The Effect of Chromite Ore Mineralogy on Reduction Mechanism and Reducibility

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Abstract

The mineralogy and structure of different chromite ores have been studied, both before and after oxidation. The mineralogy is described and correlated to the reducibility determined in reduction experiments.

Reduction experiments were carried out in a thermobalance apparatus at 1700 °C and at 1500 °C. Graphite crucibles were used and the gas atmosphere was CO.

The reduction rate seems to be affected by the mineralogical properities of the ore. It is also affected by oxidation. The effect on reduction rate and mechanism depends mainly on the composition of the chromite spinel.

Introduction

Kinetics and reduction mechanisms for reduction of chromite ores have been studied by several authors. The suggested reduction mechanisms are:

1 Solid state reduction of chromite ore to metal.
2 Chromite ore dissolves in slag and CrO_x in the slag is reduced to metal
    - Dissolution of chromite in the slag determines the reduction rate, or
    - Reduction of dissolved CrO_x determines the reduction rate
3 A combination of solid state reduction and dissolution of ore in slag.

Eric[1], Barcza et al.[2] and Urquhart[3] describe a combination of solid state reduction and dissolution in the slag as the rate determining mechanism. They believe that solid state reduction dominates at the temperatures below 1400-1500 °C, and dissolution in slag dominates above this temperature range. Xu and Dai[4] suggest that the reduction always take place in solid state while Neuschütz et al.[5] has found that above 1200 °C, the chromite ore is dissolved in the slag and then reduced to metal. Erasmus[6] has studied the effect of pre oxidation of different South African ores. He reports slight differences between the different ores, and that pre oxidation has a beneficial effect on the kinetics and extent of subsequent reduction.

The reduction rate of 6 different ores and their corresponding sinters have been studied in the present investigation. The aim has been to provide information about mechanisms and reducibility dependent on the ore mineralogy before and after preoxidation

Description of the ores

Ore samples

Six different ores from four different mines, presented in Table 1, were investigated by Malvik and Berger[7].

Table 1: Ore Samples

Sample	Ores
1147	Turkish fines
1153	Turkish concentrate
1149	Kahzak fines
1150	Brazilian concentrate
1157	South African concentrate
1158	South African fines

The same ores were oxidized and sintered at 1600 °C They where heated rapidly to the sintering temperature, followed by fast cooling. The atmosphere was air at a total pressure of 1atm. Turkish fines (1147) and South African fines (1158) were also sintered at 1400 °C. Samples in the fraction 0.147-1.16 mm were prepared from all ores and sinter for further investigations and reduction experiments.

Table 2 Chemical analysis of ores and composition of chromite minerals

Ore	%	% MgO		% Al_2O_3		% Cr_2O_3		% Fe as FeO		Cr/Fe	
	Chromite	Total ore	Chromite	Total ore	Chromite	Total ore	Chromite	Total ore	Chromite	Total ore	Chromite
1147	70	20,4	14,8	9,8	12,4	41,6	57,7	15,3	16,6	2,39	3,05
1153		18,1	14,2	9,7	12,8	45,9	56,0	16,5	14,6	2,45	3,37
1149	70	22,1	14,8	7,9	10,3	45,7	59,7	12,6	13,1	3,40	4,03
1150 Y	90-95	5,8	6,4	9,2	11,2	51,0	56,7	23,2	23,3	1,97	2,14
1150 G			9,8		13,3		56,5		20,5		2,43
1157		9,0	8,9	14,0	16,1	40,8	46,4	23,9	24,5	1,62	1,66
1158 Y	80	10,3	8,7	11,7	16,2	38,6	46,4	24,4	25,4	1,49	1,61
1158 G			9,9		16,1		45,3		26,7		1,50

Ore mineralogy

The chemical composition of the ores was determined. Polished thin sections were examined by microscope in transmissive and reflective light and analyzed with Electron Microprobe Analyzer (EPMA). The compositions of the ore and of the chromite mineral differ, as shown in Table 2. In addition the amount of and types of gangue minerals vary between the ores.

The Brazilian concentrate and South African fines, contain exsolution phases, one gray compact (G), and one yellowish (Y) with many cracks. This is illustrated in Figure 1 to Figure 4.


Figure 1 South African fines

0,5mm


Figure 2 Sintered South African fines

0,1mm

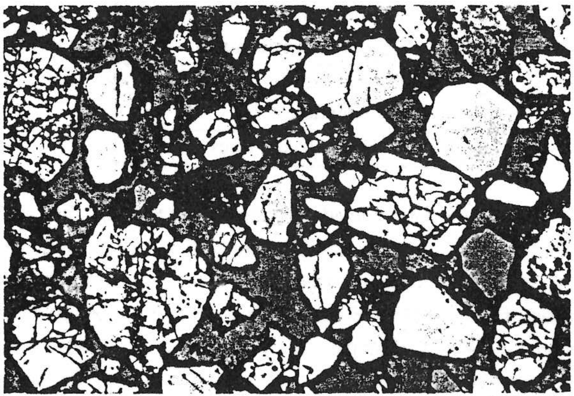
Figure 3 Brazilian concentrate

0,5mm

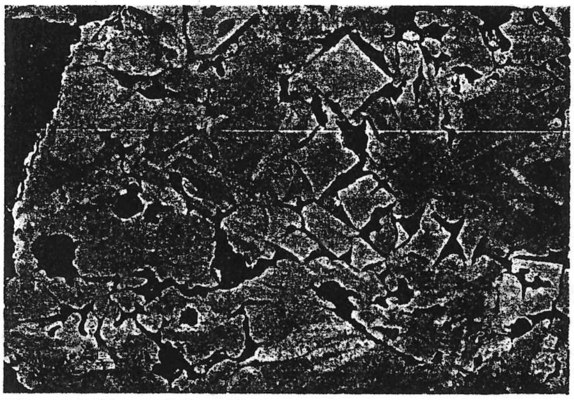
Figure 4 Sintered Brazilian concentrate

0,1mm

Table 3 Molecular formula for chromite spinel in ores and for main phase in the corresponding sinters

Ore	Chromite molecular formula, ores	Chromite molecular formula, sinters
1147	$(Fe_{0,31}Mg_{0,69})(Fe_{0,06}Cr_{0,71}Al_{0,23})_2O_4$	$(Fe_{0,13}Mg_{0,87})(Fe_{0,14}Cr_{0,60}Al_{0,26})_2O_4$
1153	$(Fe_{0,31}Mg_{0,69})(Fe_{0,04}Cr_{0,72}Al_{0,24})_2O_4$	$(Fe_{0,16}Mg_{0,84})(Fe_{0,07}Cr_{0,70}Al_{0,23})_2O_4$
1149	$(Fe_{0,29}Mg_{0,71})(Fe_{0,03}Cr_{0,77}Al_{0,20})_2O_4$	$(Fe_{0,16}Mg_{0,84})(Fe_{0,07}Cr_{0,75}Al_{0,18})_2O_4$
1150 Y	$(Fe_{0,67}Mg_{0,33})(Cr_{0,77}Al_{0,23})_2O_4$	$(Fe_{0,54}Mg_{0,46})(Fe_{0,12}Cr_{0,66}Al_{0,18})_2O_4$
1150 G	$(Fe_{0,52}Mg_{0,48})(Fe_{0,02}Cr_{0,73}Al_{0,20})_2O_4$	$(Fe_{0,50}Mg_{0,50})(Fe_{0,06}Cr_{0,77}Al_{0,17})_2O_4$
1157	$(Fe_{0,56}Mg_{0,44})(Fe_{0,06}Cr_{0,62}Al_{0,32})_2O_4$	$(Fe_{0,45}Mg_{0,54})(Cr_{0,76}Al_{0,24})_2O_4$
1158 Y	$(Fe_{0,57}Mg_{0,43})(Fe_{0,07}Cr_{0,62}Al_{0,32})_2O_4$	$(Fe_{0,30}Mg_{0,70})(Fe_{0,10}Cr_{0,70}Al_{0,20})_2O_4$
1158 G	$(Fe_{0,53}Mg_{0,47})(Fe_{0,10}Cr_{0,59}Al_{0,31})_2O_4$	

The molecular formula for the different ores and sinters have been calculated and are presented in Table 3. The calculation is based on the assumption that the ore mineral is a stoichiometric normal spinel, where Fe is the only element that occurs in two valences, Fe^{2+} and Fe^{3+}.

There is only a small content of ferric iron in the different chromite spinels. The amount of ferrous iron at tetrahedral sites varies from around 0,30 in Kahzak (1149) and Turkish (1147) fines to 0,67 in one of the phases of the Brazilian concentrate (1150). All ores except the South African ores (1157 +1158) contain around 0,70-0,77 mol Cr in the octahedral sites. A consequence of the lower Cr content in the spinels of South African ores is a correspondingly higher Al content.

The gangue minerals were melted during the sintring operation, and after solidification they appeared as forsterite and spinel crystals. Skeleton crystals of magnetite were also found in the gangue as shown in Figure 5. The iron in the magnetite may either come from iron in gangue minerals or from the chromite spinels.

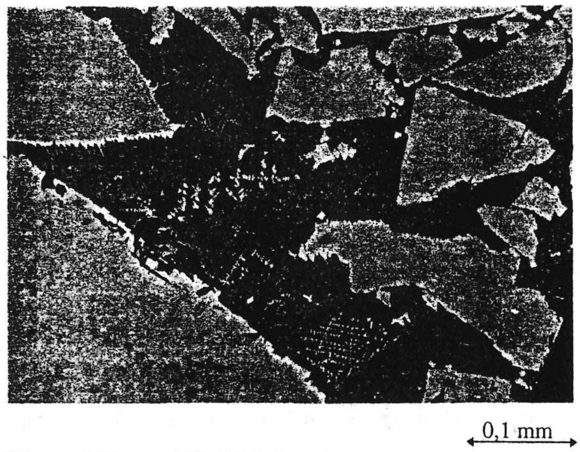

Figure 5 Sintered Turkish fines in reflective light.

Oxidation of the ores has changed the composition of the chromite spinels. As can be seen from Table 3, some Fe^{2+} in all the ores are oxidized to Fe^{3+}, and is assumed to occupy octahedral sites in the crystal. The Al-content in the main phase has decreased. The content of Mg^{2+} and of Fe^{3+} has increased in all the spinels. In South African and Brazilian concentrate there is extensive exsolution of the chromite spinels as already shown in Pictures 2 and 4. Since the amount of the different phases is unknown, it is impossible to say if elements are redistributed inside the ore grain, or transported either from gangue to ore, or vice versa.

The grains of all sintered ore fines are coated with a rim of spinel that, except for the Kahzak fines, has a high iron content and probably is magnetite. The lighter rim around the grains can be seen in Figure 5. This lighter rim is not observed in sintered concentrates.

Reduction experiments

Experimental

Ore samples in size fraction 0,147-1,16 mm, prepared by crushing and grinding were used in all experiments. The experimental setup is schematically shown in Figure 6, and the graphite tube furnace in Figure 7

Graphite crucibles, 35mm in diameter, and 40 mm high were used. Ten grams of ore was used in all experiments. Industrial coke was used as reduction material, and bauxite and quartz were added as fluxes. The crucible charged with materials was suspended in a thermobalance and the weight recorded every 30 second. In all the experiments more than stoichiometric amounts of coke were used.

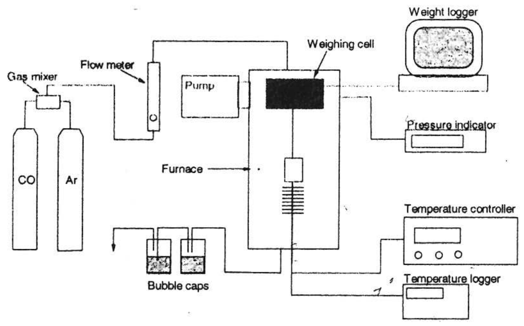

Figure 6. Sketch showing the experimental apparatus

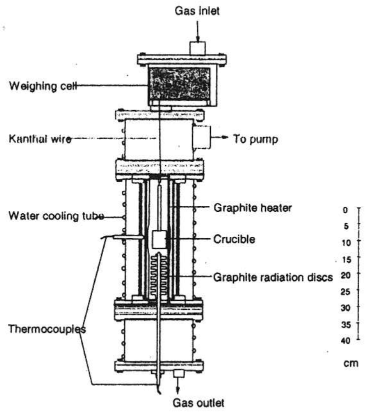

Figure 7 The graphite tube furnace.

The reduction experiments were conducted isothermally in CO-gas atmosphere. The gas flow was approximately 0,4 l/min. The furnace reached the temperature in about 10 minutes. Most experiments were run for 5 hours. The samples were cooled in Ar-gas.

The total weightloss was registered during the experiments. The degree of reduction was calculated and is shown as a function of time for different ores in the following figures. 100 % degree of reduction is defined as the weightloss due to complete reduction of all the iron and chromium oxides. Corrections were made for losses of ignition. Some SiO_2 is will also be reduced to Si_{met} and SiO-gas, and some MgO may be reduced to Mg-gas. This will give an extra weightloss, and has in some cases led to more than 100% degree of reduction. The inclination of the reduction curves is a measure of the reduction rate,

Comparison of different ore types.

Reduction rates for different ores at 1500 °C without addition of fluxes are compared in Figure 8. Brazilian concentrate exhibits the highest reduction rate and South African fines the lowest initial reduction rate. For South African concentrate the reduction will proceed in nearly the same way as for South African fines, but the initial reduction rate is higher.

Reduction rate for the same ores at 1700 °C, with addition of fluxes are shown in Figure 9. Some data points are missing in the curve for Brazilian concentrate. However the figure indicates that this ore has the highest reduction rate also at 1700 °C. Initial reduction of South African concentrate is delayed compared to the other ores which seem to have nearly the same reduction rate.

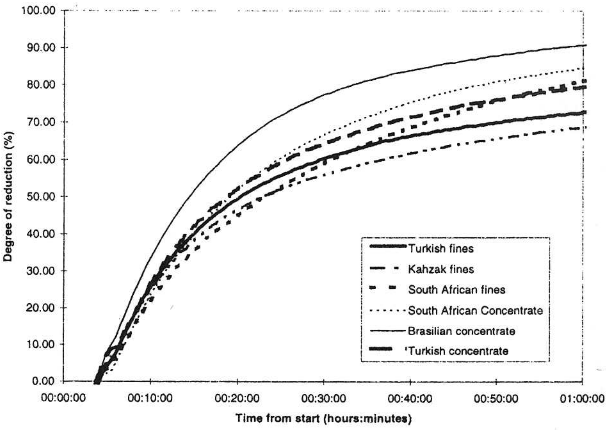

Figure 8. Reduction rate of different ores at 1500 °C without flux addition.

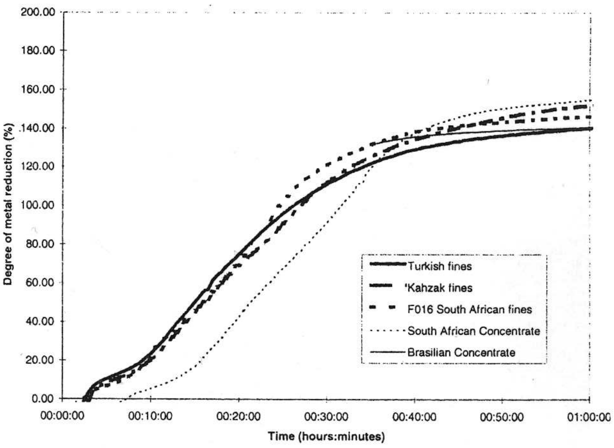

Figure 9 Reduction rate of different ores at 1700 °C with flux addition.

Reduction rates of different sinters are compared in Figure 10. The two sintered concentrates show the highest reduction rates, with South African concentrate as the highest of these two. The sintered ore fines have nearly the same initial reduction rate, but reach different degrees of reduction. The reduction rate is not affected by a change in sintering temperature from 1400 °C to 1600 °C.

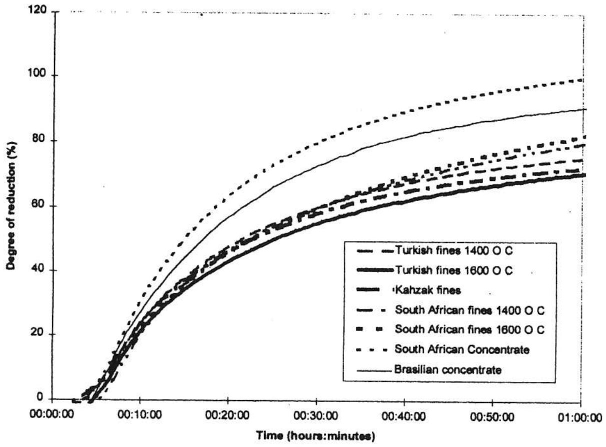

Figure 10. Reduction of different sinters at 1500 °C.

Sintering increases the reduction rate of the South African concentrate as shown in Figure 11, while it slightly decreases the reduction rate for Turkish fines. The reduction rates of the other ores are not affected by the sintering.

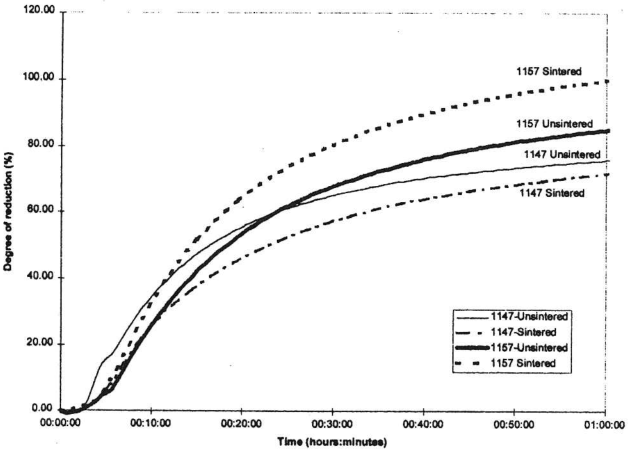

Figure 11. Reduction of South African concentrate (1157), Turkish fines(1147) and their sinters at 1500 °C

The composition of the initial gangue minerals and MgO and Al_2O_3 from the ore mineral will determine the compositions and the amount of slag to be formed. The final slag compositions from unfluxed ores are shown in Table 4.

Table 4 Slag composition after complete reduction for different ores without flux addition.

Ore	% SiO_2	%Al_2O_3	%MgO
Turkish fines	29	27	44
Turkish concentrate	26	30	44
Russian fines	29	23	48
South African fines	32	40	28
South African concentrate	22	50	28
Brazilian concentrate	31	47	22

Weightloss caused by formation of Si_{Met} and SiO- and Mg-gas depends on the content of SiO_2 and MgO in the slag. It is most pronounced with high temperatures and long reduction time. Since the slag composition change continuously during reduction, these effects will vary with time, and the variation differs from ore to ore. The importance of these properities will be further investigated.

Discussion

The chromite ores show slightly different reduction rates. This indicates that the reduction rate is affected by mineralogical properities of the ores caused by different compositions of the chromite spinels or different amount and type of gangue minerals or a combination of these. The experiments also show that the reduction rate is changed as a result of the oxidation which takes place during sintring of the ores. The rate controlling mechanism is probably either solid state reduction of iron and chromium from the ore, or dissolution of the ore in the slag phase.

High content of Fe^{2+} in the chromite spinels seems to result in higher reduction rates. Brazilian concentrate is an example of this

High content of Al^{3+} in the chromite spinel seems to result in lower reduction rates. For example the Al^{3+} content of the chromite spinel of the South African concentrate was lowered as a result of oxidation and sintring, and the reduction rate increased. Further, the South African ore has a higher Al^{3+} content in the chromite spinel than the Brazilian ore and shows a lower initial reduction rate even though the content of ferrous iron is nearly the same. The effect of the Al^{3+} content can be explained as a rate retarding effect on the dissolution of the chromite spinel in the slag, or by the lowered activity of chromium, which accompanies the higher aluminum content in the chromite spinel.

A rim of magnetite was formed around the chromite grains of the oxidized ore fines except Kahzak fines. The rim of magnetite may be responsible for the lowered reduction rate of the oxidized Turkish fines compared with original ore fines. Any retarding effect of the rim formation in the oxidized South African ore fines may be hidden by the rate increasing effect of the lowered Al-content

The concentrates of Turkish and South African ores contain less gangue mineral than their corresponding ore fines, this as a result of preceding ore dressing processes. The concentrates show higher reduction rates, and reach a higher degree of reduction than the ore fines. This difference indicates that either the amount of, or the composition of slag being formed, affects the reduction rate. According to Neuschütz et al.[5] the effect of increasing amounts of slag was expected to be the opposite as addition of fluxes and increasing SiO_2 content was reported tc increase the reduction rate. In our experiments, the concentrates that contain less slag, and has the lowest SiO_2- content has the highest reduction rate. The slag composition will affect both the amounts of CrO_x dissolved in the slag and the kinetics when it is reduced from the slag. It will also be of importance when Cr and Fe are reduced directly from solid ore since MgO and Al_2O_3 from the chromite spinels then has to dissolve in the slag.

Conclusions

The reduction rate varies between different ore types. These variations seem to be dependent of composition of the chromite spinel and of the composition of the gangue minerals. Pre oxidation will change the reduction rate. Its effect varies from ore to ore, and is dependent on the composition of the chromite spinel.

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