stirring. An increase in the rotational speed beyond 570 r/min towards 950 r/min had no appreciable effect on the reduction process. They concluded that, with an increase in the rotational speed to 570 r/min, the rate-limiting step in the reaction mechanism changes from mass transfer in the liquid phase to chemical reaction.

Barmin *et al.*[4] found that, for samples with a carbon content of higher than 2 per cent, there was no variation in the reduction rate with varying rotational speeds.

The reduction reactions of chromite $FeO.Cr_2O_3$ or $FeCr_2O_4$ can be ideally formulated as

$$FeCr_2O_{4(s)} + C = Fe_{(l)} + 2Cr_{(l)} + 4CO_{(g)}. \qquad [1]$$

There are three phases in the above equation, and it is therefore insufficient to represent the reduction mechanism. The reaction must consist of a series of steps involving chemical reaction and the transport of reactants and products to and from reaction sites.

The present investigation, concerning the general class of reactions between solid oxide, molten metal, and gas, is directed at the establishment and understanding of the mechanism of reduction avoiding the formation of a solid carbide layer. The effects of the addition of silicon and carbon saturation of the melt were considered, and liquid alloys with less chromium, approaching the composition of stainless steel, were used. Ongoing experimental work, including scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray-diffraction and metallographic analyses, is being carried out on the reacted samples to elucidate the effect of each parameter, and to establish the reaction mechanism.

Equipment and Experimental Procedure

Details of the equipment and experimental procedure are outlined below.

Reduction Furnace

The reduction furnace (Figure 1) is a stable 50 kW, 3 kHz induction unit. The furnace chamber consists of a fused-silica tube 500 mm long, with an external diameter of 120 mm and an internal diameter of 114 mm. The lower end of the tube is closed. The top end is closed by a water-cooled brass plate, with an O-ring between the silica tube and brass plate to ensure gas-tightness. A dense graphite crucible was used as the heating element. Another crucible, of graphite or alumina with a length of 68 mm and an internal diameter of 47 mm, containing the charged melt *was placed* within the heating element. A graphite cover was used as a radiation shield. The space between the heating element and the silica tube, as well as the bottom part of the silica tube, was packed with lampblack for insulation. Care was taken to ensure a uniform temperature within the alumina crucible.

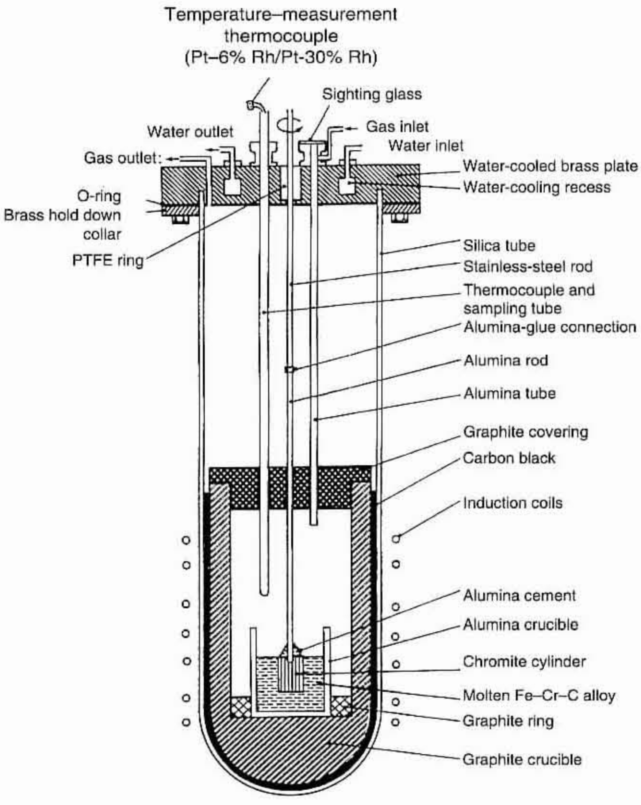

FIGURE 1. Schematic representation of the reduction furnace

A type B (Pt–6%/Pt–30% Rh) thermocouple was used for temperature measurements. Because of the stability of the induction furnace, it was seldom necessary to make adjustments in the power setting after the initial adjustment had been made. Temperature-profile tests showed that the temperature of the system during a run did not vary by more than about 10 °C from the initial setting, and the temperature in the region from the bottom of the crucible to the top varied by no more than 2 °C. The furnace assembly was gas-tight and, during the experiments, the pressure in the system was slightly above the ambient atmospheric pressure. An inert argon atmosphere was maintained within the furnace chamber. The flowrate of the gas, which was measured with a capillary flowmeter, was 2100 cm^3/min. Before it entered the system, the gas was dried in a drying chamber filled with anhydrous $Mg(ClO_4)_2$ as a desiccant, as well as silica gel. The gas then entered a furnace containing copper chips, which were maintained at 500 °C, for deoxidation. The gas was introduced into the reaction chamber through a junction to an alumina inlet tube with an internal diameter of 5 mm. The lower end of the inlet tube was located 30 mm above the surface of the melt, while the the top end was closed by a sighting glass through which the interior of the furnace could be observed.

The chromite spinel cylinder was rotated at a controlled speed about its long axis by a drive system. The various rotational speeds were obtained from a calibrated variable-speed electric motor, which was connected to the stainless-steel rod by means of a flexible attachment. The rotational speed was checked from readings of a hand-tachometer attached to the shaft of the electric motor. The stainless-steel rod could be raised or lowered by about 6 cm so that the chromite spinel cylinder could be removed from or immersed in the liquid bath. Samples were taken through the sampling hole with a fused-silica tube, one end of which was fitted to an aspirator bulb. The sampling hole was otherwise kept closed with the alumina thermocouple-protection tube.

Production of Chromite Spinel Cylinders

The chromite spinel cylinders were prepared from tabled and pulverized LG-6 chromite powders. Table I lists the screen analyses of the chromite fines, and Table II shows the chemical compositions. After pulverization, the powder was formed into dry cylinders, without binders, by uniaxial pressing in a steel mould under a pressure of 10 t. This was followed by sintering under argon, at a flowrate of 2100 cm^3/min, at 1400 °C for 3 hours in the reduction furnace.

TABLE I
SCREEN ANALYSIS OF PULVERIZED CHROMITE

Sieve size		% retained	Cum. % retained	Cum. % passing
Tyler mesh	μm			
65	208	0,000	0,000	100,000
100	147	0,250	0,250	99,750
150	104	4,065	4,315	95,685
200	74	10,463	14,778	85,222
270	53	12,058	26,836	73,134
400	38	12,634	39,470	60,530
- 400	—	60,530	100,000	0,000

TABLE II
ANALYSIS OF THE AS-RECEIVED, PULVERIZED, AND SINTERED CHROMITE (IN PERCENTAGES BY MASS)

Chromite	MgO	Al_2O_3	SiO_2	CaO	TiO_2	Cr_2O_3	Fe_2O_3	FeO
As–received	10,38	13,41	<0,60	<0,20	0,403	46,25	28,09	17,9
Pulverized	10,59	14,57	<0,60	<0,20	0,438	46,18	26,06	18,6
Sintered	10,59	14,37	<0,60	<0,20	0,429	46,11	28,34	18,6

Compositions of Master Alloys

The furnace charges were pre-melted iron–carbon and iron–chromium–carbon alloys, with the necessary additions of spectroscopic-grade graphite and laboratory-reagent-grade iron, chromium, and silicon powders. Three master alloys were prepared from mixed electrolytic iron, electrolytic chromium, and graphite. The mixed material was melted in a vacuum induction furnace under an inert argon atmosphere. Chemical analyses of the master alloys are given in Table III.

Procedure

The rotating chromite cylinders were submerged in a liquid bath of iron–chromium–carbon–silicon alloy contained in a graphite or alumina crucible. The course of the reduction was followed by chemical analyses of the melt, which were used in the construction of chromium-metallization curves.

TABLE III
ANALYSES OF THE MASTER ALLOYS
(PERCENTAGES BY MASS)

Alloy	C	Cr	Fe
A1	4	0	96
A2	3	10	87
A3	5	20	75

In a typical experiment, about 350 g of an iron–chromium–carbon-silicon alloy was charged into the crucible while the spinel cylinder was withdrawn so that the lower tip of the cylinder would be 30 mm above the surface of the liquid metal when the charge had melted. The reaction furnace was then sealed and filled with argon gas. As the furnace temperature was raised gradually until the desired level was reached, the chromite cylinder became preheated. After the charge had melted, the thermocouple was immersed in the liquid alloy and kept there until the system reached a steady temperature; then the initial sample for chemical analyses was taken. The chromite cylinder was then immersed in the melt until its lower end was 10 mm above the bottom of the crucible, and rotated at the desired speed for a specified period of time. The length and diameter of the cylinders were 17 mm and 15,6 mm respectively, and the whole cylinder was exposed to the molten alloy except the top surface, which was coated with alumina cement. Samples were taken at predetermined time intervals of 15, 30, 60, 120, 180, and 240 minutes. The argon flow was increased during the sampling operation to prevent air from entering the furnace chamber.

On completion of a run, the cylinder was raised from the melt while argon flushing was continued until the system had cooled to room temperature. The metal samples were analysed for carbon, chromium, silicon, and iron.

Chemical Analyses

The chemical analyses, as given by the Analytical Science Division of Mintek, are as follows.

(1) Chromium and iron were determined by atomic-emission spectroscopy using an inductively coupled plasma (ICP), with an accuracy of better than 1 per cent.

(2) Carbon was determined by the Leco technique, with an accuracy of 0,02 to 1 per cent.

(3) Silicon was determined by a spectroscopic ICP technique, with an accuracy range of 4 to 20 per cent. The higher accuracies were obtained at higher concentrations of silicon.

Results and Discussion

The three main variables considered were the effect of stirring, the composition of the liquid alloy, and time. The results were analysed with reference to the degree of chromium reduction into the metal phase from the chromite cylinder. This quantity, Cr(R), is defined as

$$Cr(R) = (Cr_f – Cr_i) \cdot M_{alloy}/Cr_{sc},$$

where Cr_f and Cr_i are the final and initial chromium concentrations, M_{alloy} is the mass of the melt, and Cr_{sc} is the mass of chromium in the spinel cylinder.

The change in the silicon content of the alloy as the reduction proceeds is defined as mass % Si (t/t_O), which is simply the mass of silicon at time t divided by the initial mass of silicon in the liquid metal.

The Effect of Rotation

The effect of the rotational speed of the chromite cylinder on the reduction process in iron–carbon alloys was tested in two types of alloys: one contained 4,7 per cent carbon, and the other was carbon saturated. The alloys were tested separately at stirring rates of 100, 200, 400, 600, and 800 r/min, and at a temperature of 1600 °C.

Because of the difficulty encountered in the determination of the decarburization rates in the carbon-saturated systems (carbon was continuously fed into the metal bath), the chromium reduced from the oxide cylinder was taken as a basis for the measurement of the reduction rate.

When the carbon content was 4,7 per cent, the rotational speed was effective to a certain extent, as shown in Figure 2. An increase in the rotational speed from 100 to 600 r/min had a very slight effect (about 0,5 per cent) on the percentage reduction of chromium into the metal phase from the spinel cylinder. Rotational speeds greater than 600 r/min had no appreciable effect on the reduction, and the curves obtained for rotational speeds of 600 r/min and 800 r/min more or less merged into one another.

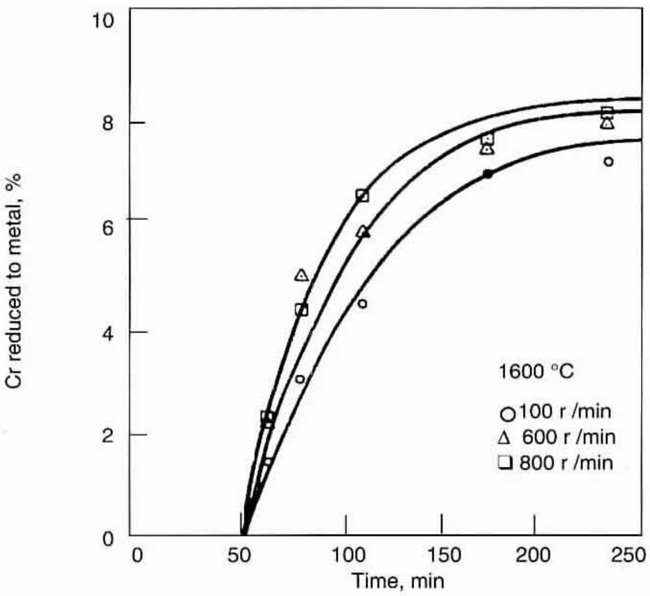

FIGURE 2. Effect of rotation on the reduction of chromite in an Fe–C (4,7% C) alloy

When the iron–carbon alloy was saturated with carbon by use of a graphite crucible, the effect of rotational speed was even less on the reduction process. The experiments conducted at 400, 600, and 800 r/min produced approximately the same results, and the curves of Cr(R) versus time plotted for each case almost merged into one another (Figure 3).

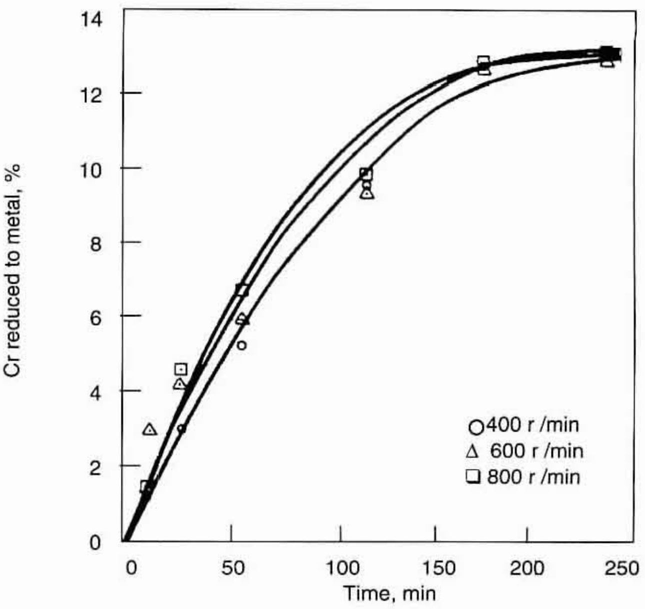

FIGURE 3. Effect of rotation on the reduction of chromite in a carbon-saturated Fe–C alloy

The effect of rotation on the reduction of chromite in carbon-saturated, silicon-containing iron–chromium alloys was investigated in a series of experiments with an alloy containing 20 per cent chromium and 0,5 per cent silicon. The temperature was 1600 °C, and the rotational speed varied from 200 to 800 r/min (Figure 4). In the early part of the reaction (up to about 40 minutes), the difference between the extent of reaction for each particular stirring rate was less pronounced than in the later stages, especially at rotational speeds of less than 600 r/min.

It appears that, during the reduction of chromite in Fe–(Cr)–C alloys in the absence of silicon, a kinetic barrier artificially stops the reaction at very low reduction levels.

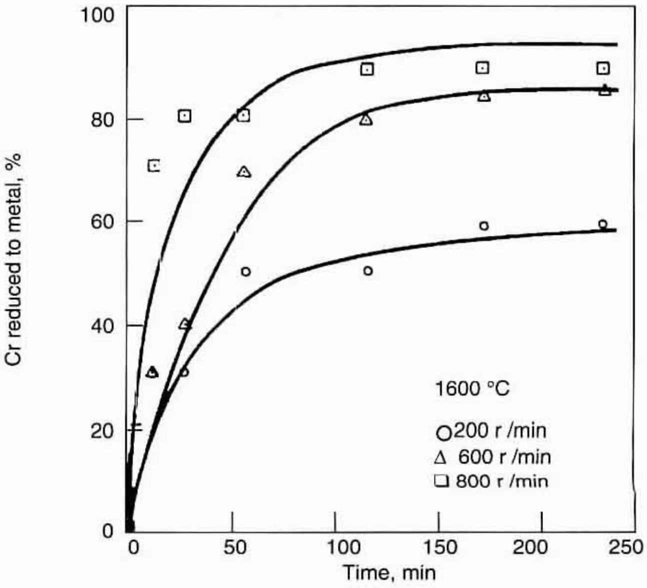

FIGURE 4. Effect of rotation on the reduction of chromite in a carbon-saturated iron alloy containing 20 per cent chromium and 0,5 per cent silicon

This effect is explained later. This phenomenon probably causes a switch in the reaction mechanism at the early stages from a process controlled by mass transport to a chemical reaction where stirring has no effect. This is in accordance with the results of Eric and Uslu[1]. However, it seems that, in the presence of silicon, such a kinetic barrier is either non-existent or destroyed by silicon, as evidenced by an increase in the rate and extent of chromite reduction with an increase in stirring rate.

The Effect of Composition

To investigate the effect of composition on the reduction of chromite, each species was considered separately. The following five groups of compositions were chosen:

1. Fe–C alloys containing 4,7 per cent carbon and carbon-saturated Fe-C alloys
2. Fe–Cr–C alloys containing 10 and 20 per cent chromium, with the carbon levels at saturation and under saturation for each chromium concentration
3. Fe–Cr–C–Si carbon-saturated and unsaturated alloys containing 10 and 20 per cent chromium
4. Fe–Si alloys containing 0,5 and 1 per cent silicon
5. Fe–Cr–Si alloys containing 10 and 20 per cent chromium.

Figure 5 shows the effect of the carbon content of iron–carbon melts on the reduction rate at 600 r/min. The final degree of reduction obtained with the saturated melt is 1,5 times greater than that with the melt containing 4,7 per cent carbon. In the early part of each run, up to about 30 minutes of reaction time, the reduction rate for both the carbon concentrations was approximately the same. In the carbon-saturated case, the carbon activity was always unity. In the case of an unsaturated alloy, once the carbon activity had reached a critical value, the reduction rate decreased.

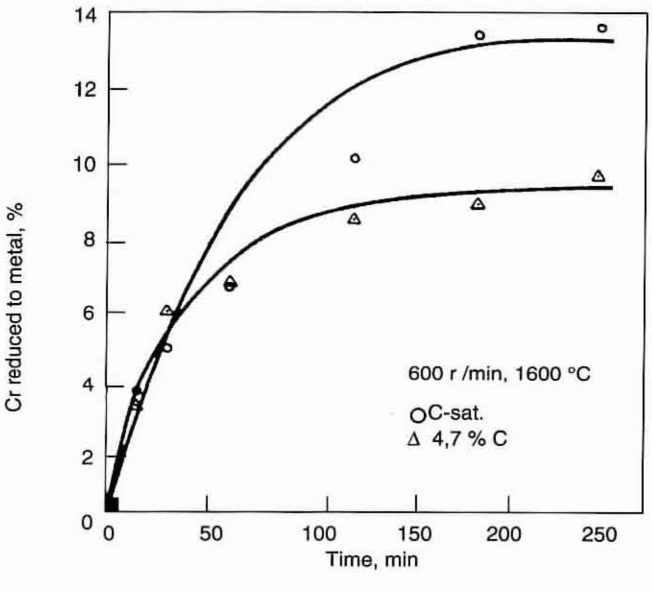

FIGURE 5. Effect of carbon content on the reduction of chromite in an Fe–C alloy

Figure 6 shows the effect of chromium content on the reduction rate of chromite in a carbon-saturated alloy. The reduction rate increased as the chromium concentration in the melt increased. This may appear contradictory to the chromium–activity relationship in the system, but this could be explained by the higher saturated-carbon content of the higher chromium-containing alloy. This is further confirmed by the results of Eric and Uslu[1].

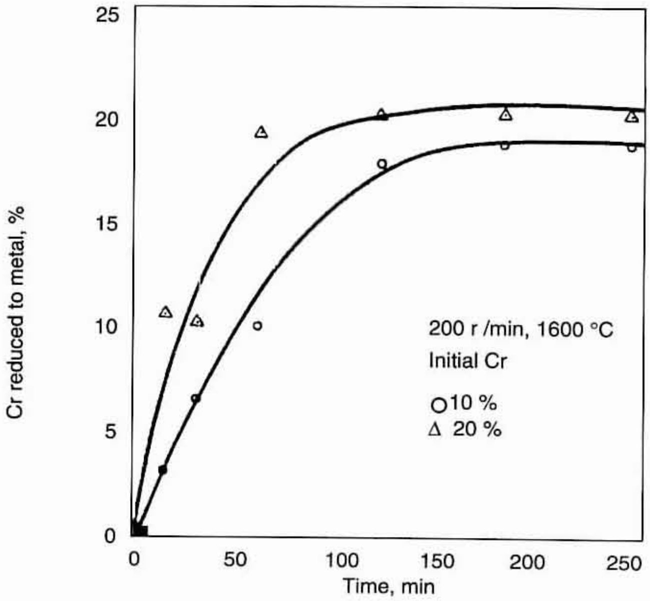

FIGURE 6. Effect of initial chromium content on the reduction rate of a carbon-saturated Fe–Cr alloy

In their study, although the iron–chromium–carbon melt was not saturated with respect to carbon, the ratio of the initial to the final carbon activity in the system first increased with an increase in the chromium content, peaking around a chromium content of 50 per cent, and

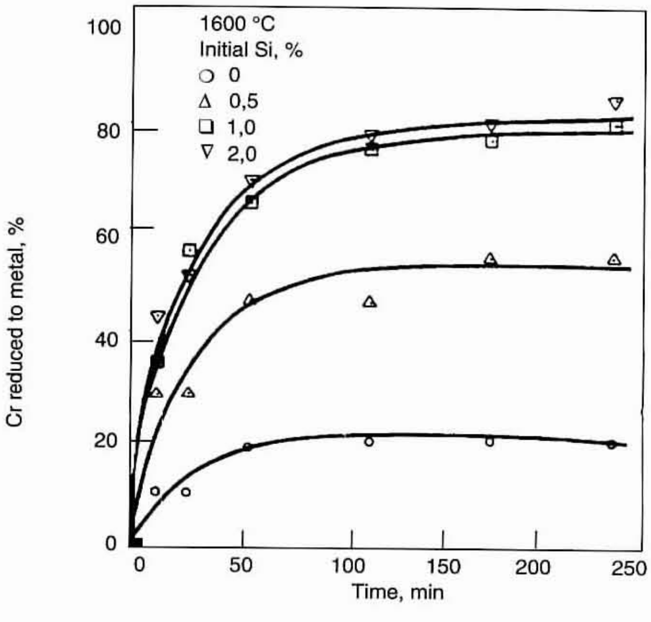

FIGURE 7. Effect of silicon on the reduction of chromite in a carbon-saturated iron alloy containing 20 per cent chromium

then decreasing.

The effect of silicon on the reduction of chromite in a 20 per cent chromium, carbon-saturated iron–chromium–carbon alloy at 200 r /min is shown in Figure 7. As the amount of silicon was increased from zero to 1 per cent, a vast change occurred in the reduction. Increases in the silicon concentration from 1 to 2 per cent did not appreciably affect the reduction.

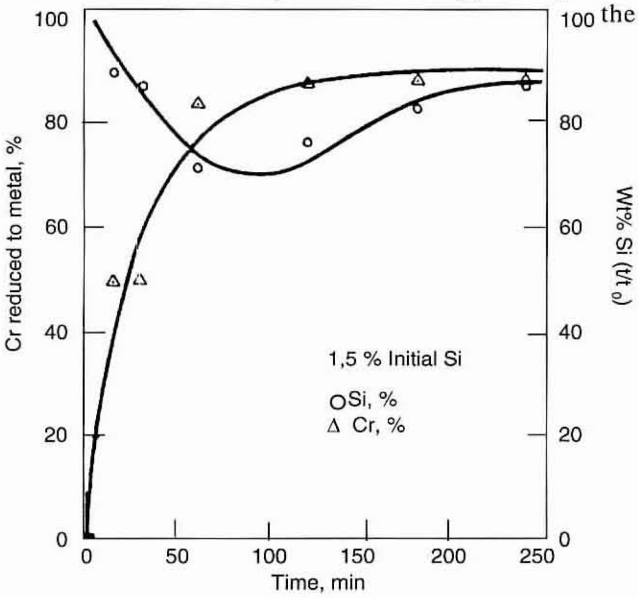

FIGURE 8. Change in the silicon content of a carbon-saturated iron alloy containing 10 per cent chromium with the reduction of chromite

Figure 8 shows the changes in the silicon and chromium concentrations of a carbon-saturated 10 per cent chromium iron–chromium–carbon alloy as a function of time, as the reaction proceeds. The fluctuation in the silicon concentration might be explained as follows.

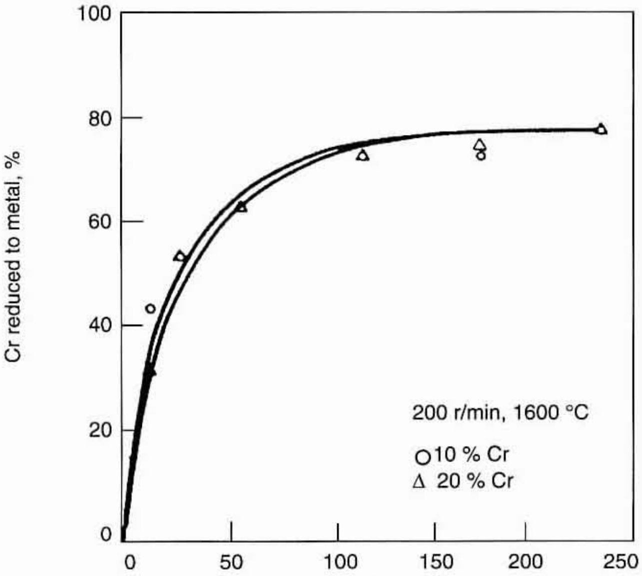

FIGURE 9. Effect, on the reduction of chromite, of the initial chromium content of a carbon-saturated Fe–Cr alloy containing 1 per cent silicon

At the beginning of the reaction, silicon in the alloy started to reduce the oxides in the cylinder, and SiO_2, formed as a product of this reduction process, entered the slag phase. After about 100 minutes, probably because of the high carbon concentration and hence the unit carbon activity in the melt, silicon in the slag phase started to be reduced back into the metal phase, causing an increase in the silicon concentration. This proposed mechanism requires further investigation.

Figure 9 shows the effect of the initial chromium content of the 1 per cent silicon, carbon-saturated iron–chromium–carbon alloy on the reduction at 200 r/min. In the presence of silicon, the change in the chromium content of the alloy had no effect on the reduction rate.

Figure 10 shows the effect of carbon content on the reduction of chromite in a 10 per cent chromium, 1 per cent silicon iron–chromium–carbon alloy. Again, the change in the carbon content of the melt did not affect the rate of reduction.

Figures 9 and 10 indicate the dominant role played by silicon in contrast to carbon in the reduction of chromite.

In the systems containing no silicon, the reduction rate was considerably faster at the early part of the process; then it slowed down and finally stopped. In the carbon-saturation case (in the absence of silicon), because its activity remains at unity, it enhanced the reduction of chromite considerably. Even in the systems with 4,7 per cent carbon (again in the absence of silicon), the final carbon content of the melt after the reduction had stopped was far above the thermodynamically expected carbon values. This enforces the suggestion that there is an artificial equilibrium, possibly due to a kinetic barrier, for the system to reach a stable thermodynamic equilibrium. It is apparent that (as deduced from Figures 9 and 10), in the presence of silicon, such a kinetic barrier was overcome, resulting in high reduction rates and extent. Further experimental work, metallographic analysis, SEM, and EDS are being carried out to investigate this phenomenon.

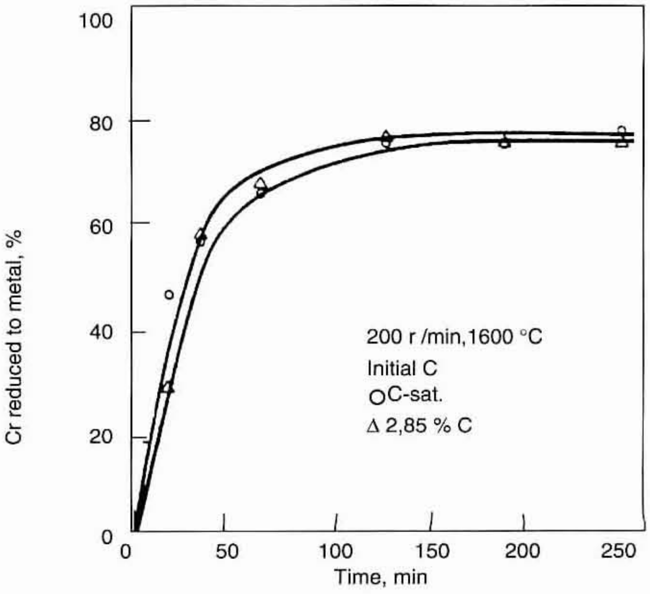

FIGURE 10. Effect of carbon content on the reduction of chromite in an Fe–C alloy containing 10 per cent chromium and 1 per cent silicon

Conclusion

The investigation showed that the rotational speed had no significant effect on the reduction rate in the systems with iron–carbon alloys. In the presence of silicon, however, the stirring rate was effective in increasing the reduction rate and extent.

The carbon saturation of the iron–carbon melts resulted in a reduction 1,5 times higher than that obtained with a 4,7 per cent carbon iron-carbon alloy. An increase in the chromium content of the carbon-saturated iron–chromium–carbon alloy from 10 to 20 per cent also increased the reduction, but not significantly. The addition of silicon improved the reduction rate drastically, causing about 80 per cent of the chromium to be reduced from the spinel. In the presence of silicon, the variations in the chromium content in the range 10 to 20 per cent and in the carbon content from 2,85 per cent to saturation had no appreciable effect on the reduction.

In the systems containing Fe–(Cr)–C alloys, the maximum reduction obtained was about 20 per cent. After the reduction had stopped, it was observed that the amount of carbon in the melt was much higher than the expected thermodynamic equilibrium values. This might be due to a kinetic barrier resulting in an artificial equilibrium. Further experimental work, metallographic analysis, SEM, and EDS are being carried out to explain this phenomenon and to establish a reduction mechanism for the systems under consideration.

From a practical point of view, it is apparent that, when solid chromite is added to an iron–(chromium)–carbon bath, the recovery of chromium units into the melt and decarburization are extremely limited due to poor reaction rates and extent. However, if silicon is present in the melt, the chromium recovery improves drastically and a certain silicon removal is achieved.

Acknowledgments

The authors thank Mintek and the Ferro Alloys Producers' Association of South Africa for co-sponsoring this work. This paper is published by permission of Mintek.

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