Chromium Recovery from Ferro-Chromium Slags

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Abstract

An experimental study was conducted to study the pyrometallurgical recovery of chromium from ferrochromium slags containing undissoulved or partially dissolved chromite particles using carbon as reductant. The available results confirmed that chromium (along with iron) could be recovered with this procedure to a high degree within about three hours. High basicity slags promoted the dissolution-reduction process. The alloy phase formed as globules and droplets at the graphite crucible walls and were also dispersed within the slag phase. Thus the pyrometallurgical reactor design must allow proper settling conditions for the alloy phase.

Introduction

Chromium as an alloying element is produced in the form of high carbon ferrochromium by smelting of chromite ores in the submerged arc furnaces. The invention of AOD(argon oxygen decarburisation) made the direct use of the high carbon ferrochromium possible instead of the low carbon ferrochromium in the stainless steel making process. By this means, a new field of consumption became available for South African chromite ores which are used for production of high carbon charge chrome alloy containing more than 6 % carbon. Chromium recovery is a very important problem in the smelting process and is a function of the smelting behaviour and the reducibility of the ore. Previous studies indicate that the chromium losses to slag mainly occur in the form of metal droplets and small particles of partially reduced and undissolved chromite [1,2,3]. An investigation on the slags obtained from plants showed that more than 60% of the chromium in the slag was in the form of undissolved or partially reduced chromite particles[1]. In another study, it was stated that, depending on the physico chemical properties of slags, mechanical entrainment of alloy prills can lead to excessive loss of metallics in the slag phase[2]. Experimental studies showed that MgO and Al_2O_3 contents of the slag played an important role in the dissolution of chromite in the slag[3,4]. Slags having higher MgO and Al_2O_3 contents had lower capacity of dissolving chromite[3]. The effect of CaO/SiO_2 ratio of the slag was found considerably important[3]. In another study, the reduction rate of chromite increased with fluxing reaction [5]. In a recent study[6] done on the reduction of solid chromite in liquid Fe-Cr-Si-C alloy, the reduction rate increased with addition of slag into the system. The reduction rate also increased with Si content of the alloy [6]. The dissolution of chromite in liquid slags was studied and the chemical dissolution was found as the limiting factor[7]. Reduction of trivalent Cr to divalent Cr in molten basic slags was studied to determine the effect of oxygen partial pressure, basicity and temperature on the distribution ratio of Cr^{3+} to Cr^{2+}. Valency of Cr in a slag depended on the basicity ratio[8]. A work done on this subject showed that chromium existed predominantly in the divalent state under reducing conditions[9]. Thermodynamics of chromium oxide was studied in the system of $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3$, and very little Cr (in the range of ppm) was found in the slag at 1650°C [10].

The purpose of this work is to study the reducibility of the chromite particles in the ferro-chromium slags in order to increase the chromium recovery in the process.

Experimental

Work is conducted to study the dissolution behaviour of chromite particles in the ferro-chromium slags. To achieve this purpose the following is considered:

1. Alterations of the slag composition in order to dissolve chromite particles in the slag to render them amenable for reduction from the liquid slag by solid carbon reductant.
2. Study of the parameters affecting the mechanistics and kinetics of the dissolution and reduction process.

Apparatus

An induction furnace with a transparent quartz-silica reaction chamber employing a graphite crucible as the heating element , a water top cooled brass plate enabling argon flushing, sampling and temperature measurement is used (Figure 1). The furnace is a 50 kW , 3kHz induction unit. Another graphite crucible is located as sampler holder inside the bigger graphite crucible used as heating element. Temperature is controlled by a type B (Pt- 6% / Pt-30% Rh) thermocouple suspended through the quartz silica tube to the graphite crucible containing the sample. Carbon black is filled between the fused silica tube and heating graphite crucible for insulation purpose.

Preparation of Samples

Slag compositions were chosen to be within the ranges practiced in the submerged arc furnaces. Synthetic slags were prepared to have the compositions listed in Table 1. Pure CaO, SiO_2, MgO and Al_2O_3 were weighed in required amounts and mixed homogeneously under acetone in a mortar. They were formed into pellets and than sintered. The sintered (and homogenized) pellets were then broken into appropriate sizes to fill the graphite crucibles. Approximately 300 g of each sample was placed in a graphite crucible and melted in the induction furnace under argon atmosphere prior the actual runs. LG6 chromite ore was ground and screened to have the particle size within the range of -1.00 +0.50 mm. Chemical composition of the ore is given in Table 2.

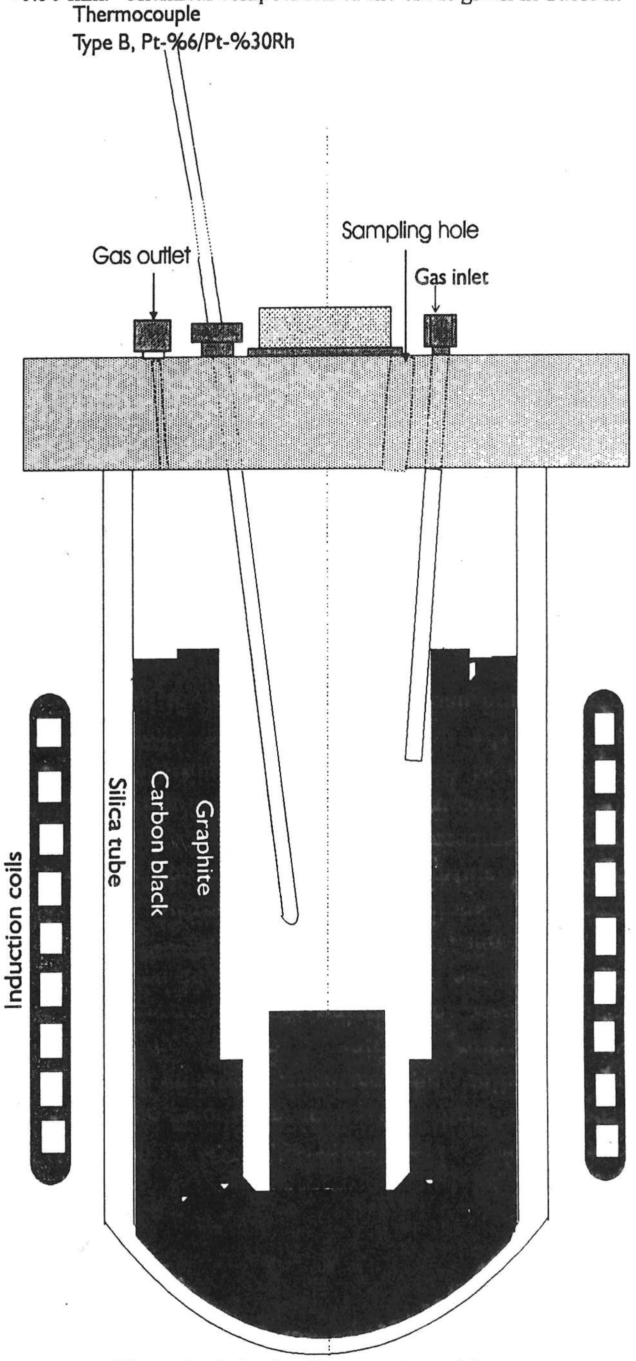

Figure 1. Induction Furnace Assembly

Table 1. Initial composition of the slag samples (in mass percent)

Sample No	Al_2O_3	MgO	SiO_2	CaO
SP 1	10	7.5	50	32.5
SP 2	10	7.5	65	17.5
SP 3	20	7.5	50	22.5
SP 4	20	7.5	65	7.5
SP 5	10	5	57.5	27.5
SP 6	10	10	57.5	22.5
SP 7	20	5	57.5	17.5
SP 8	20	10	57.5	12.5
SP 9	15	5	50	30
SP 10	15	10	50	25
SP 11	15	5	65	15
SP 12	15	10	65	10
SP 13	15	7.5	57.5	20
SP 14	15	7.5	57.5	20
SP 15	15	7.55	57.5	20

Table 2. Chemical analysis of LG6 chromite ore (in mass percent)

FeO	Fe_2O_3	Cr_2O_3	MgO	Al_2O_3	SiO_2	TiO_2	V_2O_5
18.0	8.3	46.6	10.3	14.1	0.79	0.54	0.31

Procedure

Graphite crucible containing the slag sample is located in the induction furnace. The sample is heated under the flow of argon atmosphere until it becomes fully molten. Chromite ore particles weighing 20 % of the charge is poured into the molten slag through an alumina bore passing through the brass plate. This is taken as zero time for the experiment. Samples are taken by means of a steel rod passing through the sampling hole of the brass plate at 15, 30, 45, 60, 90, 120, 150, 180 , 210 and 240 minutes of intervals.

Analytical Work

The samples are subjected to chemical analysis for the constituents of Cr_2O_3 , Fe(total as FeO), FeO, SiO_2, CaO, MgO, Al_2O_3 and for Cr(metal), Fe(metal) and Si(metal) when possible at Mintek. The samples are examined under optical microscope for the formation of metallic phase. The sectional samples are also subjected to SEM-EDAX studies.

Results and Discussion

Preliminary tests has shown that the system was in a reliable working order with no leaks through the silica tube and the temperature was controllable at levels above the melting points of the slag samples which are measured generally between 1500°C to 1600°C within ±10°C accuracy range. The graphite crucible acted as reducing agent. The samples taken at 15 to 30 minute intervals are subjected to chemical analysis in order to determine the changes in the concentrations of FeO,CrO,MgO, SiO_2 and Al_2O_3 in the slags with respect to time.

The process involves two steps: the dissolution of the chromite particles in the slag and the reduction of the dissolved chromite by solid carbon at crucible walls. The kinetics of the process should therefore be considered in two parts as the dissolution rate of chromite and the reduction rate of chromite. The dissolution process mainly depends on the composition of the slag phase. The main variables influencing the reduction rate of chromite are slag composition, concentration gradients, stirring rate, reduction potential, and temperature. In this work no stirring was employed and temperature and reduction potential were kept constant. Therfore, the variables affecting the reduction rate of chromite is again slag composition and concentration gradients.

During dissolution process, the reactions take place between the liquid slag and the solid chromite particles. The reaction interface is the area of contact between the liquid slag and the chromite particles. The dissolution rate is therefore proportional to the particle surface area. The other factors controlling the dissolution rate. are the concentration gradients of the elements which are supposed to be transferred between chromite and slag phases.

Graphite crucible holding the sample is the only source for carbon in the above reactions. The interface for the reduction reaction is therefore the area of contact between the the graphite crucible and the liquid sample. The reduction starts as soon as the chromite is dissolved in the slag and the reducible oxides of the dissolved chromite reach the graphite-slag reaction interface.

The reducible oxides in the chromite ore are FeO, Fe_2O_3 and Cr_2O_3. The total dissolution and reduction can be calculated by the chemical analysis of the reducible oxides. When samples are taken from the slag phase containing dissolved chromite, the change in the above oxides which are not initially present in the slag phase can be used to calculate the dissolution-reduction percentage.

During dissolution part, chromite is dissolved in the slag forming a slag phase containing Cr_2O_3 and FeO additional to the oxides of the initial slag. Cr_2O_3, during this stage, is assumed to be immediately reduced to CrO due to the highly reducing conditions which shows that, both reduction and dissolution take place at the same time. Figure 2 shows the calculated total percentages of dissolution and reduction with time for several selected slag samples. Figures 3 and 4 show the dissolution-reduction percentages for slag samples 3 and 5 respectively in terms of the chromium and iron components. Both of these components- as expected- first increase in the slag phase where dissolution process is dominant and then decrease as reduction process becomes more pronounced.

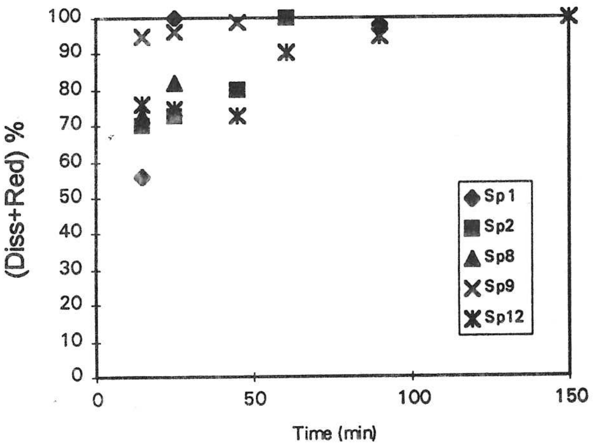

Figure 2. Reuction-Dissolution of chromite in slags

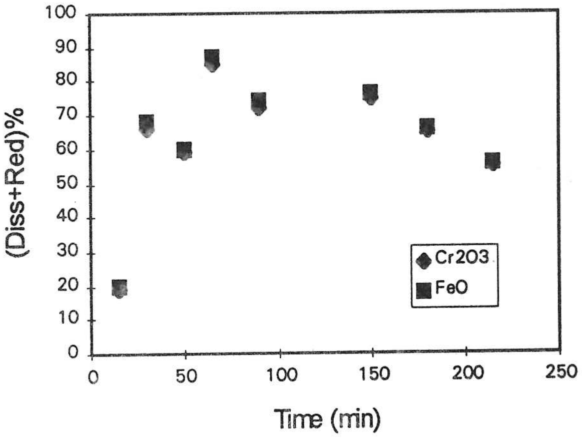

Figure 3. Dissolution and reduction of chromite in Sample 3.

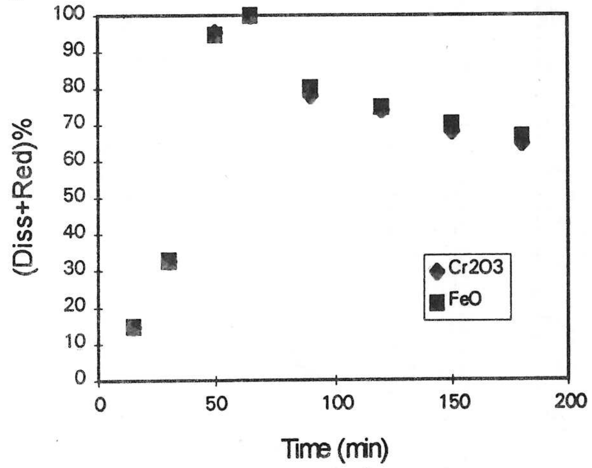

Figure 4. Dissolution and reduction of chromite in Sample 5.

Basicity plays an important role in both dissolution and reduction processes as can be seen in Figure 5 where 60 and 120 minutes data are plotted as a function of basicity. As the basicity increases, reduction-dissolution increases. This is in aggrement with the known fact that chromium losses in silicate slags decrease with an increase in basicity under reducing conditions.

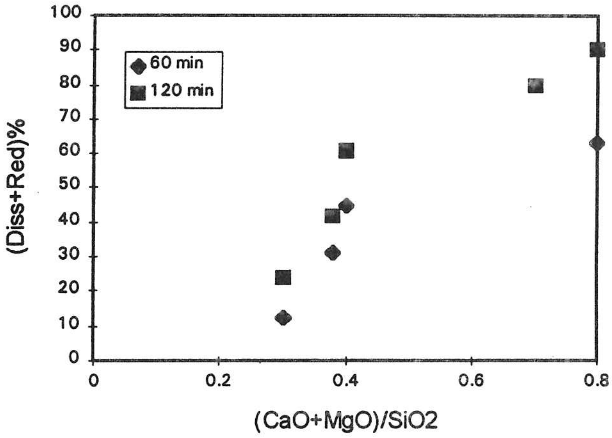

Figure 5. Effect of basicity on dissolution- reduction of chromite

Conclusion

Dissolution of chromite in the slag is accompanied with the reduction of Cr_2O_3 to CrO and then to Cr metal and FeO to Fe metal. Basicity of the slag increases the dissolution-reduction percentage. The alloy phase is formed as metallic globules at the walls of the graphite crucible as well as droplets. Despite the fact that experimental work is not complete yet, the available results confirm that a major portion of chromium (along with iron) can be recovered from ferrochromium slags by a pyrometallurgical treatment using carbon as a reduction. However, the reactor must be designed in such a way that settling of the alloy phase formed must be achieved to high degrees.

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