INFACON 7, Trondheim, Norway, June 1995
Eds.: Tuset, Tveit and Page
Publishers: FFF, Trondheim, Norway

EFFECT OF FLUX ADDITIONS ON THE KINETICS OF CHROMITE ORE REDUCTION WITH CARBON

D. Neuschütz*), P. Janßen*), G. Friedrich**) and A. Wiechowski**)
*) Lehrstuhl für Theoretische Hüttenkunde, **) Institut für Mineralogie
und Lagerstättenlehre, Rheinisch-Westfälische Technische Hochschule
Aachen, D-52056 Aachen, Germany

ABSTRACT

The reduction kinetics of a South African chromite fine ore from Lebowa was determined thermogravimetrically with the addition of graphite powder and different fluxes composed of 3 to 4 of the components SiO_2, CaO, Al_2O_3, MgO and CaF_2. Three g of ore, 2 g of carbon and 1 g of flux were intimately mixed and heated steadily up to 1450°C. The non-isothermal reduction rate was calculated from the bulk mass loss measured continuously. A number of runs were interrupted for sampling at different stages of reduction. The reduction was always accelerated by the addition of fluxes. Furthermore, samples containing a flux showed two stages of acceleration with temperature, the first one starting at 1020 to 1120°C, the second one at 1200 to 1320°C, while fluxless samples only exhibited the first stage which did not start before 1200°C. Electron microprobe analyses revealed more complex non-metallic regions in partially reduced fluxed samples. Theses regions apparently contain ternary compounds like $CaO \cdot MgO \cdot SiO_2$. The first acceleration effect is therefore attributed to the solid-state formation of ternary oxides. This apparently leads to surface roughening and to more frequent microcracking of the chromite grains, thus facilitating metal phase nucleation. The second effect is attributed to the formation of liquid slags. They enhance the reduction by dissolving part of the $MgO \cdot Al_2O_3$ surrounding the unreduced chromite and by accelerating the transport of Cr ions to the reductant. Through the addition of fluxes the temperature for 90% reduction of Lebowa chromite fines was lowered by up to 150 degrees.

INTRODUCTION

The kinetics and mechanism of the carbothermic reduction of chromite ore have repeatedly been the subject of detailed investigations [1...12] in view of their importance in producing ferrochromium in the submerged-arc furnace, in smelting reduction processes, or in the rotary kiln. It is generally observed that the addition of silica accelerates the metallization, most probably through the formation of a liquid slag [1,8,11]. At 1500 to 1600°C the addition of a complex slag enhances the reduction rate considerably [1,7]. This effect is attributed to a preferable dissolution of chromites in the slag and a relatively easy reduction of the chromium from liquid slag. It is also suggested that the slag dissolves some of the $MgO \cdot Al_2O_3$ spinel which forms as a dense solid shell around the chromite grains during reduction [8]. In general, the beneficial influence of flux additions is attributed to the earlier formation of a liquid slag phase which is able to dissolve either solid diffusion barriers or chromite [1,8,11].

The present work was carried out to investigate the influence of multi-component fluxes on the reduction kinetics of South African chromite ore from Lebowa at temperatures above and below the melting temperature of the mixture of gangue and flux. It includes preliminary tests carried out by Neuhaus [13].

EXPERIMENTAL

The reduction kinetics of chromite ore from Lebowa with carbon as reductant was investigated in laboratory tests making use of a thermobalance, Fig. 1. Mixtures of 3 g of Lebowa chromite ore, 2 g of graphite, and 1 g of flux, were reacted in a graphite crucible under a flowing gas containing 20 % CO + 80% Ar. The temperature curve applied was a rough approximation of the heating curve of the solid feed in a rotary kiln process; i.e. from 20 to 500°C in 30 min; at 500°C for 15 min; from 500 to 950°C in 15 min and from 950 to 1450°C with 90 K/h. When 1450°C were reached, the sample was cooled down in the furnace by turning off the electric power and flushing with inert gas. Within 2 hours, 700°C were reached.

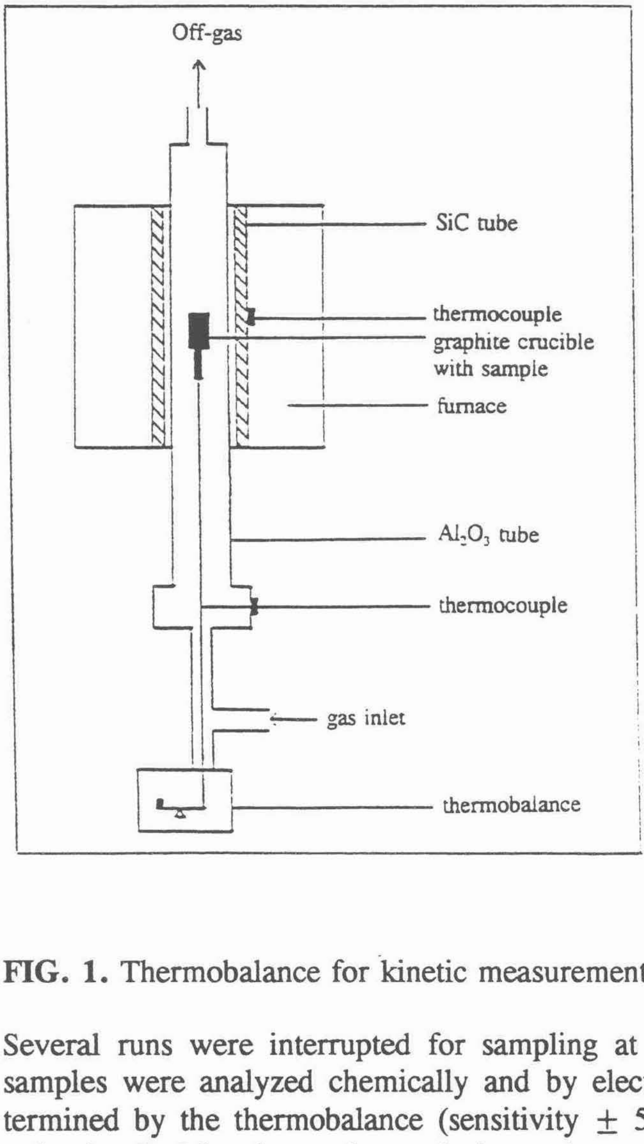


FIG. 1. Thermobalance for kinetic measurements

Several runs were interrupted for sampling at different stages of the reduction and the samples were analyzed chemically and by electron microprobe. Bulk mass losses as determined by the thermobalance (sensitivity ± 5mg) were used to calculate the degree of reduction R. Mass losses due to drying and to volatilization during heating were determined in separate runs and deduced from the resulting mass changes. R = 100 % refers to the complete reduction of iron and chromium oxides. Since in the later stage of reduction SiO_2 also starts to be reduced, R can reach values above 100 %.

TABLE 1: Chemical composition and grain size distribution of the Lebowa ore

Composition (mass-%)		**Grain size distribution:**	
46.0%	Cr_2O_3	< 40 μm	1%
25.5%	FeO	40-75	17%
14.2%	Al_2O_3	75-100	1%
10.0%	MgO	100-160	30%
1.1%	SiO_2	160-250	34%
0.6%	TiO_2	250-630	18%
0.35%	V_2O_5		
0.25%	MnO		
0.2%	CaO		
0.1%	NiO		

Chemical composition and grain size distribution of the Lebowa chromite ore are given in Table 1. Graphite powder of spectrographic purity (99,9% C) was used as reductant. The fluxes added to the ore-graphite mixture were chosen according to their eutectic melting temperature as well as their different chemical composition. Table 2 summarizes the various flux compositions used in our experiments. Flux 1 is a siliceous mixture of SiO_2, CaO, Al_2O_3 and MgO; flux 2 is highly siliceous containing SiO_2, MgO and Al_2O_3, but no lime; fluxes 3 to 5 are all basic, flux 3 and 4 are composed of CaO, CaF_2 and SiO_2 with flux 3 having a higher CaO:SiO_2 ratio; flux 5 contains Al_2O_3 in place of SiO_2.

The mass ratio of flux to ore chosen for the laboratory experiments was relatively high in view of practical operation. It was intentionally chosen to demonstrate the kinetic effects as clearly as possible. This ratio needs to be optimized with respect to economic feasibility.

TABLE 2: Flux compositions (mass-%)

Flux no.	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**CaF_2**
1	26.3	47.7	17.8	8.2	-
2	-	62.8	16.4	20.8	-
3	45.3	13.4	-	-	41.3
4	41.0	25.7	-	-	33.3
5	38.7	-	32.0	-	29.3

RESULTS

Thermogravimetry

The reduction kinetics of Lebowa chromite fines with pulverized graphite were determined under non-isothermal conditions as a function of different flux additions. From the mass loss measured by the thermobalance, the degree of reduction of (Fe + Cr) was calculated as a function of time and (correspondingly) temperature. The results are summarized in Figure 2. Note that reduction degrees can reach values above 100% due to SiO_2 reduction.

The sample with no flux additon showed by far the slowest reduction, which started at about 1100°C reaching 25% at 1265°C, 50% at 1320°C and 90% at 1450°C.

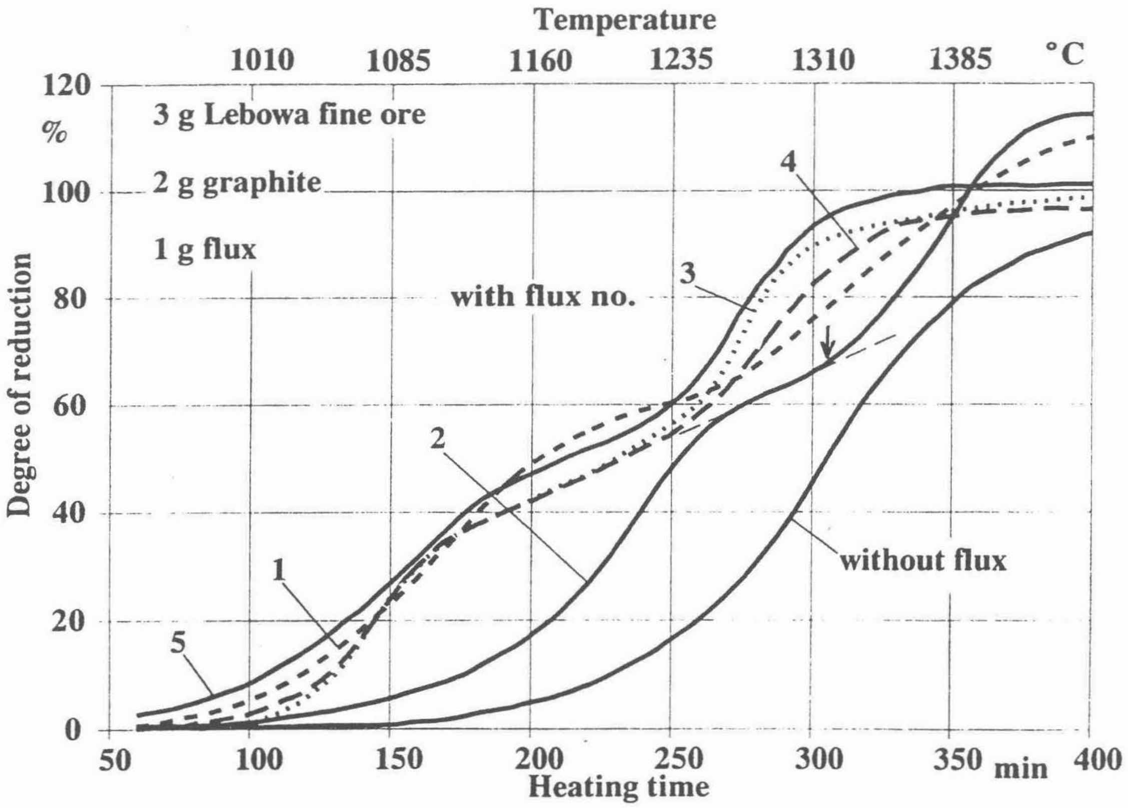


FIG. 2. Reduction rates of chromite fines with carbon in the presence of different fluxes
Note: Reduction degrees above 100% are due to SiO_2 reduction !

TABLE 3: Onset temperatures of acceleration stages

Sample	First acceleration stage	Second acceleration stage
without flux	1200°C	-
with flux 1	1040°C	1270°C (R = 61%)
" 2	1120°C	1320°C (R = 65%)
" 3	1050°C	1200°C (R = 46%)
" 4	1050°C	1210°C (R = 48%)
" 5	1020°C	1225°C (R = 55%)

A higher reduction rate was obtained with flux 2 (containing no CaO), where 25% reduction were reached at 1185°C, 50% at 1240°C, and 90% at 1375°C. All other flux additions resulted in even stronger acceleration of the reduction: 25% reduction were already obtained at about 1090°C, 50% at 1150 - 1220°C, and 90% at 1310 - 1350°C. The shape of the reduction curves of samples containing fluxes differs markedly from the curve obtained for the flux-free sample. The latter shows only one stage of acceleration (between 0 and 50% reduction) while all other samples reveal a second stage of acceleration which starts at 50 to 65% reduction.

Although the first acceleration actually starts at zero reduction, we arbitrarily define 10% reduction as its starting point. The onset of the second stage is taken as the temperature where the reduction curve deviates from the straight line when extrapolated between two stages. For illustration, Fig. 2 contains a vertical arrow pointing at the onset temperature of the second stage in the curve for flux no. 2. The onset temperatures of the two acceleration stages are listed in Table 3.

Microprobe Analyses

A selection of samples taken at different reduction stages were analyzed with the electron microprobe. The chemical compositions of the multi-component oxidic phases of samples reduced in the presence of fluxes 1 and 4 are given in Table 4.

TABLE 4: Composition of multi-component oxidic phases in samples reduced in the presence of fluxes 1 and 4

Flux no.	Degree of reduction R	Phase no.	Composition (mass-%)					
			CaO	SiO_2	Al_2O_3	MgO	Cr_2O_3	CaF_2
1	63%	1	x	(x)	x	(x)	-	-
"	85%	2	10	20	45	22	3	-
"	> 100%	3	28	47	21	4	-	-
4	54%	4	46	42	-	12	-	-
"	"	5	35	39	-	25	-	-
"	"	6	25	56	-	19	-	-
"	"	7	51	30	3	-	-	15
"	97%	8	51	33	-	3	-	13
"	"	9	31.5	41.5	-	27	-	-
"	"	10	38.5	28.5	29.3	3.6	-	-

x = major, (x) = minor component

A fluxless sample at 40% reduction shows the typical picture of partial chromite reduction, Fig. 3. The unreacted chromite core is surrounded by a relatively dense rim of spinel made up of ca. 56% Cr_2O_3, 22% Al_2O_3, 14% MgO, and 8% FeO. Outside the rim, isolated metal droplets are found being composed of (Fe,Cr) carbides and alloys. No other oxidic phases were found in the partially reduced sample. As is known from previous investigations [8], the gangue components will form $MgO{\cdot}Al_2O_3$ spinel and a very small amount of siliceous slag in the final stage of reduction.

Samples with flux 1: Samples were taken from 3 runs at 63, 85 and > 100 % reduction. At 63% reduction, a narrow zone between the Mg-rich chromite rim and the metallic particles was identified containing Al_2O_3 and CaO and in smaller quantities MgO and SiO_2. The sample reduced to 85% contained $MgO{\cdot}Al_2O_3$, Mg-silicates and, between the metal particles, a porous "phase" composed of 22% MgO, 45% Al_2O_3, 20% SiO_2, 10% CaO and 3% Cr_2O_3. In the completely reduced sample, $MgO{\cdot}Al_2O_3$, Mg-silicates with 47-55% MgO, and Casilicate ($CaO{\cdot}SiO_2$) containing several percent of Al_2O_3 and MgO, were identified. A major "slag phase" was found to be composed of 32% (CaO + MgO), 47% SiO_2, and 21% Al_2O_3.

Samples with flux 4: A sample reduced to 54% contained as ternary phase Ca-Mg-silicates with varying compositions ranging from 12 to 25 % MgO, from 25 to 46 % CaO, and from 38 to 56 % SiO_2. The fluoride was found in a phase composed of 15 % CaF_2, 51 % CaO, 30 % SiO_2, and 3 % Al_2O_3. A completely reduced sample (R = 97 %) contained the CaF_2 in a very similar composition, namely 13 % CaF_2, 51% CaO, 33 % SiO_2, and 3 % MgO. Ca-Mg-silicates containing 27,3 % MgO, 41,6 % SiO_2, and 31,5 % CaO (phase 9), or 29,3 % Al_2O_3, ca. 42 % (CaO+MgO), and 28,5 % SiO_2 (phase 10) occur as larger particles. In addition, phases containing $MgO{\cdot}Al_2O_3$ and Mg-silicate are found.

DISCUSSION

Reduction experiments of Lebowa chromite ore in the presence of flux revealed two stages of acceleration with temperature. For the second stage, the onset temperatures were in the range 1200 to 1320°C, and the corresponding degrees of reduction were between 46 and 65%. It is suggested that this second acceleration is caused by the formation of eutectic melts in the multi-component nonmetallic systems. The overall composition of the non-reducible components as obtained by adding up the gangue and the flux components of a sample are listed in Table 5, together with the lowest melting eutectic compositions [14] of the corresponding systems. In this context SiO_2 was taken as a non-reducible component. A comparison of onset temperatures of the second acceleration stage with eutectic temperatures shows relatively good agreement, Table 6. For the fluxless sample, the second acceleration

TABLE 5: Overall compositions of non-reducible sample components and corresponding lowest melting eutectic compositions [14]

Flux no.	Composition of		Temp. of eutectic	mass-%				
	sample	eutectic		CaO	SiO_2	Al_2O_3	MgO	CaF_2
1	x			15,1	29,1	34,3	21,5	-
		x	1235°C	34	45	11	10	-
2	x			0.3	37.5	33.4	28.8	-
		x	1365°C	-	53	21	26	-
3	x			26.0	9.5	24.1	17.0	23.4
		x	1115°C	55	11	-	-	34
4	x			23.6	16.4	24.1	17.0	18.9
		x	1115°C	44	18	-	-	38
5	x			22.3	1.9	42.3	17.0	16.6
		x	1230°C	40	-	20	-	40
without flux	x			0.8	4.3	55.7	39.2	-
		x	1480°C	-	45	38	17	-

stage was not observed (Fig.3), because its onset temperature was above our range of investigations.

TABLE 6: Comparison of onset temperatures of second acceleration stages and eutectic temperatures of non-reducible sample components

Flux no.	Onset temp. (°C)	Eutectic temp. (°C)
no flux	> 1450	1480
2	1320	1365
1	1270	1235
5	1225	1230
4	1210	1115
3	1200	1115

While the second stage of acceleration may be correlated to the formation of a liquid slag phase, the onset temperatures of the first acceleration lie well below the lowest eutectic temperatures of the relevant nonmetallic systems. It is therefore concluded that solid-state reactions between flux and gangue may be responsible for the accelerations observed in this stage.

Figures 3, 4 and 5 show micrographs of partially reduced chromite grains, namely a flux-free sample (Fig. 3, 1300°C, R = 40 %), a sample containing flux 4 (Fig. 4, 1170°C, R = 54 %), and a sample containing flux 1 (Fig. 5, 1230°C, R = 63 %).

In all three cases, the unreacted chromite core (lighter grey) is surrounded by a zone of Mg-Al-Cr spinel (darker grey) and metallic phase (white). In the absence of flux addition, the metal forms relatively few, spherical particles at the outer rim of the grain. Only a small number of cracks are observed in the dark zone. These cracks which are filled with metal do hardly ever penetrate into the core. With fluxes added, the metal phase covers the whole grain in the form of small irregular fibres which also extend into the darker zone. The number of cracks is larger and they penetrate into the core more frequently. With fluxes present, the chromite surface has obviously been roughened considerably, more cracks have formed and the nucleation of the metal phase has definitely been facilitated.

Obviously, the differences in reduction behavior are related to the effect of the additives. It is therefore assumed that in the presence of fluxes, ternary phases are formed in the solid state at temperatures above 1000°C. Their formation causes mechanical stress affecting the chromite grains leading to microcracks and roughening of the grain surfaces.

From the compositions of the multi-component nonmetallic phases detected in samples containing fluxes (Table 4), a number of possible ternary compounds can be deduced which are listed in Table 7. Apparently, samples reduced with flux 1 contain monticellite and anorthite, while in samples with flux 4, merwinite, diopside, and gehlenite are assumed to have formed in addition to monticellite. The formation of all of these compounds is thermodynamically probable if reactions start from $MgO \cdot Al_2O_3$ and free silica and lime. The relevant reactions and their $\Delta G°$ values for 1400 K, which are all negative, are listed in Table 8 [15]. In the case of flux 2, the formation of cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ is assumed as the only relevant ternary oxide since flux 2 does not contain any lime.

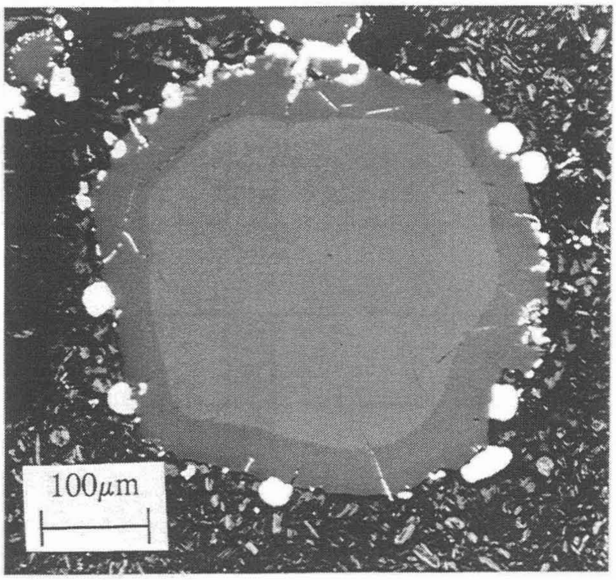
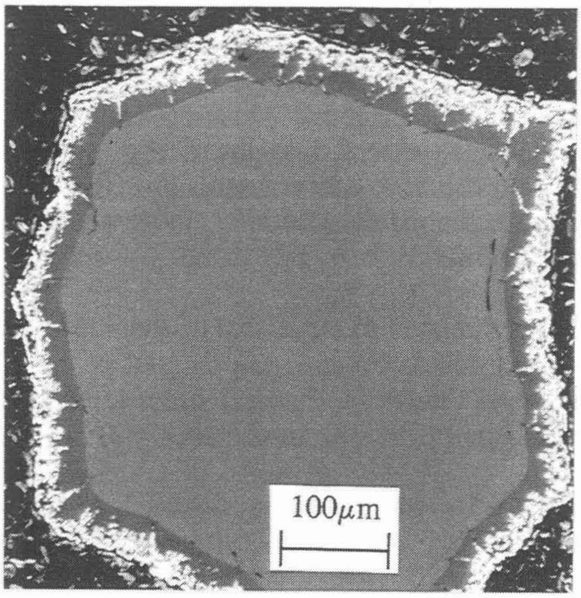


FIG. 3: Chromite ore reduced to R = 40 % without fluxes. Unreacted chromite ore (lighter grey) surrounded by Cr-rich spinel (dark grey) and by isolated spherical metal particles (white). Occasionally, metal is also found in cracks.



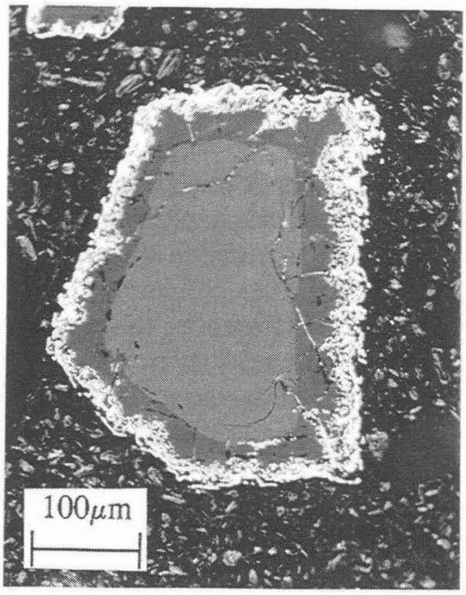


FIG. 4:Chromite ore reduced to R = 54 % in the presence of flux 4. Numerous small metal particles form a nearly dense rim around the unreacted core and the Cr-rich spinel zone.

FIG. 5:Chromite ore reduced to R = 63 % in the presence of flux 1. Again, small metal particles form a nearly dense rim around the core and the Cr-rich spinel zone. Numerous metal-filled cracks are found in the grain.

TABLE 7: Ternary compounds assumed in samples according to compositions listed in Table 4

Flux no.	Phase no. (Table 4)	Assumed compounds
1	2	$CaO{\cdot}MgO{\cdot}SiO_2$ (monticellite) + $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ (anorthite) (+ $MgO{\cdot}Al_2O_3$)
1	3	$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ + $CaO{\cdot}SiO_2$ (eutectic mixture)
4	4	$3CaO{\cdot}MgO{\cdot}2\frac{1}{2}SiO_2$ (merwinite)
4	5	$CaO{\cdot}MgO{\cdot}SiO_2$
4	6	$CaO{\cdot}MgO{\cdot}2SiO_2$ (diopside)
4	7	$2CaO{\cdot}SiO_2$ (84%) + CaF_2 (16%)
4	8	similar to phase no. 7
4	9	close to $CaO{\cdot}MgO{\cdot}SiO_2$
4	10	$2CaO{\cdot}Al_2O_3{\cdot}SiO_2$ (gehlenite)

TABLE 8: Formation reactions of ternary nonmetallic compounds and their free enthalpies of formation at 1400 K [15]

Reaction no.	Reaction	ΔG° (1400 K) kJ
(1)	$MgO{\cdot}Al_2O_3 + 2\ CaO + 3\ SiO_2 = CaO{\cdot}MgO{\cdot}SiO_2 + CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	- 224.2
(2)	$MgO{\cdot}Al_2O_3 + 3\ CaO + 2\ SiO_2 = CaO{\cdot}MgO{\cdot}SiO_2 + 2CaO{\cdot}Al_2O_3{\cdot}SiO_2$	- 276.5
(3)	$MgO{\cdot}Al_2O_3 + 3\ CaO + 2\ SiO_2 = MgO{\cdot}3CaO{\cdot}2SiO_2 + Al_2O_3$	- 245.6
(4)	$MgO{\cdot}Al_2O_3 + CaO + 2\ SiO_2 = MgO{\cdot}3CaO{\cdot}2SiO_2 + Al_2O_3$	- 112.8
(5)	$MgO{\cdot}Al_2O_3 + 2\frac{1}{2}\ SiO_2 = \frac{1}{2}\ (2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2)$	-33.8

CONCLUSIONS

The reduction of chromite ore fines with carbon in the temperature range 1000 to 1450°C is accelerated in the presence of fluxes containing at least three of the components CaO, SiO_2, Al_2O_3, MgO, CaF_2. The acceleration takes place in two stages:

(1) The first effect is noticeable at 1000 to 1100°C when all phases are still solid, and is attributed to the solid-state formation of ternary oxides leading to surface roughening of the chromite grains and facilitating metal phase nucleation. In addition, a higher number of microcracks in the chromite grains is observed. In fluxless samples, reduction only starts around 1200°C.

(2) The second effect is found at 1200 to 1300°C and can directly be related to the formation of liquid eutectics of the nonmetallic components. Liquid slag dissolves part of the $MgO \cdot Al_2O_3$ spinel which formed around unreduced chromite grains and acted as a diffusion barrier. It may also enhance the reduction of chromium oxide by dissolving it and transporting the chromium ions more quickly to the nearest carbon grain for reduction. In the absence of fluxes, the lowest slag eutectic temperature is 1480°C.

Through the addition of fluxes the temperature for 90% reduction of Lebowa chromite fines can be lowered by up to 150 degrees.

REFERENCES

[1] Urquhart, R.C., Jochens, P.R. and Howat, D.D.: A laboratory investigation of the smelting mechanisms associated with the production of high-carbon ferrochromium, Proceedings INFACON 1974, Johannesburg, pp. 231-245, 1974.

[2] Katayama, H.G., and Tokuda, M.: The reduction behavior of synthetic chromites by carbon, Trans. ISIJ, vol. 20, pp. 154-162, 1980.

[3] Wedepohl, A.: The mineralogy of the reduction of chromium ore in a plasma furnace, Mintek 50, Proceedings International Conference of Mineral Science and Technology, Sandton, March 1984, vol. 2, pp. 905-912, 1985.

[4] Fernandes, T.R.C.: Chromite Mineralogy and Metallurgical Behavior, Mintek 50, Proceedings International Conference of Mineral Science and Technology, Sandton, March 1984, vol. 2, pp. 913-921, 1985.

[5] Katayama, H.G., Tokuda, M. and Ohtani, M.: Promotion of the Carbothermic Reduction of Chromium Ore by the Addition of Borates, Tetsu to Hagane vol 72, pp. 1513-1520, 1986.

[6] Slatter, D. and Ford, M.: Reactions and phase relationships in a d.c. arc plasma furnace producing ferrochromium. Proceedings INFACON 5, pp. 103-111, New Orleans, 1989

[7] Katayama, H., Kuwabara, M., Hirata, H. and Izawa, T.: Production of ferrochromium by smelting reduction with top and bottom blowing converter, Proceedings SRNC-90, Pohang, Korea, pp. 297-306,1990.

[8] Neuschütz, D.: Kinetic aspects of chromite ore reduction with coal at 1200 to 1550°C, Proceedings INFACON 6, Vol.1, pp. 65-70, Johannesburg, SAIMM, 1992.

[9] Van Vuuren, C.P.J., Bodenstein, J.J., Sciarone, M. and Kestens, P.: The reduction of synthetic iron chromite in the presence of various metal oxides - a thermoanalytical study, Proceedings INFACON 6, Vol.1, pp. 51-56, Johannesburg, SAIMM, 1992.

[10] Niayesh, M.J. and Dippenaar, R.J.: The solid-state reduction of chromite, Proceedings INFACON 6, Vol.1, pp. 57-64, Johannesburg, SAIMM, 1992.

[11] Weber, P. and Eric, R.H.: Solid-sate fluxed reduction of LG-6 chromite from the Bushveld Complex, Proceedings INFACON 6, Vol.1, pp. 71-78, Johannesburg, SAIMM, 1992.

[12] Xu, S. and Dai, W.: The melting behaviour of chromite ores and the formation of slag in the production of high-carbon ferrochromium, Proceedings INFACON 6, Vol.1, pp. 87-92, Johannesburg, SAIMM, 1992.

[13] Neuhaus, R.: Der Einfluß der chemischen Zusammensetzung der Schlackenphase auf die Reduktionsgeschwindigkeit von Chromerzen, Diplomarbeit, März 1993, Institut für Mineralogie und Lagerstättenlehre, RWTH Aachen.

[14] Phase Diagrams for Ceramists, The American Ceramic Society, Columbus, Ohio, 1964, 1969, 1975, 1981, 1983.

[15] Barin, I.: Thermochemical Data of Pure Substances, Weinheim, 1989.