

Dissolution and reduction of chromite ore in ferrochromium slags

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Abstract - The dissolution and reduction of a natural chromite ore in molten ferrochromium slag was studied. The chemical composition (by mass) of the chromite ore was: 46.6% Cr₂O₃, 8.3% Fe₂O₃, 18.0% FeO, 10.3% MgO, and 14.1% Al₂O₃. The slag samples were synthetically prepared in the composition range 50-65% SiO₂, 7.5-32.5% CaO, 5-10% MgO, and 10-20% Al₂O₃ (by mass). The basicity ratio (CaO/SiO₂) varied between 0.3 and 0.65. The slag was contained in a graphite crucible, and melted in an induction furnace operating at 1650°C under an argon atmosphere. The chromite ore having a particle size range of (-1.0+0.5) mm was fed into the molten slag. The process involved both the dissolution and reduction stages, as the reducible oxide components of the chromite ore were reduced by the carbon of the graphite crucible. The metallic globules of Fe and Cr were seen mostly on the walls of the graphite crucible. The dissolution process started immediately as the chromite ore was fed into the molten slag, and was followed by reduction of iron and chromium oxides. Due to the fact that the chromite ore was fed in granular form, as expected, a greater contact area was created which influenced the dissolution / reduction reaction between the ore and the slag. The slag composition played a significant role in the dissolution and reduction process. The results showed that the increase in the basicity ratio of the slag increased the dissolution and reduction rates.

Keywords: dissolution , reduction , chromite , ferrochromium, slags

INTRODUCTION

High-carbon ferrochromium is produced predominately by the smelting of chromite ores with the addition of coke and fluxing materials in submerged arc furnaces. The alloy may later be refined into a medium-carbon ferrochromium, in order to be used as an alloying addition in manufacturing chromium-containing alloy steels, including stainless steels (Izawa, 1992). The use of the AOD (argon oxygen decarburization) process made possible the replacement of low-carbon ferrochromium alloy with high-carbon ferrochromium alloy, particularly in the production of stainless steel, where a very low carbon content is required. The efficiency of the high-carbon ferrochromium production process regarding the recovery of chromium from ores hence became fundamentally important (Urquhart, 1972; Hayes, 2004).

It was reported in the literature that the higher proportion of the chromium losses to slags was found in the form of the chromite ore particles which existed in the slag phase either in partially reduced, dissolved, or undissolved form, and the rest was found in the form of alloy droplets which were trapped in the slag (Curr, 1990).

The ferrochromium slags contain between 3 and 15% Cr₂O₃. The chromium loss at such considerable levels leads to the necessity for further treatment of the slags to increase the chromium recovery (Oosthuyzen, 1982).

The physico-chemical properties of slags, such as viscosity, density, melting point, and surface tension, have influence on the separation of slag from the metal phase, whereas

the chemical properties of the slag play a role in the reduction behaviour of the chromite particles in the slag (Jansson, 2002). The dissolution of chromite started from the surface of the ore particle, whereas the reduction started at the graphite surface. High SiO₂ and low MgO promoted the reduction (Katayama, 1989). The composition of the slag phase, the content of each component, the basicity ratio, and the ratio of one specific component to another, influence the recovery of chromium from the slag in various ways, which requires a detailed knowledge to understand better the influence of such parameters on the chromium recovery (Ossin, 1975; Demir, 1998).

The dissolution rate of chromite into a slag was found to be temperature dependent and controlled by the compositions of both the chromite ore and the slag. The dissolution rate increased with increasing basicity ratio of the slag, as well as with increasing Al₂O₃ and decreasing SiO₂. An increase in the MgO content became more influential when it replaced CaO (Demir, 1998).

The chemical dissolution rate was found to be the limiting factor in the dissolution of chromite in liquid slags (Roos, 1981). The valency of Cr in slags, which was also expressed as the distribution ratio of Cr³⁺ to Cr²⁺, was found to depend on the temperature, oxygen partial pressure, and the basicity of the slag (Rankin, 1978).

The purpose of the present study was to investigate the reducibility potential of the chromite particles entrapped in the ferrochromium slags. The influence of each slag component as well as the slag composition on the extent of dissolution and reduction of chromite particles present in the ferrochromium slags are studied.

EXPERIMENTAL

Experimental work was scheduled to study the dissolution and reduction characteristics of chromite ores in the ferrochromium slags, in the presence of carbon, under an argon atmosphere, at smelting temperatures. A series of slag samples with different compositions were prepared by changing the mass percentage of each oxide component in the slag in such a way that the overall slag composition would be within the acceptable ranges encountered in the ferrochromium industry (Demir, 1998). The parameters influencing the dissolution and reduction behaviour of chromite ores in the synthetically prepared slags were studied accordingly.

Experimental Technique

A 50 kW, 3.0 kHz induction furnace using a graphite crucible as the heating element was used in the experiments. The isolated reaction chamber was designed by using a transparent fused quartz reaction tube with a length of 50 cm, and an internal diameter of 12 cm. The reaction tube is sealed using a rubber bellows at the bottom, and the top region was isolated with a water-cooled brass plate designed with the tubular holes for sample collection, temperature measurement, and inlet and outlet for argon gas. The graphite crucible (heating element) was placed inside the reaction tube, and the space between the reaction tube and the graphite heating element was filled with carbon black for insulation purposes. Another graphite crucible (sample holder), smaller in size, was placed inside the larger graphite crucible (heating element). The temperature was controlled by using a B-type thermocouple (Pt-6% Rh / Pt-30% Rh) suspended through the reaction tube located just above the graphite sample crucible. The reaction chamber was flushed continuously with argon gas (99.999% purity) at a rate of 2 l/min in order to create an inert gas atmosphere in the reaction zone during experiments. A stainless steel rod, which was passed through the sampling hole, was used to collect

samples at particular intervals of reaction time during the runs. The details of the experimental system are presented elsewhere (Kucukkaragoz, 1998).

Experimental procedure

A slag sample with a mass of approximately 300 g was placed in the graphite crucible which was then located inside the graphite crucible (heating element) positioned in the reaction chamber of the fused silica tube in the induction furnace. The system was isolated by closing the top plate, and argon was flushed through the silica tube before the induction furnace was switched on to heat the reaction zone to the set temperature. Once the slag was molten completely, the ground chromite ore weighing 20% of the total charge (1 part of ore to 4 parts of slag) was added into the molten slag by using an alumina tube passing through the sampling hole. This is taken as zero time for the experimental run. The samples taken out of the silica tube were quenched immediately in water. The quenched samples were then subjected to analysis. The graphite crucible (sample holder) was taken out of the induction furnace at the end of a run and was inspected for any metal formation on the interior surface of the crucible.

Ore and synthetic slag preparation

The slag samples were prepared synthetically by mixing the pure oxides (98.5% purity supplied by ACE (Associated Chemical Enterprises CC)) within the compositional range of the ferrochromium slags produced in the industry. The principal slag components were SiO₂, CaO, MgO, and Al₂O₃. The compositions of the prepared slags are illustrated in Table 1. The oxides CaO, SiO₂, MgO, and Al₂O₃ were weighed in the required proportions and mixed homogeneously under acetone in an agate mortar. The mixture was then pressed into the form of pellets and sintered (homogenized) under an air atmosphere in a muffle furnace at 1200°C. The sintered pellets were then broken into smaller sizes and 300±5 g of each slag type was placed in the graphite crucible and melted in the induction furnace under an argon atmosphere. The chromite ore (LG-6 from the Bushveld Complex) was ground and screened to have a particle size range of -1.0 + 0.5 mm, and charged in solid form into the molten slag in the induction furnace. The chemical composition of the chromite ore is given in Table 2.

Analytical work

The reacted samples were taken out of the graphite crucible and subjected to chemical analysis using ICP/M (inductively coupled plasma emission spectrometry) conducted at Mintek for the components Cr₂O₃, Fe (total as FeO), FeO, SiO₂, CaO, MgO, Al₂O₃, and for metallic Cr, Fe, and Si, when possible. The graphite crucible with possible metal formation accumulated on the interior surface was kept for further inspection after each run.

RESULTS AND DISCUSSION

The components of the reaction system consisted of the synthetically prepared slag (Table 1), the natural chromite ore (Table 2), the graphite crucible (with carbon as reductant) and the metallic phase. When the chromite ore was charged into the molten slag, it dissolved in the slag, and as a consequence changed its overall composition. The chemical composition of each reacted sample taken at a pre-determined interval of time during an experimental run indicated that the overall slag composition changed with respect to reaction time. The CaO/SiO₂ ratio of the slag phase did not, however, change throughout a run, as the natural chromite ore added into the system did not contain any CaO and SiO₂ in considerable amounts.

Table 1: Initial composition of the synthetically prepared slag samples
(Maximum liquidus temperature is T= 1550°C)

Sample No	CaO (%)	SiO ₂ (%)	MgO (%)	Al ₂ O ₃ (%)	CaO/SiO ₂ (Basicity)
1	10	65	10	15	0.15
2	12.5	57.5	10	20	0.21
3	17.5	65	7.5	10	0.27
4	17.5	57.5	5	20	0.30
5	22.5	57.5	10	10	0.39
6	22.5	50	7.5	20	0.45
7	27.5	57.5	5	10	0.48
8	30	50	5	15	0.60
9	32.5	50	7.5	10	0.65
10	20	57.5	7.5	15	0.35

Table 2: Chemical composition of LG6 chromite ore (mass %)

FeO	Fe ₂ O ₃	Cr ₂ O ₃	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	V ₂ O ₅
18.0	8.3	46.6	10.3	14.1	0.79	0.54	0.31

Table 3: Theoretically calculated composition of a reacted sample (80% of Slag No.8 + 20% chromite ore) assumed to have a 100% dissolution with no reduction

FeO(total)	Cr ₂ O ₃	MgO	Al ₂ O ₃	SiO ₂	CaO
5.14	9.38	6.10	14.92	40.28	24.17

The theoretical composition of each sample formed by mixing chromite into the slag was calculated stoichiometrically, an example of which is given in Table 3. The calculations were based on a mass ratio of 80% slag + 20% chromite ore. The chemical composition of a reacted sample taken during a run was compared with the theoretically calculated one to indicate at which time of reaction the dissolution stage was completed and the molten slag was assumed to have a uniform composition. The extent of dissolution and reduction in total can be calculated according to the chemical analysis of the reacted samples taken out of the molten slag at pre-determined periods of reaction time. The results are illustrated in Figures 1 to 4.

The dissolution process started when the ore particles were charged into the molten slag, changing the composition of the slag phase which varied depending on the composition of both of the ore and the slag used in the run (Curr, 1990; Demir, 1998; Urquhart, 1972). The Fe and Cr concentration of the slag phase remained approximately constant during the stage of the process in which the dissolution process was considered dominant, as can be seen in the concentration-time plots of Figures 1 to 4. The oxides Fe₂O₃ and Cr₂O₃ originating from the chromite ore were most probably reduced to FeO and CrO due to the highly reducing conditions prevailing, which implies that a part of the overall reduction which was not producing a metallic phase took place simultaneously during this stage. Due to their higher dissolution levels in the slag phase, the reducible cations of chromite, namely Fe²⁺ and Cr²⁺, together with anion O²⁻ hence would have an additional driving force for their transfer in the slag phase to be eventually reduced by the reactions taking place at the interior surface of the graphite crucible. The dissolution progressed with each chromite ore particle for a certain period of reaction time until the sample was taken out of the molten charge which indicated that depending on the particle size and time,

a part of each particle was left in undissolved form in the slag. The portion of the chromite ore particles which were not completely dissolved in the molten slag gradually decreased with reaction time and the degree of dissolution would eventually depend on the solubility limit of the chromite ore in the ferrochromium slags.

The reduction of the reducible oxides, FeO and CrO, to metallic form took place at the reaction interface between the molten slag and the graphite crucible. The reduction progressed through the transfer of the reacting species; oxygen anions associated with the cations of the reducible oxides FeO and CrO to the reaction interface (contact surface area between graphite crucible and the molten slag) where they reacted with carbon to form the metallic phase which was accumulated on the interior surface of the graphite crucible. Some of the metallic prills were entrapped in the slag phase within the region close to the reaction zone. The slag phase also contained the undissolved chromite ore particles.

The changes in FeO and Cr₂O₃ contents taking place during the dissolution and reduction process with respect to reaction time are seen in Figures 1 to 4. The FeO and Cr₂O₃ contents of the slag increased during the stage where the dissolution process was dominant and decreased during the stage where the reduction process was dominant.

According to the graphs presented in Figures 1 to 4, the dissolution stage can be assumed to be completed within approximately the first 15 to 60 minutes of reaction time. During this time the reducible oxides reached their maximum contents throughout the slag phase, while the initial stage of reduction during which the higher oxides of iron and chromium were reduced to FeO and CrO, was completed simultaneously. After this stage, the reducible oxides decreased in their contents, as they were reduced to the metallic state as a result of the reactions taking place on the graphite-slag reaction interface.

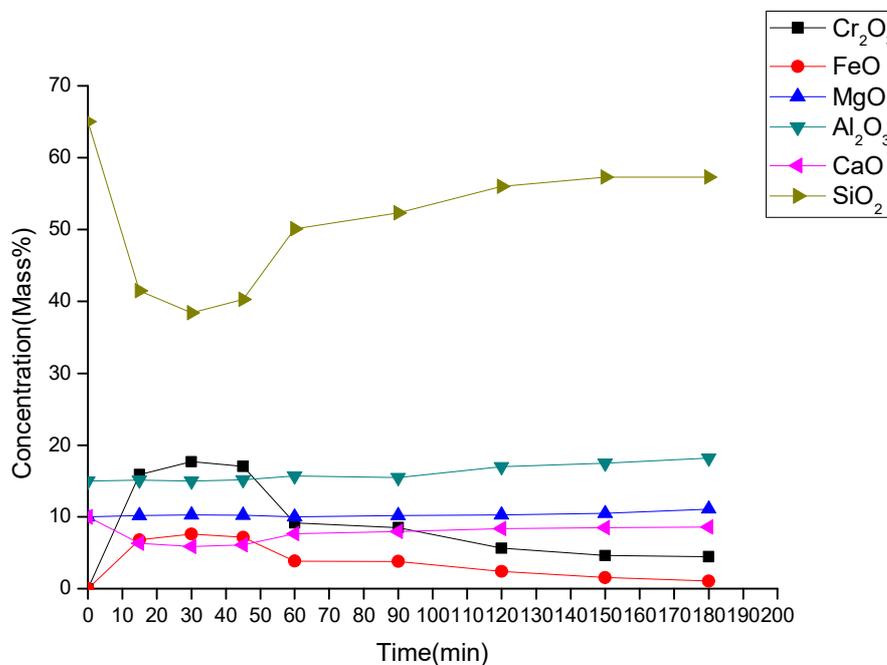


Figure 1: Concentration-time plots of slag constituents (the dissolution dominant stage up to 45 minutes and the reduction dominant stage between 45 to 180 minutes). Slag No.1, Basicity 0.15.

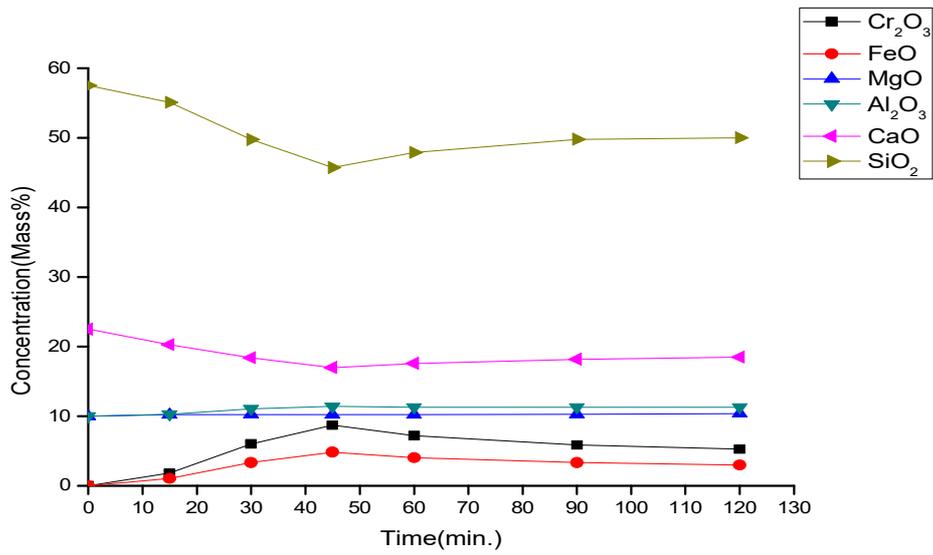


Figure 2: Concentration-time plots of slag constituents (the dissolution dominant stage up to 45 minutes and the reduction dominant stage between 45 to 120 minutes) . Slag No.5, Basicity 0.39.

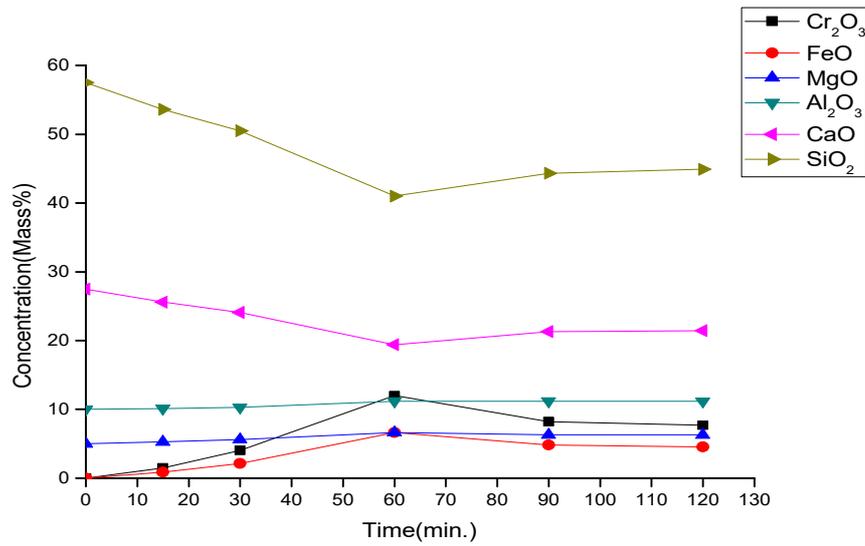


Figure 3: Concentration-time plots of slag constituents (the dissolution dominant stage up to 60 minutes and the reduction dominant stage between 60 to 120 minutes. Slag No.7, Basicity 0.48.

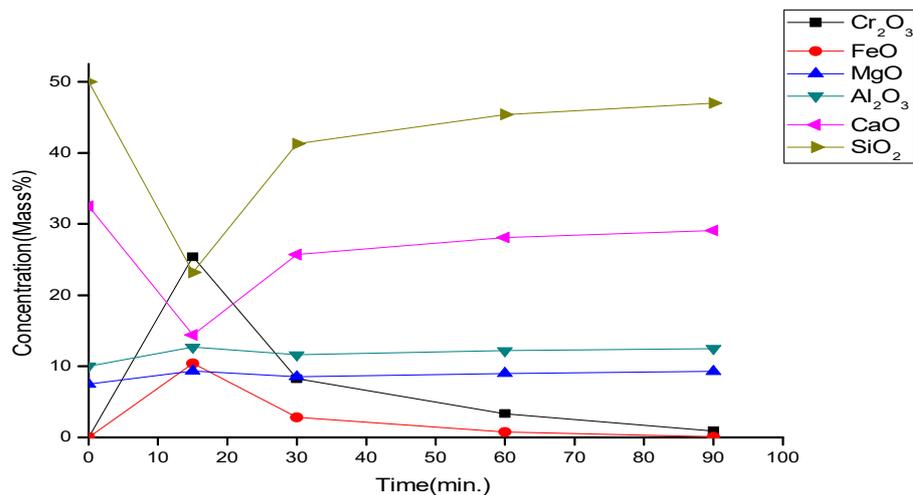


Figure 4: Concentration-time plots of slag constituents (the dissolution dominant stage up to 15 minutes and the reduction dominant stage between 15 to 90 minutes. Slag No.9, Basicity 0.65.

Basicity of the slags had a very strong role in both dissolution and reduction processes, as can be seen in Figure 5. The total dissolution and reduction percentage increased with increasing basicity of the slags. This result was in agreement with the fact that the chromium losses can be decreased by increasing the basicity of silicate slags when treated under reducing conditions (Curr, 1990; Demir, 1998). The dissolution and reduction percentage values against the basicity were calculated for each of the dissolution dominant and reduction dominant stages of the process. The complexity of the calculations arose from the fact that the chemical analysis of the reacted samples provided data only on the total contents of each oxide present in the system regardless of their origins whether from the dissolved or undissolved chromite. This complexity presents difficulty for defining the actual procedure of calculating the exact dissolution and reduction percentages obtained in the process. The results in Figure 5 were calculated on the basis of two procedures using the extreme values obtained, disregarding the reaction time. These two procedures are: (1) the highest mass percentage values of FeO and Cr₂O₃ obtained during the dissolution dominant stage and (2) the lowest mass percentage values of FeO and Cr₂O₃ obtained during the reduction dominant stage. The values (Tables 1 and 2) were compared with the overall mass percentage values given in Table 3, and the reduction percentage values were then calculated accordingly (Table 4). If the dissolution percentage value obtained experimentally is higher than the overall value given for the corresponding oxide in Table 3, then it is assumed that there was too much of the undissolved chromite present in the system which influenced the analysis wrongly, in which case the next highest but lower than the overall value is used in the calculations provided the value is obtained within the dissolution dominant stage. A summarized form of the calculations is given below whereas the example of detailed calculations can be found elsewhere (Demir, 1998).

Calculations for Slag No.1 (Table 1) mixed with chromite ore :

X = Mass of Slag Y = Mass of Chromite ore

X = 4 Y (80% Slag + 20% Chromite Ore)

X + Y = 375 g (the total mass of mixed sample used in each experiment)

Mass balance calculations for Cr₂O₃:

$$0.466 (Y) = (0.0916) (375)$$

where 0.466 and 0.0916 are the mass fractions (46.6% and 9.16%) of Cr₂O₃ in the chromite ore and in the reacted slag respectively, and 375 g shows the total mass of each sample (X+Y) as given above.

The calculated value of Y indicates the portion of the initial 75 g of chromite ore which was dissolved in the slag during the dissolution dominant stage. The value of Y (Y= 73.71) calculated above shows that the chromite was mostly dissolved and partly reduced in the slag at the ratio of 73.71 / 74 (around 99%) up to t = 60 minutes of reaction time within the dissolution dominant stage.

The dissolution and reduction percentage for Cr₂O₃ achieved during the second stage (reduction dominant stage) can be calculated using the following equation:

$$(\text{Reduction and Dissolution}) \% = (9.16 - 4.48 / 9.16) = 51 \%$$

where 9.16% and 4.48% are the mass percentage values for Cr₂O₃ obtained from the chemical analysis of the reacted samples taken out of the molten charge at the beginning and at the end of the reduction dominant stage.

Table 4: Effect of varying basicity of slags on the dissolution and reduction percentage (calculations based on the chemical analysis of the reacted samples)

Basicity (CaO/SiO ₂)	Mass % (Cr ₂ O ₃)	Mass% (FeO)	(Diss.+Red.)% (Cr ₂ O ₃)	(Diss.+Red.)% (FeO)
0.30	7.32	4.08	22	21
0.45	5.26	2.96	44	42
0.48	4.05	2.13	56	58
0.60	3.40	0.55	64	89
0.65	0.9	0.1	90	98

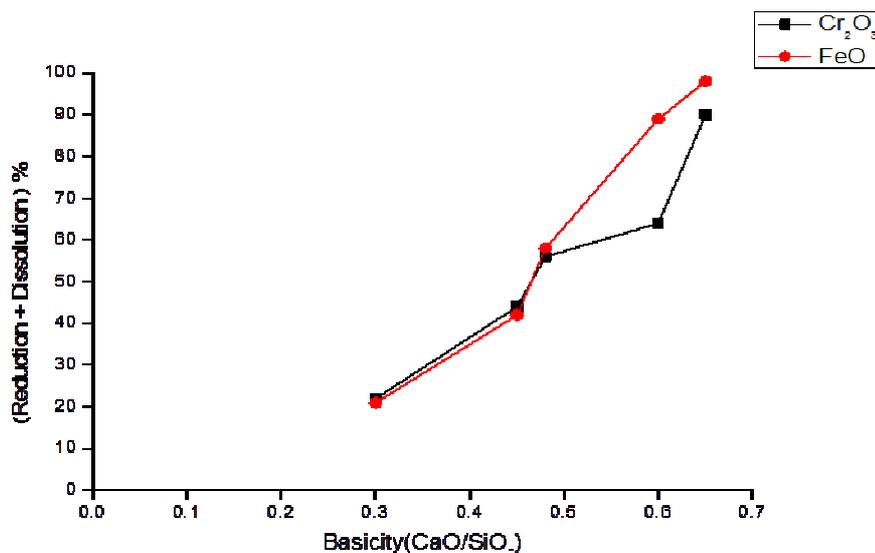
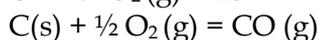
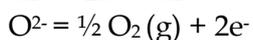
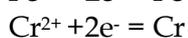


Figure 5: Effect of Basicity Ratio (CaO/SiO₂) on the dissolution and reduction of the reducible oxides of chromite in slag

According to the examination of the samples and the analytical results obtained, the overall process involved the following stages:

- a. Dissolution of chromite ore started immediately as the ore was charged into the slag, and the dissolution dominant stage of the process took place presumably within the first 60 minutes of reaction time. A portion of the undissolved chromite ore particles were entrapped in the slag phase. Reduction of the chromite ore took place simultaneously with the dissolution process and involved the reduction of reducible oxides initially from Fe^{3+} and Cr^{3+} states to Fe^{2+} and Cr^{2+} states.
- b. Transfer of oxygen anions (O^{2-}) associated with the cations of the reducible oxides (Fe^{2+} and Cr^{2+}) to the reaction interface between the slag phase and the interior surface of the graphite crucible.
- c. The following reactions are assumed to take place at the graphite-slag reaction interface.



- d. Formation and growth of a metallic phase mostly accumulated on the interior surface of the graphite crucible.
- e. Entrapment of a portion of the metallic phase in the slag within a region close to the reaction interface.

Under the present experimental conditions, the composition and the basicity of the slag phase were considered as the most important variables which influenced the dissolution and reduction behaviour of chromite ores in the slags. The influence of the concentrations of the dissolving species in the slag and chromite can be considered as another important variable which should be studied separately.

CONCLUSION

The dissolution of chromite ores in ferrochromium slags resulted in simultaneous reduction of the reducible higher oxides of iron to FeO , and Cr_2O_3 to CrO , and then to metallic Fe and Cr . The alloy phase involving Fe and Cr was formed as a metallic phase accumulated on the interior wall of graphite crucible. An increase in the basicity (CaO/SiO_2) of the slags studied (in the range 0.15 to 0.65) increased the extent of both the dissolution and reduction especially in reducing conditions. According to the results obtained, a considerable portion of chromium along with iron can be recovered from the ferrochromium slags by using carbon as a reductant under suitable conditions such as designing a process in which the settling of alloy phase is achieved to a high degree.

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REFERENCES

- Curr T.R. 1990. The dissolution of a Transvaal chromite in liquid silicate slags under an inert atmosphere at 1550°C and 1650°C, MSc Thesis, University of the Witwatersrand, Johannesburg.
- Demir O. 1998. Dissolution of chromite in liquid slags, PhD Thesis, University of the Witwatersrand, Johannesburg.
- Ding W. and Olsen S.E. 1996. Reaction equilibria in the production of manganese ferroalloys, *Metallurgical and Materials Transactions B*, Vol.27B, pp. 5-17.
- Hayes P.C. 2004. Aspects of SAF smelting of ferrochrome, *Infacon X, Tenth International Ferroalloys Congress*, Cape Town, South Africa, 1-4 February 2004, pp.1-4.
- Izawa T., Katayama H., and Sano N. 1992. Smelting reduction of chromite ore in an oxygen converter, *Infacon 6: Proceedings of the 1st International Chromium Steel and Alloys Congress*, Cape Town, 8-11 March 1992, Vol.2, pp.245-252.
- Jansson A., Brabie V., Fabo E., and Jansson S. 2002. Slag formation and its role in the ferrochromium production, *Scandinavian Journal of Metallurgy*, 31, pp.314-320.
- Katayama H.G., Satch M., and Tokuda, M. 1989. Dissolution and reduction behaviours of chromite ore in molten slag, *Tetsu-to Hagane*, 75(10), pp.1883-1890.
- Kucukkaragoz C.S., Akdogan G., and Eric R.H. 1998. Chromium recovery from ferro-chromium slags, *Infacon 8: 8th International Ferroalloys Congress Proceedings*, Beijing, 7-10 June 1998, pp.180-183.
- Oosthuizen E.J. and Viljoen E.A. 1982. *Proc. XIV. Int. Mineral Processing Congress*, Toronto.
- Ossin D.I. 1975. PhD Thesis, University of the Witwatersrand, Johannesburg.
- Rankin W.J. and Biswas A.K. 1978. *J. Inst of Mining and Metallurgy*, pp.C60-C70.
- Roos E.H. 1981. Measurement by use of the rotating cylinder technique of the rate of the solution of Winterveld chromite ore in slag, MSc Dissertation, University of the Witwatersrand, Johannesburg.
- Urquhart R.C. 1972. A study of the production of high-carbon ferrochromium in the submerged-arc furnace, PhD Thesis, University of the Witwatersrand, Johannesburg.



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