

Kinetic Aspects of Chromite Ore Reduction with Coal at 1200 to 1550°C

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The reactions that take place in the novel CODIR process for chromite fines were investigated by means of laboratory reduction tests carried out with United States and South African chromite-ore fines mixed with equal amounts of anthracite coal and 6 per cent silica. Reduction rates from 1200 to 1550°C were determined thermogravimetrically, and the product phases were identified by microprobe analysis. The reduction sequence with time and increasing temperature is Fe–Cr–Si, with wide regions of overlap for chromium and silicon. Two hours at 1550°C are sufficient for the complete metallization of all three oxides.

The lower reduction rate observed for the US chromite could be attributed mainly to its larger grain size. Solid products ($\text{MgO}\cdot\text{Cr}_2\text{O}_3$ and $\text{MgO}\cdot\text{Al}_2\text{O}_3$) are formed as shells around unreacted $\text{FeO}\cdot\text{Cr}_2\text{O}_3$, requiring solid-state diffusion for the chromium reduction to proceed.

Additions of silica clearly accelerated the reduction of chromium in both ores. Silica increases the amount of liquid slag in the burden, thus removing part of the solid layers of $\text{MgO}\cdot\text{Al}_2\text{O}_3$. Silica may also be beneficial by acting as a solvent for CrO formed from Cr_2O_3 in the presence of carbon. Apparently, chromium is easily reduced to the metal from $\text{CrO}\cdot\text{SiO}_2$ melts.

Irrespective of the ore type, the reduction yielded a metal that, after cooling, contained three distinct phases: Fe–Cr–Si, Cr–Fe–C, and Cr–Fe–Si–C. The non-metallic products were $\text{MgO}\cdot\text{Al}_2\text{O}_3$ and a siliceous slag. The intimate mixture of metal and slag droplets with solid spinel and char particles gives rise to the pasty state of the product, which is considered beneficial in the technical process.

Introduction

Of the world's ferrochromium production, 72 per cent is used in stainless-steel making. Therefore, the production figures for both ferrochromium and stainless steel show a very close proportionality, and their annual growth rates since 1975 have both averaged¹ around 3 per cent. Ferrochromium is conventionally made from lumpy chromite ores in submerged-arc furnaces with a power consumption of about 4000 kWh/per tonne of ferrochromium. Increasing costs of electrical energy and a reduced availability of lumpy ores have prompted a number of process improvements, such as the Outokumpu process, which has a preliminary pelletizing stage that cuts the consumption of electrical energy down to about 3000 kWh/t; or the Showa Denko process, which includes the prereduction of pellets in a rotary kiln, with an energy consumption of about 2000 kWh/t.

A different approach has been tested in Japan in a joint effort by the major Japanese steelmakers². A top- and bottom-blown steel converter was used to produce ferrochromium from ore fines, coal, and oxygen without any direct input of electrical energy. The required energy is

produced by the combustion of CO to CO_2 directly above the melt. This smelting reduction technology is currently being developed in several countries for the production of hot metal from iron ore and coal without coke ovens and blast furnaces.

The CODIR Chromite Process

While the converter technology for the production of ferrochromium will require several more years of development, the CODIR process for chromite fines¹, Figure 1, conceived and tested by Krupp in the 1980's and now commercialized by Mannesmann Demag, has found its first industrial application in South Africa.

In a rotary kiln, 4.8 m in diameter by 80 m long, chromite fines and coal are reacted at temperatures up to 1450°C to produce a semi-solid material consisting of highly metallized ferrochromium, slag, gangue, and char. Phase separation is carried out subsequently in an electric furnace. The design capacity of the rotary kiln is 120 kt of ferrochromium per year for a material with a 90 per cent reduction of iron plus chromium. The target consumption of electrical energy for the CODIR ferrochromium process,

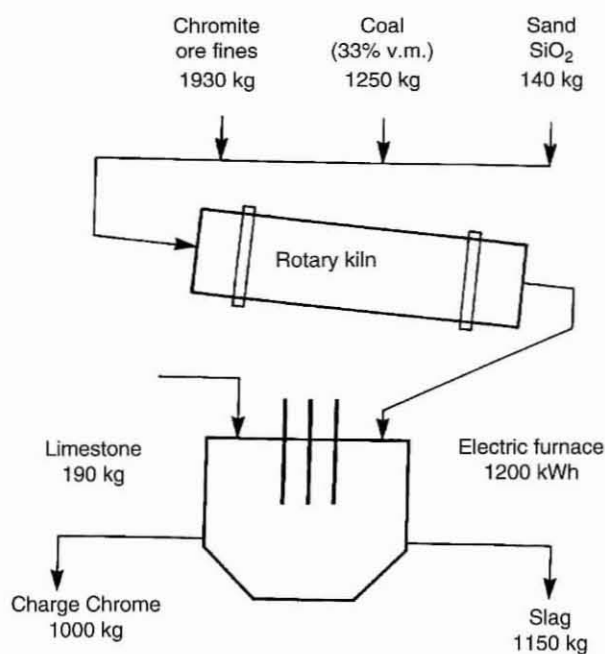


FIGURE 1. Typical consumption figures for the CODIR coal-based ferrochromium process

including the melting stage, is 1200 kWh per tonne of ferrochromium.

The CODIR process aims at the almost complete reduction of both iron and chromium in the rotary kiln. This requires sufficiently high temperatures and an intimate contact between chromite grains and carbon over the entire residence time in the kiln.

To meet these goals, the burden is transformed into a 'pasty' state, with some of the phases molten and others solid, so that the specific surface area of the oxygen-sensitive metal phases decreases, but macroscopic phase separation does not take place.

In order to gain some information on the complex reactions proceeding in the kiln, laboratory tests were carried out with similar burden compositions, temperatures, and residence times. The results of these investigations are described in the following sections.

Basic investigations on the reduction behaviour of chromites have previously been presented by several researchers³⁻¹⁰.

Experimental

Mixtures of 4 g of chromite ore, 4 g of coal, and 0,24 g of silica (analyses and grain sizes in Tables I to III) were reacted in a graphite crucible (height 48 mm, inner diameter 17 mm) at temperatures up to 1550°C. The measurement of mass loss was followed by thermogravimetric analysis. The total mass loss was about $2 \text{ g} \pm 5 \text{ mg}$. The furnace was flushed continuously with 10 per cent CO plus 90 per cent Ar at a total flowrate of 50 l/h (at standard conditions). Several runs were interrupted for sampling at different stages of the reduction. Samples were analysed chemically and by microprobe. The mass loss caused by the loss of moisture and volatile matter from the coal was determined in a separate calibrating run and deducted from the mass losses measured in the chromite-reduction runs.

TABLE I
COMPOSITION OF CHROMITES

	SA % by mass	US % by mass
Cr ₂ O ₃	45	41
FeO	26	23
Cr/Fe	1,52	1,58
Al ₂ O ₃	14,0	17,2
MgO	8,2	13,4
SiO ₂	8,2	5,5
CaO	0,41	0,45
TiO ₂	0,41	0,42
MnO	1,22	0,20
S	0,008	0,01
P	0,01	0,008

TABLE II
SIZE DISTRIBUTION OF CHROMITES AND SILICA

Size fraction μm	Distribution, % by mass		
	Chromite ore		Silica
	SA	US	
>630	1	1	3
250-630	36	55	55
160-250	32	30	33
100-160	20	9	8
40-100	10	4,5	1
<40	1	0,5	0,3

TABLE III
COMPOSITION AND SIZE DISTRIBUTION OF COAL

9% volatile matter 9% ash 0,084% S 0,03% P Basicity of ash: $\frac{\text{CaO} + \text{MgO}}{\text{Al}_2\text{O}_3 + \text{SiO}_2} = 0,6$	Size fraction μm	Distribution, % by mass
	100-160	2
	75-100	1
	40-75	33
	<40	64

The temperature-time programme used was chosen as an idealized approximation of the situation in the hot zone of the kiln: the samples were heated to 1200°C in 60 minutes, held at that temperature for 60 minutes, heated to the desired final temperature (between 1300 and 1550°C) within 5 to 15 minutes, and held there for up to 150 minutes. Upon completion of the run, the samples were cooled in the furnace at an increased Ar flowrate of 300 l/h.

The degree of reduction was determined from the oxygen content of the samples. It was assumed that the metallic Fe-Cr phase contained 3 per cent silicon and 7 per cent carbon, that MgO, Al₂O₃, and CaO were not reduced, and that there was no silicon loss via SiO volatilization. The same assumptions were used in the evaluation of the thermogravimetric results. The reduction degrees (in

percentages) of four samples based on thermogravimetry and on chemical analysis gave satisfactory agreement:

Sample	1	2	3	4
Thermogravimetry	18	19	62	72
Chemical analysis	23	16	63	72

Results

Thermogravimetric Investigations

Figure 2 shows a set of mass-loss curves for three final temperatures between 1350 and 1480°C. During the first stage of the runs, the temperatures were kept at 1200°C for one hour, and the masses of the samples stopped decreasing after some time. This indicates that some selective reduction of FeO, but no reduction of Cr₂O₃ or SiO₂, had taken place. When the temperature was increased, reduction continued at a rate that depended strongly on temperature. Above 1400°C the mass loss reached values much higher than could be accounted for by the reduction of FeO and Cr₂O₃ alone, indicating that SiO₂ was also reduced.

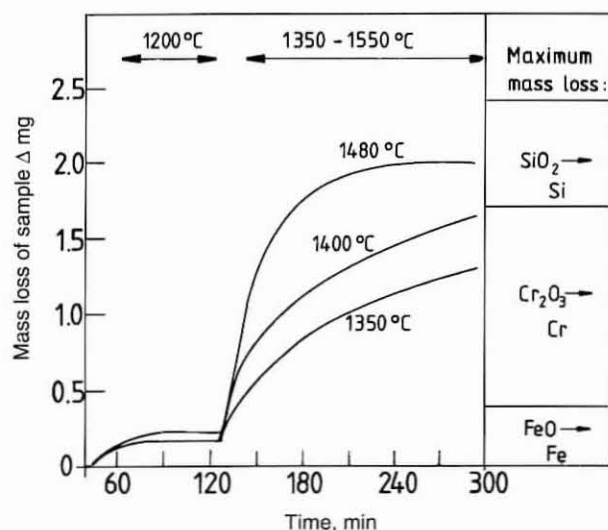


FIGURE 2. Reduction rates of South African chromite with anthracite plus 6 per cent silica (temperature held at 1200°C for 1 hour, and raised to final value within 5 to 15 minutes)

The reduction behaviour of United States and South African ores are compared in Figure 3. The SA ore is more easily reduced at all temperatures. For the same degree of reduction, the US ore requires almost twice the time for the SA ore. Since the chemical and the mineralogical compositions of the two ores are not very different, this may be due to the difference in average grain size of the ores. Therefore, the influence of grain size on reduction rate was tested for both ores.

In the case of the US ore, fractions larger than 315 μm and smaller than 160 μm were prepared and reduced. Figure 4 shows the results for these fractions and for the original ore at 1480°C. Since the size separation did affect the chemical composition of the fractions, the comparison was made on the basis of relative degrees of reduction. The observed differences in reduction rates are much larger than the deviations in composition. Thus, the time required to

raise the reduction degree from 50 to 80 per cent increased with the average grain size as follows: 12 minutes (130 μm), 26 minutes (260 μm), 34 minutes (360 μm). In the case of the SA ore, the chemical compositions of the size fractions were nearly identical to those of the original ore. The fractions are listed in Table IV. Figure 5 shows the reduction rates of the four SA ore fractions treated at 1400°C. Again, the strong influence of grain size on reduction kinetics is evident.

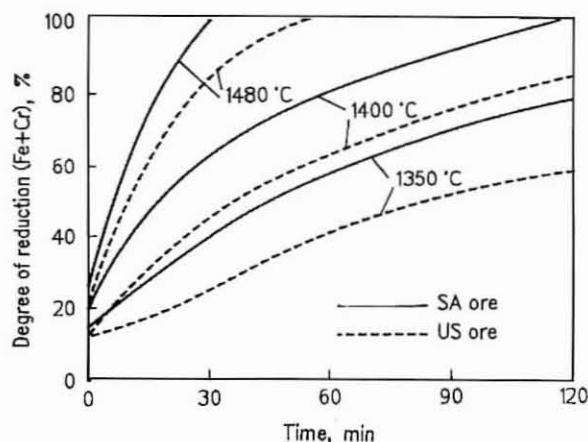


FIGURE 3. Reduction rates at constant final temperatures for two different chromites

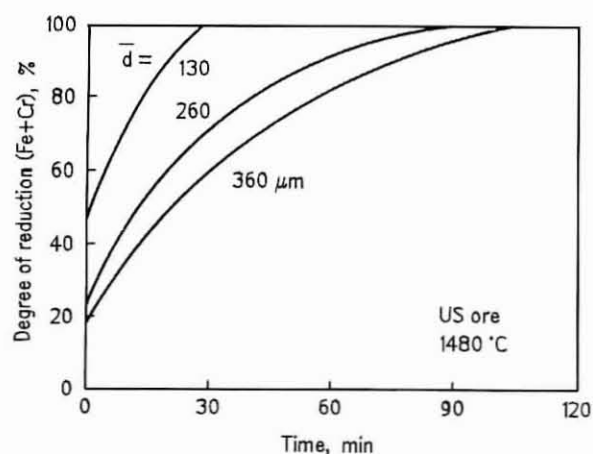


FIGURE 4. Influence of grain size on the reduction rate of United States ore

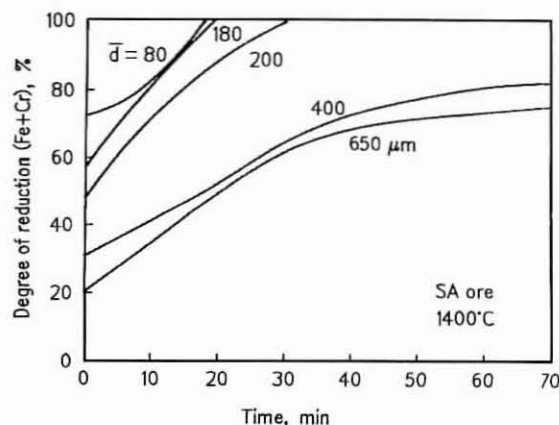


FIGURE 5. Influence of grain size on the reduction rate of South African ore

TABLE IV
SIZE FRACTIONS OF SOUTH AFRICAN ORE PREPARED FOR REDUCTION TESTS (FIGURE 5)

Sample no.	Size fraction, μm	Average size, μm
1	Original ore	200
2	<100	80
3	100–250	180
4	250–630	400
5	>630	650

All the tests were carried out with a constant silica addition of 6 per cent by mass relative to the ore. The beneficial effect of silica was tested with both ores at 1480°C (Figure 6). In the reduction range of 50 to 100 per cent, the addition of silica causes a remarkably higher reaction rate. A series of test runs with the SA ore showed that an increase in the silica additions from 0 to 12 per cent had very little influence on the degree of prereduction at 1200°C while, at 1400°C, the silica strongly enhanced the rate and the final degree of reduction. The difference in rate between silica additions of 0 and 3 per cent was very marked.

Microprobe Analyses

Microprobe analyses were carried out on a number of samples reduced under different conditions to obtain information on the reduction sequence and the formation of phases. Selected micrographs are shown in Figures 7 to 10.

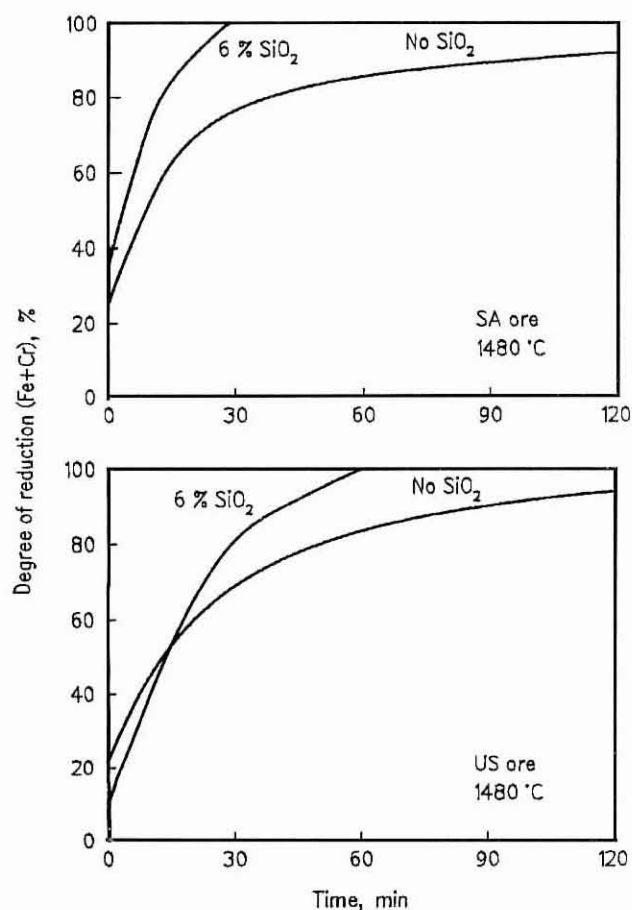
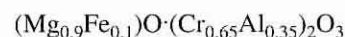


FIGURE 6. Effect of silica addition on reduction rate of South African ore (above) and United States ore (below)

At 1200°C, FeO is reduced selectively from $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ to form an iron phase with about 5 per cent chromium and a chromite spinel, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$. Silica is not reduced at all. Figure 7 shows unreduced $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ in the centre, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ as the darker-grey zone surrounding the core, and the metal phase ($\text{Fe} + 5\% \text{Cr}$) as white seams. It should be noted that $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ is used here to refer to a spinel that, besides MgO and Cr_2O_3 , contains considerable amounts of FeO and Al_2O_3 . On the basis of several microprobe analyses of different partially reduced samples, the formula



would describe the composition more precisely, as can be seen from the following comparison in % by mass:

Constituent	Analysis, %	Formula, %
MgO	18–23	20,4
FeO	1–6	4,0
Cr_2O_3	53–59	55,5
Al_2O_3	17–22	20,1

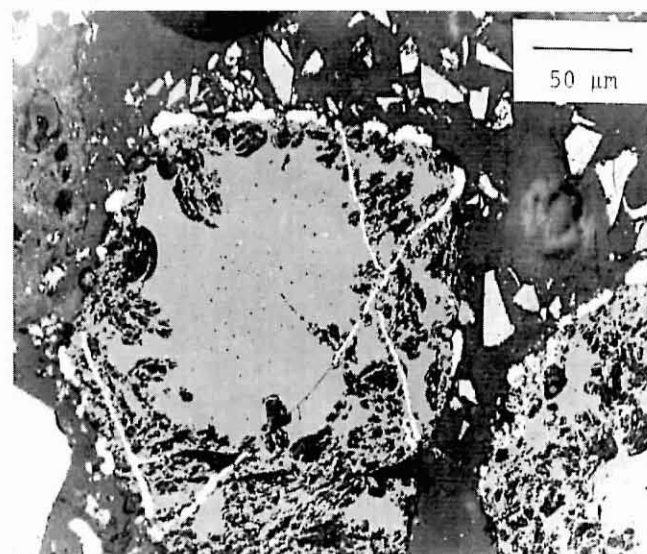


FIGURE 7. Slightly reduced chromite grain (1200°C). Core of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ surrounded by darker and porous $\text{MgO} \cdot \text{Cr}_2\text{O}_3$. White seams are metal phase ($\text{Fe} + 5\% \text{Cr}$)

At 1350°C, the following three phases could be distinguished analytically in the metallic particles, appearing as a white homogeneous phase in Figure 8:

- (a) 74% Fe, 18% Cr, 8% Si (no C)
- (b) 60% Cr, 35% Fe, + C (no Si)
- (c) 52% Fe, 36% Cr, 3% Si, + C.

(The microprobe analysed only qualitatively for carbon.) The grain shown in Figure 8 contains a core of unreduced $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, a porous shell of $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ surrounding the core, then a layer of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel, and finally a thick outer zone made up of slag with a composition of 50 to 59 per cent SiO_2 , 21 to 24 per cent Al_2O_3 , 15 to 25 per cent MgO, and 4 per cent CaO. It can be assumed that the metal and slag phases are liquid at 1350°C, while the $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, and $\text{MgO} \cdot \text{Al}_2\text{O}_3$, as well as the char, remain solid.

At 1480°C and higher, three co-existing metallic phases could be detected side by side having the approximate compositions:

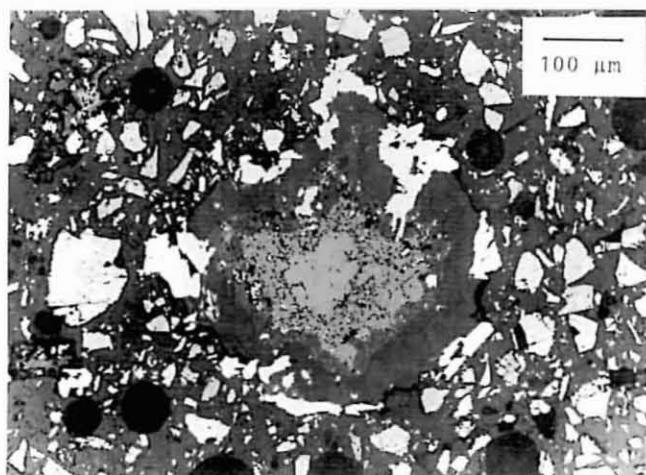


FIGURE 8. Partly reduced chromite grain (1350°C). Core of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ surrounded by $\text{MgO} \cdot \text{Cr}_2\text{O}_3$, then $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and finally a thick slag layer containing white metal particles. Grey chunks are char

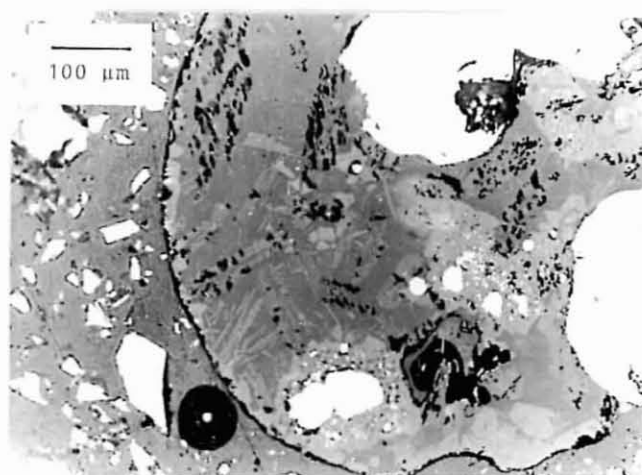


FIGURE 10. Slag droplet formed at 1480°C containing crystals of forsterite and (lighter) $\text{MgO} \cdot \text{Al}_2\text{O}_3$, and metal droplets (white)

- (a) 65% Fe, 20% Cr, 12% Si (no C)
- (b) 75% Cr, 20% Fe, + C (no Si)
- (c) 50% Fe, 30% Cr, 12% Si, + C.

Figure 9 shows a metal droplet, after reduction at 1550°C, containing three phases with these approximate compositions. The final non-metallic products at 1480°C and higher are $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and the slag as mentioned above. Figure 10 shows a slag droplet containing $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel crystals. The adjacent metal droplets are again made up of the different phases shown in Figure 9.

Figure 11 summarizes the phases observed at various temperatures. The chromium and silicon contents of the metallic phases increase with the temperature of reduction. The sequence of reduction with time and temperature is Fe–Cr–Si, with wide regions of overlap. While at 1200°C

the only metal phase formed is iron containing 5 per cent chromium, three metallic phases are detected after reduction at or above 1350°C, namely Fe–Cr–Si, Cr–Fe–C, and a quaternary Cr–Fe–Si–C phase. Generally, the Cr/Fe and the Si/Fe ratios in these phases increase with the higher reduction temperatures.

Since the metallic phases are very probably liquid at the reduction temperature, they may be formed as one single liquid phase and separate into three co-existing phases only upon cooling.

Discussion

The observed reduction sequence Fe–Cr–Si is in agreement with the thermodynamic stability of the respective oxides.

The reduction rate is strongly influenced by temperature, grain size, and silica additions. As demonstrated by the micrographs (e.g. Figure 8), solid-state reactions are

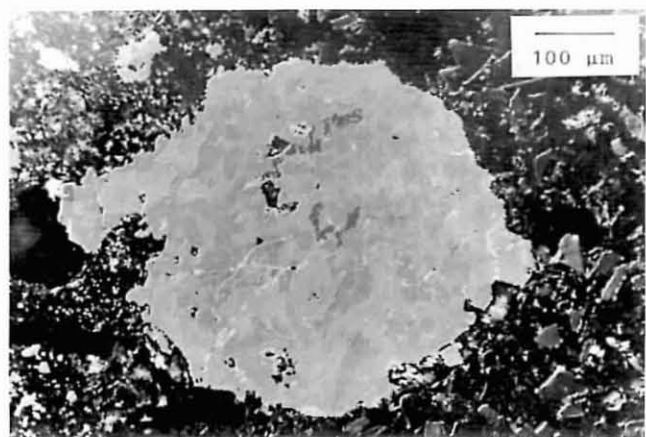


FIGURE 9. Metal droplet formed at 1550°C, consisting (after solidification) of three different phases: Cr–Fe–C, Fe–Cr–Si, Cr–Fe–Si–C

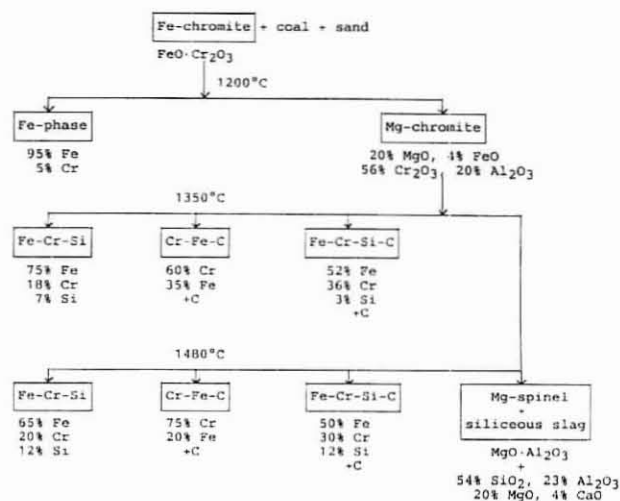
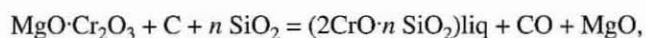


FIGURE 11. Metallic and non-metallic phases identified in reduced United States and South African ores at different temperatures

involved, and solid intermediate products are formed as shells around the unreacted cores. Therefore, solid-state diffusion is required for further reduction. If transport processes in the solid state have an important influence on the overall reaction rate, a smaller grain size will increase the reduction rate.

Transport processes are accelerated by the transformation of part of the solids into liquid phases. The addition of silica increases the amount of liquid slag, thus dissolving more of the $\text{MgO} \cdot \text{Al}_2\text{O}_3$ formed as a solid reaction product around unreduced chromite ores. If silica additions can decrease the thickness of these spinel shells, they will lead to a higher overall reduction rate.

Another beneficial effect of silica is reported¹¹ to be its ability to dissolve chromium monoxide to form a liquid eutectic at 1400°C with 40 per cent CrO. Under reducing conditions, Cr^{3+} in slags is to a certain extent transformed to the divalent state^{7,8,12-14}. The role of silica during the reduction of chromite can be described by the reaction.



with MgO reacting to form the spinel $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Cr}^{2+}$ must be easily reduced from the liquid $\text{CrO} \cdot \text{SiO}_2$ phase, since the silica-rich slag phase in the experiments reported here did not contain any noticeable amounts of chromium oxide.

From the results of the present investigation, neither of these alternative mechanisms for the effect of silica can be ruled out.

As seen from the micrographs, the process carried out at about 1450°C produces a liquid metal in the form of droplets less than 1 mm in diameter. Compared with that in solid-state reduction processes, the specific surface area is definitely smaller, and therefore the tendency for re-oxidation to occur is drastically decreased. The hot product is an intimate mixture of liquid metal and slag, and solid $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel and char, giving rise to what is called the 'pasty' state in the technical process. This state has the advantage of keeping the chromium-bearing species and the reductant in very close contact throughout the entire process.

Acknowledgments

Thanks are due to Professor G. Friedrich and Dr Wiechowski of RWTH Aachen for the microprobe analyses and micrographs; to Dipl.-Ing. P. Janssen of RWTH Aachen for the thermogravimetric measurements; to Dr Ulrich and W. Janssen of Mannesmann Demag for their support; and to Dr Barcza of Mintek, Professor Sano of Tokyo University, Dr Slatter of MS&A, and Professor Tokuda of Tohoku University for helpful discussions.

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