

KINETIC INVESTIGATION OF CHROMITE REDUCTION IN A HIGH-CARBON FERROCHROMIUM ALLOY BATH

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ABSTRACT

Kinetic measurements on the reduction of chromite ore from a lime-silicate slag by carbon dissolved in a high-carbon ferrochromium alloy bath were conducted at temperatures between 1500 and 1650°C. The reaction kinetics were followed by periodic sampling and chemical analysis of the reduced products. The effect of adding powdered graphite to the refining slag was assessed by the extent of reduction obtained and carbon pick-up in the alloy. The results showed that for chromium oxide saturated slags, the rate of oxidation of carbon is independent of the oxide content. Carbon diffusion from the bulk alloy to the alloy/slag interface is envisaged to be rate controlling in the initial instance. Later, the reaction appears to exhibit mixed control kinetics. However, when powdered graphite is added to the slag surface, less dissolved carbon participates in the reduction process.

INTRODUCTION

The kinetics of chromite ore reduction with carbon either in the solid or liquid state have been previously examined [1-5]. Various reaction mechanisms have been proposed on the basis of the results obtained. However, most of the reported work has not adequately dealt with the morphology of the reduction products in as much as it relates to the reaction mechanism. Furthermore, carbon saturated melts of either iron or ferrochromium have been used in a number of investigations [5,6]. This has only provided limited information on the kinetics of reduction. For example, in an environment of constantly decreasing carbon activity which is also under thermodynamic constraints, how much carbon can be oxidized under a given set of conditions.

This paper presents the results of investigations on the reduction of fluxed chromite ore by carbon dissolved in a high-carbon ferrochromium (HCF₂Cr) alloy, and also on the effect of adding powdered graphite to the slag. The study has been prompted by the need to utilize chromite fines in the partial oxidation of the carbon from a molten HCF₂Cr alloy bath prepared by remelting alloy fines.

MATERIALS AND EXPERIMENTAL PROCEDURE

Materials

The materials used in this investigation were obtained from a local ferroalloy smelter, and the chemical analysis of HCFeCr is given in Table 1 and that of chromite ore and quartz in Table 2. The HCFeCr and chromite were screened to -1 mm and -5 mm size fractions, respectively. The quartz was crushed and screened to the same size as the chromite ore. Commercial lime was used in each case to adjust slag basicity to the required value.

TABLE 1: Chemical analysis of high-carbon ferrochromium (wt%)

Cr	Fe	C	Si	S	Ti	V
64.78	26.23	6.90	1.42	0.04	0.07	0.014

TABLE 2: Chemical analysis of chromite ore and quartz (wt%)

	Chromite Ore	Quartz
Cr ₂ O ₃	50.08	-
Fe ₂ O ₃	14.82	0.44
SiO ₂	4.71	98.34
Al ₂ O ₃	10.00	-
CaO	0.30	-
MgO	17.00	-

Experimental Methods

Two sets of experiments, series A and B were devised to investigate the reduction behaviour of chromite ore in slag by carbon dissolved in HCFeCr alloy.

Series A

The effect of temperature and graphite addition was investigated using a 30kW, 4.2kHz rated induction furnace with a capacity of about 8kg. The raw materials which consisted of chromite ore, HCFeCr alloy, quartz and commercial grade lime were combined in proportions given in Table 3. The carbon content of the alloy at the end of the experiment was expected to fall below 6%. In order to achieve the desired objective, assuming 80% chromium oxide and 99% iron oxide reduction, the amount of chromite required was estimated to be 5.6% of the weight of the HCFeCr alloy. About 5kg of the alloy including a 450 ± 20 g starter block of ferrochromium were remelted in an alumina-magnesia lined induction heated crucible. At melt out, chromite ore fines blended with a lime - quartz flux to give a slag basicity of 1.2 was added to the surface of the molten alloy. The flux took 2-5 minutes to melt completely depending on the temperature of the

alloy bath (see Table 3). The time at which the flux was added was taken as zero time for the experiment.

TABLE 3: Experimental conditions for Series A

T (°C)	HCFcCr (g)	Cr ₂ O ₃ (%)	Quartz (%)	Lime (%)
1500	5 000	10	40	50
1600	5 000	10	40	50
1650	5 000	10	40	50

In some experiments, graphite powder amounting to 5% of slag weight was added to the liquid slag. Periodically, slag was sampled using a flattened piece of iron made into a spoon. Alloy samples were collected using Leco carbon analysis instrument crucibles adapted on steel rods. The alloy samples were then analyzed for Cr, Fe and other minor elements using a Siemens SRS 300 X-ray spectrometer. Carbon analysis was carried out using the Leco instrument. The slag samples were each split into two parts: for Cr₂O₃, FeO, MgO, SiO₂ and Al₂O₃ oxide analysis by X-ray fluorescence spectrometry, and the other part retained for optical microstructural observations. The total chromium content of the slag was calculated to Cr₂O₃, and divalent chromium was not determined.

The temperature was measured with a Pt-13%Rh/Pt-6%Rh sheathed thermocouple to within $\pm 10^\circ\text{C}$.

Series B Experiments

The effects of an inert atmosphere and the concentration of chromium oxide in the slag on chromite ore reduction were investigated in a 70mm deep alumina crucible with an internal diameter of 40mm. The experimental setup is illustrated in Figure 1 and the conditions of experimentation are summarized in Table 4. Resistive heating from the graphite was used to melt the HCFcCr alloy, after which a premelted slag mixed with chromite ore was added. Temperature was controlled to within $\pm 2^\circ\text{C}$ using a Eurotherm PID regulator. Slag samples were collected periodically and divided into two parts to allow for the determination of:

- (a) total chromium by XRF
- (b) divalent chromium (CrO) by oxidizing Cr²⁺ to Cr³⁺.

TABLE 4. Experimental conditions for Series B

T (°C)	HCFcCr (g)	Cr ₂ O ₃ (%)	Quartz (%)	Lime (%)
1600	146	10	40	50
1600	146	30	25	35

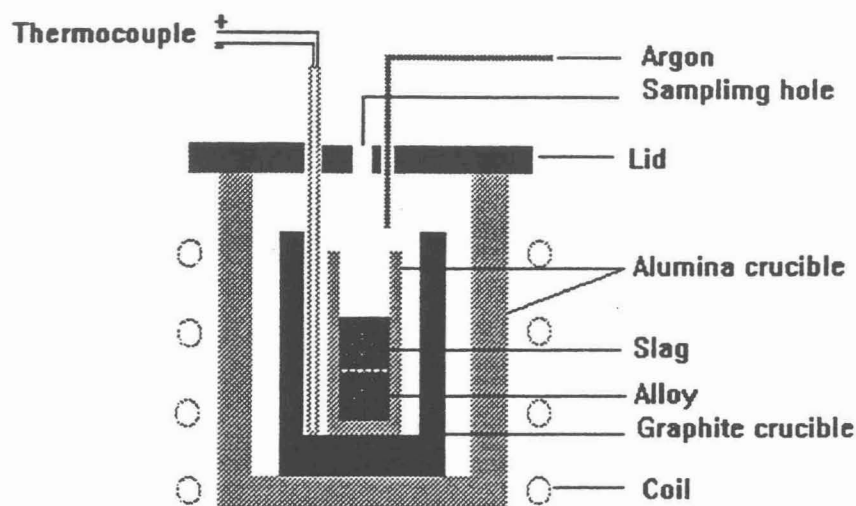


FIGURE 1. Experimental setup for Series B experiments

EXPERIMENTAL RESULTS

In Series A experiments, the reduction rate profiles of chromium oxide at three different temperatures as determined by periodic sampling of slag and its subsequent analysis are presented in Figure 2. The total chromium oxide content of the slag is observed to fall rapidly after 20 minutes before levelling off after 60 minutes, a situation associated with the attainment of equilibrium conditions. The results also show a temperature dependence of the reduction process with equilibrium conditions being attained at a much faster rate as the temperature is increased. The addition of graphite to the slag (Figure 3) reduced the time required to reach equilibrium conditions considerably. However, the general presentation of the reduction profiles remain similar to those shown in Figure 2 at treatment times between 20 - 40 minutes.

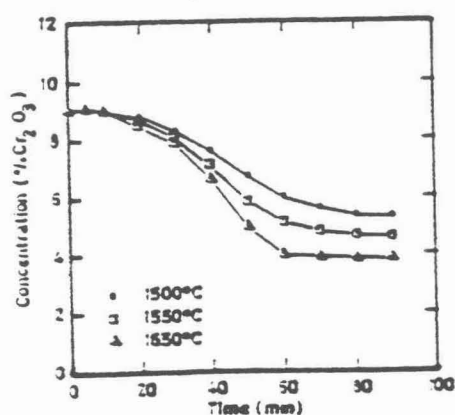


FIG. 2. Temperature dependence of Cr_2O_3 reduction. Series A.

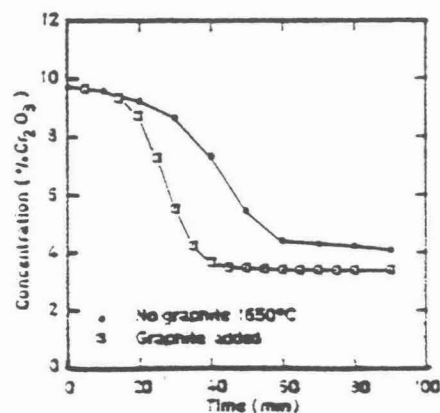


FIG.3. Effect of graphite addition on the kinetics of Cr_2O_3 reduction. Series B.

The variation of carbon in the HCFcCr alloy with time is shown in Figure 4. The upper curve is for a case in which graphite was added, while the lower curve represents a condition with no graphite. The results indicate an increase in the carbon content of the alloy which becomes significant as the treatment time is increased. This means less dissolved carbon is used in the reduction reaction.

For the Series B experiments, the results show (Figure 5) an initial increase in divalent chromium (Cr) which reaches a maximum after 20 minutes before decreasing to attain an almost constant value after 40 minutes. The trivalent chromium {Cr} (or Cr_2O_3) shows a rapid decrease in the first 40 minutes before levelling off as stable conditions are attained. The total chromium (T.Cr) initially shows a slow decrease during the conversion of {Cr} to (Cr). As the rate of reduction of (Cr) increases, (T.Cr) falls rapidly. When the initial Cr_2O_3 content in the slag is raised from 10 to 30% (Figure 6), there is a significant increase in the levels of both (T.Cr) and {Cr} while that of (Cr) increases only marginally.

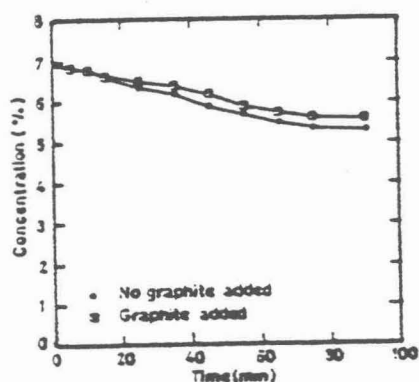


FIG. 4. Variation of carbon concentration in the alloy with reaction time. Series A

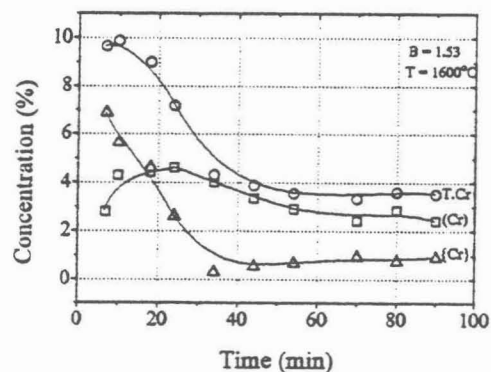


FIG. 5. Chromium distribution in the slag at 10% initial Cr_2O_3 concentration in the slag. Series B.

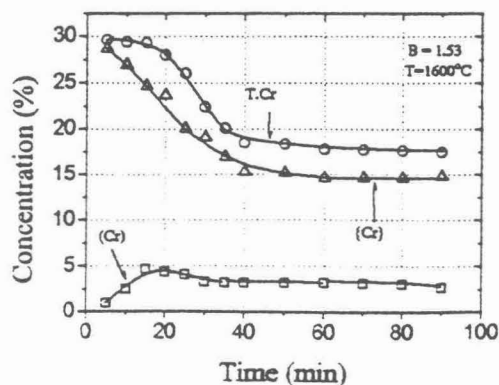


FIG. 6. Chromium distribution in the slag at 30% initial Cr_2O_3 concentration in the slag. Series B.

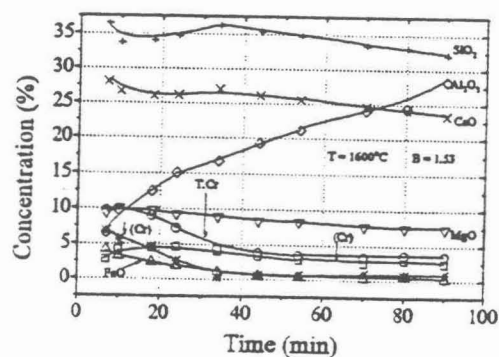
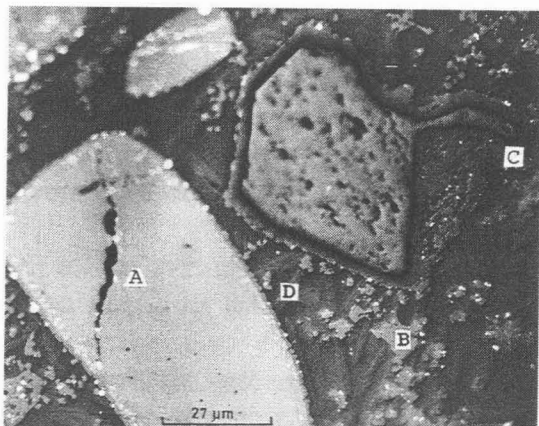
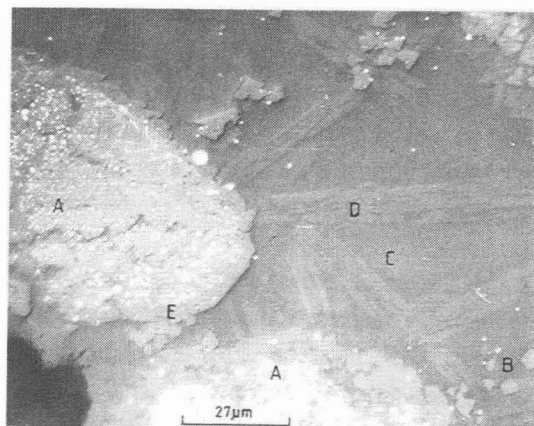


FIG. 7. Variation of total slag analysis with time. Series B.



A - chromite grain C - Slag matrix
B - chromite grain fragments
D - recrystallized slag phase

FIG. 8. Partially reduced chromite ore grains showing evidence of topochemical reduction.



E - reduced and chromium depleted shell (A-D as in FIG. 8)

FIG. 9. Fragmentation and dissolution of an extensively reduced chromite grain. Recrystallized slag phase is evident.

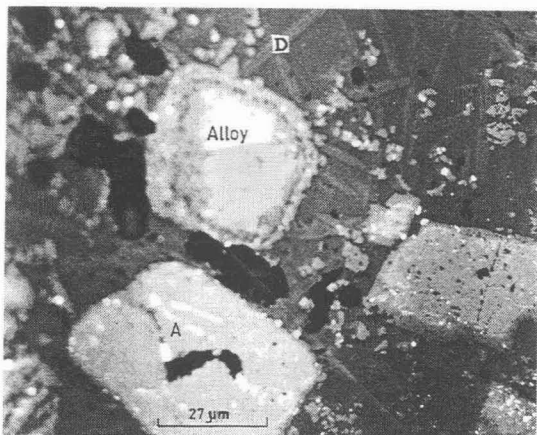


FIG. 10. Coalescence and growth of alloy particles in the interior of the reduced chromite grain.

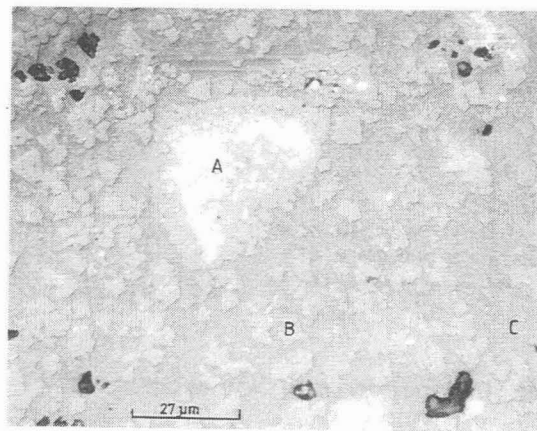


FIG. 11. Final stage of dissolution and assimilation of reduced chromite in the slag phase.

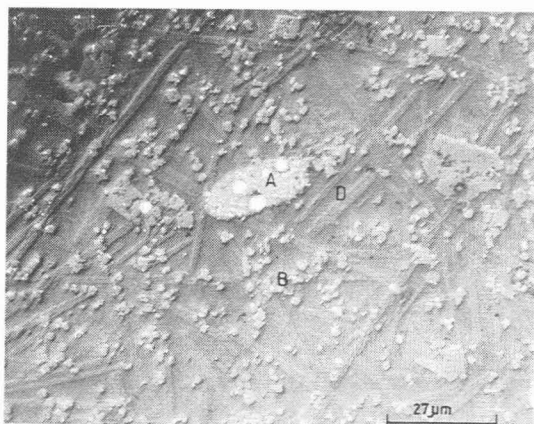


FIG. 12. Reduced chromite particles associated with sites previously occupied by chromite grains.

Analysis of the components of total slag with time is shown in Figure 7. While most slag constituents exhibit trends which seem to be in good agreement with results reported in Figures 2-6, a somewhat rapid increase in the content of Al_2O_3 is observed. This has been associated with erosion-wear of the alumina crucible by possibly excess basic constituents of the lime - silicate slag. Typical final slag analyses for Series A and B experiments are given in Table 5.

TABLE 5. Typical final slag analysis (wt %)

	T.Cr	(CrO)	MgO	Al_2O_3	SiO_2	CaO	FeO
Series A	4.6	-	12.9	16.73	27.8	38.4	0.33
Series B	3.8	2.8	10.4	30.1	32.4	23.2	0.12

Microstructures of slag samples collected during the reduction in which dissolved carbon was the sole reductant showed evidence of topochemical reduction of the partially reduced chromite grains (Figure 8). The initiation of early reduction in regions of surface deformities like cracks on the chromite grains is evident. Alloy particles produced by the reduction are seen as white beads or streaks. As the reaction proceeds, the chromite grains are observed to decrease in size as indicated by a reduction of their areas in the slag matrix (Figure 9). Fragmentation of the altered chromite grains occurs in regions of intense metallization, as the alloy product coalesces into large globules which eventually find their way into the alloy bath. Dissolution of the chromite grains is followed by the recrystallization of a new slag phase consisting of long acicular crystals in a homogeneous matrix. Furthermore, as reduction proceeds from the grain exterior inwards, there is an apparent migration of alloy particles into the grain interior, where they coalesce into larger particles (Figure 10). The microstructure of the final slag obtained after tapping and solidification in the casting mould revealed chromite particle segregation, with the size increasing with depth from the surface top. From the slag microstructure analysis, it appears that reduction in the case of a slag with 10% Cr_2O_3 , nearly goes to completion as shown in Figure 11. The assimilation of altered chromite spinels in the slag appears to be facilitated by the departure of reduced alloy species from the spinel, whereas the recrystallized phase is devoid of these. The microstructure of the slag after 90 minutes reaction time is shown in Figure 12, from which it is seen that only very small chromite particles still remain suspended in a recrystallized slag phase. To a lesser extent alloy particles are still associated with traces of chromite particles.

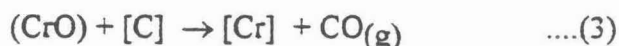
DISCUSSION

The Cr_2O_3 reduction profiles indicate a marked dependence of the reduction rate on the process temperature. However, the similarity in the general appearance of the curves suggests that the mechanism of reduction is the same and that it is independent of temperature.

The reactions taking place can be represented by:



This reaction can be subdivided into two consecutive steps:



where {} and () refer to the undissolved and dissolved species in the slag respectively, while [] refers to dissolved species in the molten alloy bath.

From equation (1), conditions which promote the reduction of chromium oxide are a high carbon activity in the alloy bath and also a high activity of Cr_2O_3 in the slag. The removal of CO as well as a low Cr content of the alloy bath are beneficial in promoting the forward reaction. However, in this work the carbon content in the alloy was fixed and the chromium content of the alloy was very high. In order to assess the efficacy and mode of participation of dissolved carbon on the Cr_2O_3 reduction rate, it was found necessary to add carbon in the form of powdered graphite to the slag. The increase in the reduction rate in the early stages following graphite addition suggests that carbon diffusion from the alloy to the alloy/slag interface is rate determining in the initial stages, becoming less important as the reaction proceeds. Reactions (2) and (3) are confirmed to be taking place by the data presented in Figures 5 and 6. According to Shantarín et al [7], the reduction of Cr^{2+} to Cr is considered to be much faster than that of Cr^{3+} as the former involves a two-electron transfer as opposed to three in the latter. Since the results indicate that carbon elimination from the alloy takes place in the initial stages of reduction, and that this is followed by a corresponding decrease in total Cr_2O_3 content of the slag, it appears reasonable to suggest that carbon loss from the alloy is due to partial reduction of Cr^{3+} . The variation in total slag with time is similar to that reported by Katayama et al [8].

Studies of microstructures of slag samples taken at various stages of the reduction reaction have indicated a thin outer core mostly devoid of alloy particles. This suggests the occurrence of topochemical reduction. Furthermore, this core is seen to be fragmenting and dissolving in the slag, after which a new slag matrix recrystallises in the form of acicular crystals. This implies that dissolution is preceded by reduction. This seems to be in good agreement with results reported by Oosthuizen and Viljoen [9] who showed that more than 60% of chromium lost to the slag is contained in the undissolved partly altered chromite grains.

CONCLUSIONS

1. The reduction of chromite ore by dissolved carbon contained in HCFeCr is controlled by carbon diffusion from the bulk of the alloy to the alloy/slag interface.
2. While the addition of powdered graphite was found to increase the rate of Cr_2O_3 reduction,

the effect was a decrease in the amount of dissolved carbon participating in the overall reduction reaction.

3. Results of microstructure examination of slag samples suggest topochemical reduction in which dissolution is preceded by reduction.

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