MICROSTRUCTURE CHANGES OF CHROMITE REDUCED WITH CO GAS

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ABSTRACT

In the present paper, microstructure changes of solid-state reduction of industrial chromite pellets and lumpy ore were investigated with SEM/EPMA. To simulate the reactions in the packed bed zone of the Submerged Arc Furnace (SAF), carbon monoxide was used as the reducing agent, with the presence of graphite in proximity to chromite. The experiments were carried out at 1500 °C. Scanning electron microscopy was used to observe and analyse the structure and composition changes of the chromite samples. It was found that reduction of lumpy ore generally took place slower than that of pellet. In all samples, chromite reduction proceeded faster in the outer part of the sample than in the centre part. The reaction mechanism is discussed on the basis of experimental results and earlier investigations. The possibilities to optimize the FeCr production process are also discussed.

1. INTRODUCTION

Submerged Arc Furnace (SAF) is often used to smelt chromite ores into ferrochrome by using carbonaceous reductants. Furnace feed contains mainly chromite (lumpy ore and pellets), reductant (coke, anthracite, char,), and flux (quartzite, dolomite, lime, etc.). The compositions and quantities of the flux added are to control the slag properties, for example liquidus temperature, viscosity and electrical conductivity, for an efficient operation of the process. The size and shape of chromite pellets, lumpy ore, coke and fluxes are controlled for a good permeability of the packed bed. The energy consumption is relatively high, and for high carbon ferrochrome the electrical energy consumption varies between 2000 kWh/t alloy with pre-reduction to 4000 kWh/t alloy without pre-reduction and feed preheating. Because of the complexity of feed and electrical-thermal-chemical interactions, large temperature gradients exist in the furnace and the temperature ranges from a few hundreds at the surface of the burden to well over 2000°C around the electrode tips. This leads to various zones and different reaction mechanisms in the furnace, as is clearly exemplified by the dig-out of furnaces with various sizes for ferrochromium production [1-3].

Because of the large temperature gradient in the Submerged Arc Furnace, quite different reduction mechanisms exist in different reaction zones. As a prerequisite to analyse the furnace, and further to simulate the reduction progress within the furnace charge, it is essential to understand the microstructure changes during the sintering and reduction processes. Due to the variation of the chromite composition, different ore types may behave in different ways and thus can have different reaction mechanisms. In previous studies the reaction kinetics of solid-state carbothermal and CO gas reduction of industrial chromite pellets have been investigated [4]. The unreacted core model was applied to analyse the reaction mechanism of carbon-containing chromite pellet, the reaction thermodynamics were assessed, and a modified grain model was developed to mathematically simulate the CO reduction of chromite pellets [5, 6]. Reviewing the information in the literature, several studies were reported on chromite reduction with carbon [4, 7-14], but only a few studies on chromite reduction with CO gas [7, 12, 14]. Chromium behaviour in the SAF for ferrochrome production, from chromite to metallic alloy, has been recently described elsewhere [15]. Reaction kinetics of the reduction

of various chromite samples have been investigated on laboratory scale [16]. In the present paper, the details of the microstructure changes of the partially reduced industrial chromite pellet and lumpy ore are further examined, and the reaction mechanism of chromite reduction in the gas – solid reaction zone is confirmed. The results are expected to provide quantitative information for the kinetic modelling of chromite reduction.

2. REACTION ZONES IN THE SAF FURNACE

Submerged Arc Furnaces for ferrochrome production are very complex in both physical and chemical aspects. In general, the furnace can be divided into six regions, as illustrated in Figure 1: (1) the loose charge packed bed region at the upper part of the furnace with a large temperature gradient, where the chromite ores are heated and reduced in solid state; (2) the smelting region around electrode tips above the coke bed and/or slag layer; (3) the coke beds under the electrodes and/or between the electrodes and the furnace wall; (4) the inactive zone adjacent to the furnace wall and above the slag/metal layer; (5) the molten slag layer, where the oxides in the ore and flux form slag, and the chromite is further dissolved into the slag to be reduced with the carbon in both slag and metal; and (6) the molten alloy layer at the bottom part of the furnace.

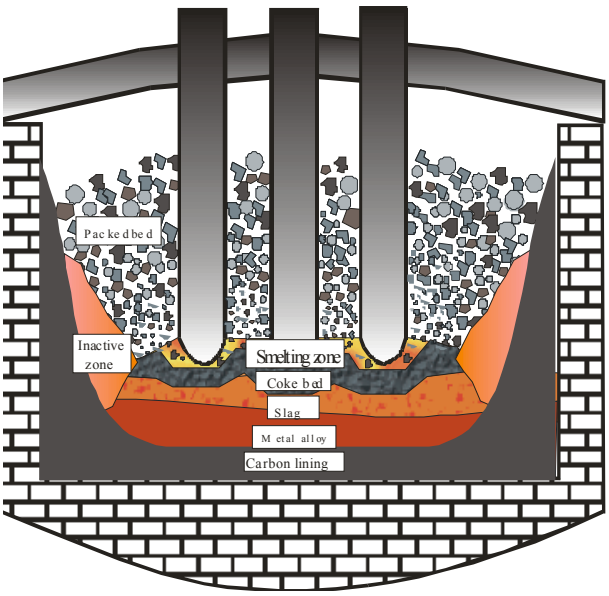


Figure 1: Schematic diagram of the reaction zones in Submerged Arc Furnace for FeCr production

The zones are classified based on the information reported in the literature [1-3], and they may vary with furnace design, size and operation conditions. For example, the size and location of the coke beds may change with the charge input and process operation, and they may not exist as a significant part in the furnace [2]. They may be present but in different locations either under the electrode tips [3] or between the electrode and the wall and between the two electrodes [1]. The ore layer indicated by Yamagishi et al. [1] demonstrated the difficulty of the melting, reduction and dissolution of the lumpy ore. This may also depend very much on the furnace scale and operation parameters, for example the energy distribution and materials flow in the furnace. In addition, the size of the inactive zone in the furnace also depends greatly on the furnace control. According to the furnace dig out investigation, it can be generally seen that the packed bed zone is large in volume, which should play a significant role if the process operation is optimized.

3. REACTIONS IN THE PACKED BED ZONE

In the packed bed, the loose charge experiences an increasing temperature environment while the charge descends, and the chromite pellet or lumpy ore is reduced by the ascending CO gas and the reduction is promoted by contacted coke particles. The continuous CO gas is mostly generated in the smelting and coke bed zones from the Boudouard reaction and the reduction reactions of the chromite pellet (or lumpy ores). It is obvious that temperature profile within the packed bed has a great influence on the rate of the solid state reduction of chromite. On the other hand, reaction kinetics of the gas and solid reduction process also plays an important role in the localised and overall energy and temperature distribution. Energy required by the carbothermic reduction reactions is supplied through the submerged arcs and electrical conduction in the solid bed and in the molten slag. The rate of solid state reduction is greatly affected by gas phase temperature distribution and gas flow pattern, chromite type as well as the compositions of the feed. It is assumed that the temperature in this region can change from a few hundred degrees up to over 1500 °C.

The reduction feasibility of the reducible constitutes in the chromite by CO gas has been thermodynamically analysed [6] in the temperature range of 700 to 1650 °C. The activities of the solid reactants and products were assumed to be unity in the calculation. It can be seen that reduction of chromite pellet with CO is a very complicated process. It starts with reduction of iron oxides, and the chromium oxides will be reduced only at high temperatures and with low CO_2 to CO ratio. By comparing the equilibrium ratio of P_{CO2}/P_{CO}, Fe_2O_3 in the chromite grains in the pellet or lumpy ore will be reduced first into magnetite $FeFe_2O_4$(s) which is easier to be reduced than iron chromite $FeCr_2O_4$(s). At the same temperature, the reduction tendency of $FeCr_2O_4$(s) is much greater than that of $MgCr_2O_4$(s), and the reduction of $MgCr_2O_4$(s) needs a higher starting temperature than that of $FeCr_2O_4$(s).

In practice, a chromite particle may undergo different reactions at different locations within a single ore lump or pellet. The chromite reduction with CO gas can proceed simultaneously in the chemical compounds of $FeFe_2O_4$, $(Fe,Cr)_2O_3$, $FeCr_2O_4$ and $MgCr_2O_4$, when the temperature is high enough. The reaction can be controlled by a complex parallel series sequence of chemical and transport steps, and the reduction reactions normally should proceed through the series from higher valence to lower valence, and finally to the metallic iron and chromium. The various reactions may also interact with one another. The reaction boundaries may be visible or indiscernible due to the various diffusion effects.
It is assumed that the direct reduction of chromite lumpy ore/pellet by carbon/coke particles is negligible in the packed bed. The chromite particles are mainly reduced by CO gas, which is constantly supplied via the Boudouard reaction. The reduction of chromite pellet with CO gas is characterized by different interrelated mechanisms and steps. The following global reactions may illustrate the overall reduction of the chromite in the packed bed:

$$FeCr_2O_4 + 4\ CO(g) = 2\ Cr + Fe + 4\ CO_2 \quad \text{Solid-state reduction with CO)} \tag{1}$$

$$CO_2(g) + C = 2\ CO(g) \quad \text{(The Boudouard reaction} \tag{2}$$

$$FeCr_2O_4 + 4\ C = 2\ Cr + Fe + 4\ CO(g) \quad \text{(Overall reaction)} \tag{3}$$

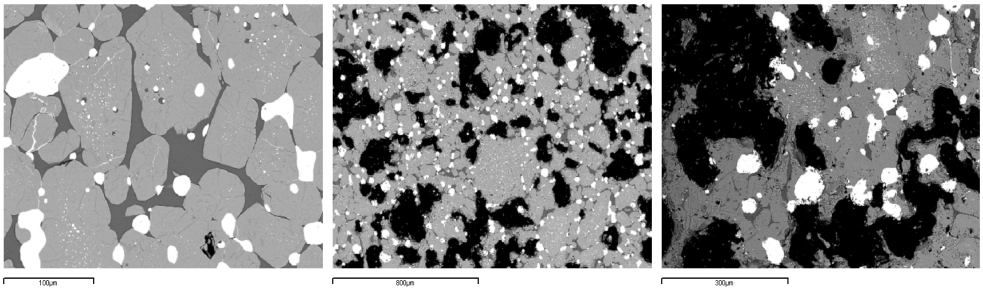
For the chromite reduction, topochemical reactions occur in the chromite, when iron oxides at the surface of the chromite particles are reduced to metal prior to chromium oxides. The fine metal beads are formed initially on the chromite surface and further along the pellet pores and the cracks within the chromite particles and lumpy ore. The reduction degree increased significantly towards the surface of chromite pellet or lumpy ore [16]. The formed metal phase is distributed at the surface of the chromite particles, also along the fissure inside chromite grains. The gangue mineral was melted and sintered around the chromite particle. Comparing to the pellet samples, the lumpy ore is nearly non-porous [16].

4. OBSERVATION OF REDUCED CHROMITE SAMPLES

Two types of chromite were investigated in this work: industrial pellets and chromite lumpy ore. Industrial pellets, lumpy ore and coke were provided by Outokumpu Stainless Steel, Tornio Works, Finland.

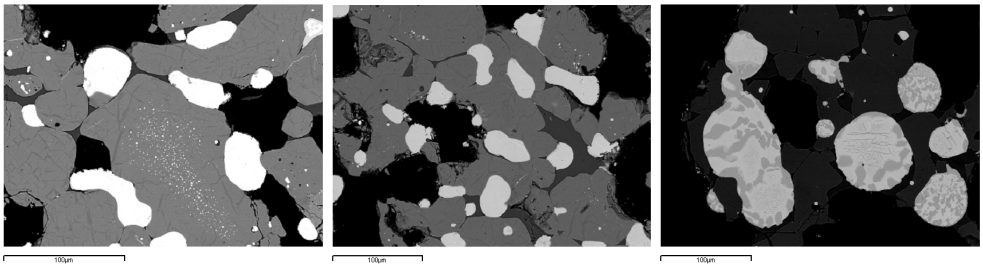
4.1 Industrial Pellets

Industrial pellets were reduced with CO at the flow rate of 2.0 l/min at 1500 °C for 4 and 16 hours, respectively. After the reaction, the samples were cooled in the furnace under N_2 atmosphere. Figures 2 and 3 illustrate the microstructure of the reduced industrial pellets at different locations after 4 hours and 16 hours reduction, respectively. More metal was formed from the reduction with longer reduction time. From the photograph taken at the surface area of the pellet reduced long time, two phases were observed and could be distinguished analytically within a single metal bead: iron based alloy – a light colour phase with composition of 23.0 wt% Cr and 75.7 wt% Fe on average, and chromium based alloy – a dark colour phase with composition of 84.9 wt% Cr and 13.6 wt% Fe, as shown in Figure 3. The major compositions in different phases within the pellets were analysed with an X-ray energy dispersive spectrometer (EDS), and are given in Table 1 and represented in Figure 4. Here each value is an average of 3 – 6 analysed points.



Pellet centre Pellet half radius Pellet surface

Figure 2: Backscattered images from different locations of an industrial pellet reduced with CO for 4 hours; white: metal phase; light grey: partially reduced chromite; dark grey; sintered gangue minerals; dark: void



Pellet centre Pellet half radius Pellet surface

Figure 3: Backscattered images from different locations of an industrial pellet reduced with CO for 16 hours; white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void; Metal phase in surface area: light colour with 23.0 wt% Cr and 75.7 wt% Fe, and dark colour with of 84.9 wt% Cr and 13.6 wt% Fe

It can be seen that the reduction degree increased significantly towards the pellet surface, as indicated from the analysis both in chromite and metal phases. By increasing the reaction time, more chromium has been reduced and dissolved into the iron based metal phase. In addition, a certain amount of silicon has also been reduced and alloyed into the FeCr metallic phase.

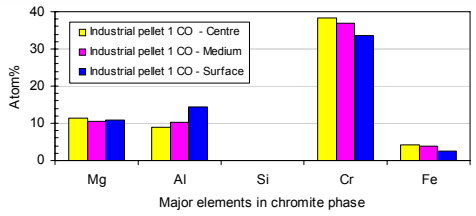
4.2 Lumpy Ore

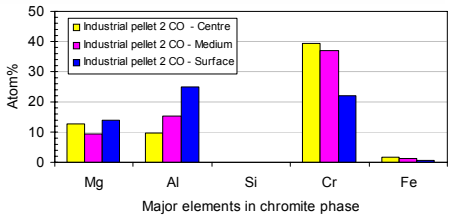
A spherical chromite lumpy ore was reduced with carbon monoxide (2 l/min) at 1500 ºC for 4 hours. In order to compare the difference resulting from solid carbon proximity, a packed bed experiment was designed to pack chromite lumpy ore (28.28 g) and coke (7.85 g) in an alumina crucible. Plenty of holes were drilled in and distributed over the wall of the crucible to maintain a homogeneous reducing atmosphere around the reacting sample. The lumpy ore contacted with solid carbon (coke) was observed to reduce much faster [16].

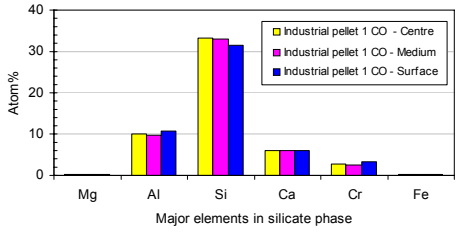
Figure 5 shows the microstructure changes of the chromite reduced by CO gas through the cross section of the spherical lumpy ore sample. For the chromite lumpy ore reduced by carbon monoxide, mainly iron oxides were reduced, less than 1.5 wt% Cr was alloyed in the metal phase, as shown in Table 2 and in Figure 6. The formed metal phase is mainly distributed at the surface of the chromite particles, also along the fissure inside chromite grains.

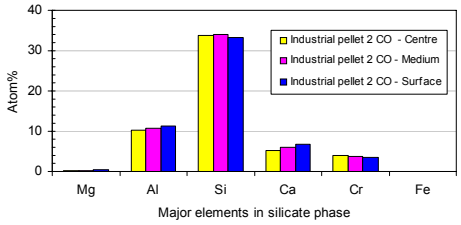
Table 1: EDS analyses of industrial pellets reduced with CO gas at 1500 °C for 4 and 16 hours

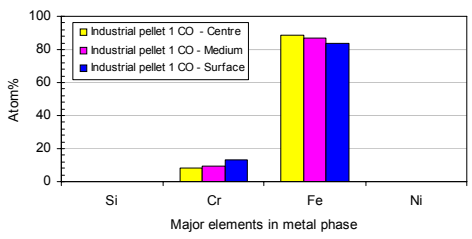
Sample	Phase	Location	Atom%						
			Mg	Al	Si	Ca	Cr	Fe	Ni
4 hrs	Chromite	Centre	11.49	8.96	0.00	---	38.41	4.09	---
		Medium	10.66	10.37	0.00	---	36.89	3.79	---
		Surface	10.74	14.55	0.06	---	33.48	2.40	---
	Silicate	Centre	0.24	9.99	33.19	5.93	2.85	0.31	---
		Medium	0.20	9.69	33.12	5.90	2.61	0.25	---
		Surface	0.30	10.85	31.56	6.11	3.33	0.25	---
	Metal	Centre	---	---	0.17	---	8.09	88.71	0.11
		Medium	---	---	0.12	---	9.59	86.89	0.00
		Surface	---	---	0.28	---	13.03	83.85	0.06
16 hrs	Chromite	Centre	12.59	9.56	0.06	---	39.41	1.75	---
		Medium	9.37	15.29	0.00	---	37.12	1.49	---
		Surface	14.01	25.01	0.11	---	22.11	0.78	---
	Silicate	Centre	0.26	10.15	33.87	5.37	4.02	0.07	---
		Medium	0.27	10.67	33.97	6.02	3.83	0.07	---
		Surface	0.42	11.30	33.27	6.68	3.54	0.06	---
	Metal	Centre	---	---	0.24	---	15.30	81.43	---
		Medium	---	---	0.33	----	20.91	75.63	---
		Surface	---	---	0.42	---	45.18	50.41	---
		Sur.light	---	---	0.64	---	23.64	72.49	---
		Sur.dark	---	---	0.00	---	83.14	12.42	---

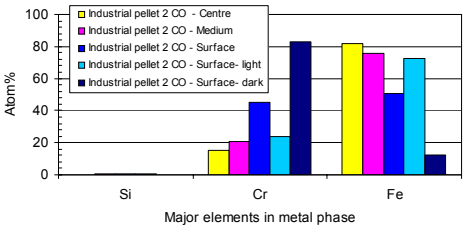








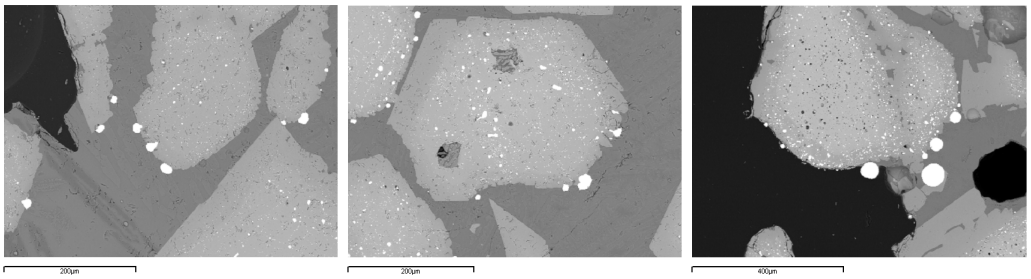




Reduced for 4 hours

Reduced for 16 hours

Figure 4: EDS analyses of industrial pellets reduced with CO gas for 4 to 16 hours, respectively



Lumpy ore centre Half radius of lumpy ore Lumpy ore surface

Figure 5: Backscattered images from different locations of the lumpy ore reduced with CO gas for 4 hours. white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void

Table 2: EDS analyses of lumpy ore reduced with CO gas

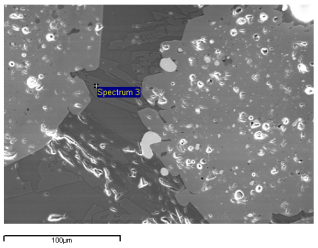
Sample	Phase	Location	Atom%						
			Mg	Al	Si	Ca	Cr	Fe	Ni
1500 °C 4 hrs	Chromite	Centre	12.08	12.59	0.06	---	33.38	6.11	---
		Medium	12.68	11.64	0.06	---	34.53	5.22	---
		Surface	13.39	14.66	0.21	---	30.86	3.69	---
	Silicate	Centre - light	7.63	5.05	25.89	13.86	0.73	2.26	---
		Centre - dark	1.69	9.85	29.98	8.75	0.19	3.43	
		Medium - light	8.59	4.62	26.19	12.98	0.73	1.82	---
		Medium - dark	1.62	10.70	30.01	8.01	0.16	1.96	
		Surface - light	7.64	5.17	27.20	11.67	1.01	1.14	---
		Surface - dark	7.69	7.99	29.37	6.80	0.32	1.14	
	Metal	Centre	---	---	0.00	---	1.71	94.31	1.25
		Medium	---	---	0.00	---	1.06	92.10	3.96
		Surface	---	---	0.19	---	1.18	95.23	0.27

The gangue mineral was melted and sintered around the chromite particle. Through observing the microstructure of the silicate phase in the reduced lumpy ore, it was found that two different silicate phases co-exist in the reduced chromite ore: the light grey with higher calcium oxide and/or magnesium oxide, as compared with that in the dark grey silicate phase, as shown in Figure 7.

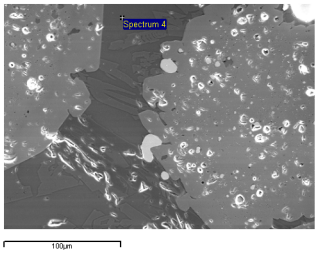
For the experiment of simulated packed bed, two reduced lumpy ore samples were selected and analysed: one closely packed and the other one loosely packed lump with coke. The results are shown in Figures 8 – 10. It proved that the presence of coke promoted Cr reduction and the highest reduction degree was obtained for the lumpy ore closely packed with coke.

Normally the larger metal beads produced contain a higher amount of Cr and Si than the smaller metal beads in the same location, for example at the surface area of the reduced lumpy ore with CO and the loosely packed coke. The analysis results are presented in Table 3 and Figure 10.

The presence of coke particles promotes chromite reduction and the highest reduction degree is obtained for the lumpy ore closely packed with coke. It can be generally concluded that the reduction of chromite with only carbon monoxide is possible in the absence of coke, but the presence of solid carbon is essential to convert the formed CO_2 gas back to CO via the Boudouard reaction.



Light grey



Dark grey

Figure 7: Two phases in silicate phase

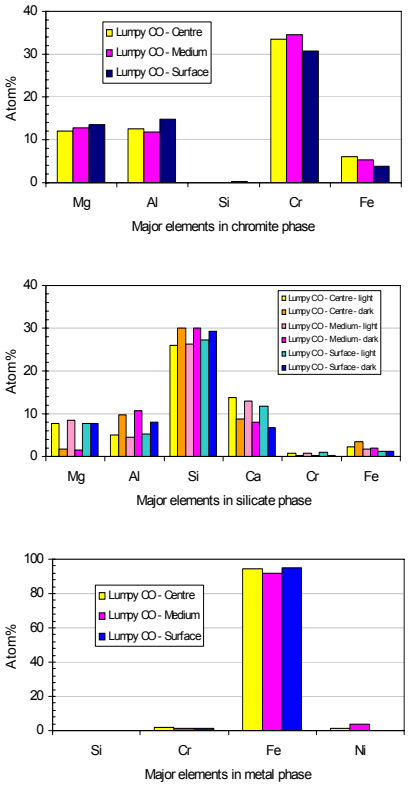
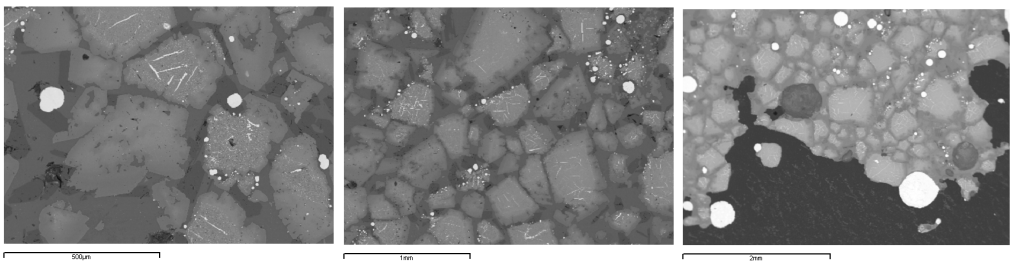


Figure 6: EDS analyses from lumpy ore sample reduced with CO gas



Lumpy ore centre Half radius of lumpy ore Lumpy ore surface

Figure 8: Backscattered images from different locations of the lumpy ore reduced with CO/coke. Closely packed bed; white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void

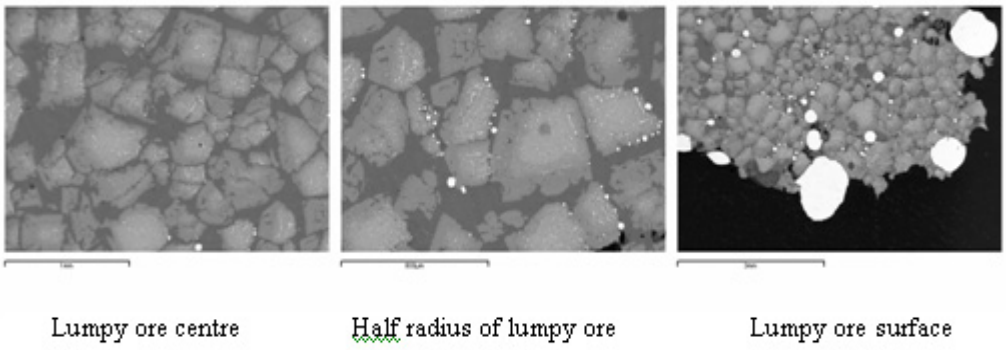


Figure 9: Backscattered images from different locations of the lumpy ore reduced with CO/coke. Loosely packed bed; white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void

Table 3: EDS analyses of lumpy ore reduced with CO/coke at 1500 °C for 4 hours

Sample	Phase	Location	Atom%						
			Mg	Al	Si	Ca	Cr	Fe	Ni
Closely packed	Chromite	Centre	16.51	21.42	0.18	---	27.10	0.35	---
		Medium	16.37	18.54	0.09	---	29.76	0.35	---
		Surface	16.60	24.40	0.16	---	22.16	0.13	---
	Silicate	Centre - light	3.90	9.40	31.76	9.11	2.20	---	---
		Centre - dark	31.49	0.00	26.12	0.08	3.19	---	
		Medium-light	4.21	9.44	30.82	8.82	2.44	---	---
		Medium-dark	31.12	0.00	25.76	0.20	3.07	---	
		Surface - light	3.63	10.42	30.43	8.62	1.71	---	---
		Surface - dark	31.00	0.04	25.46	0.08	2.74	---	
	Metal	Centre	---	---	0.83	---	19.59	73.81	2.70
		Medium	---	---	0.96	---	21.33	72.48	1.56
		Surface	---	---	0.96	---	35.12	59.28	0.00
Loosely packed	Chromite	Centre	15.28	19.07	0.05	---	26.97	0.81	---
		Medium	14.75	14.96	0.05	---	31.13	0.94	---
		Surface	15.08	16.68	0.00	---	29.98	0.53	---
	Silicate	Centre - light	29.94	0.00	24.36	0.00	3.04	0.63	---
		Centre - dark	17.38	4.22	29.36	0.10	3.94	0.24	
		Medium	13.65	4.43	31.20	0.76	3.81	0.25	---
		Surface	3.28	9.30	34.78	1.78	3.32	0.00	---
	Metal	Centre	---	---	0.33	---	6.63	89.41	0.91
		Medium	---	---	0.07	----	8.39	88.60	0.12
		Sur. - large	---	---	0.64	---	17.21	78.66	0.00
		Sur. - medium	---	---	0.60	---	13.78	82.45	0.16
		Sur. - small	---	---	0.60	---	11.76	84.48	0.00

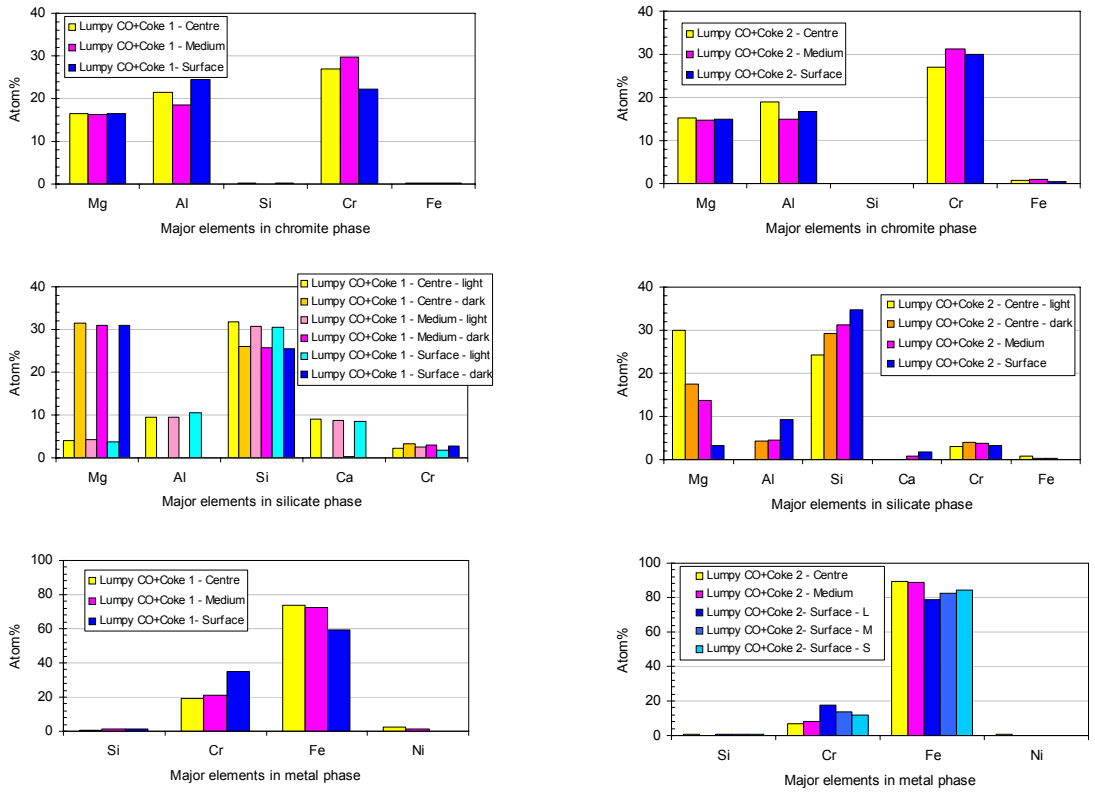
5. DISCUSSION

The raw material for ferrochrome production, natural chromite ore, is typically an iron-magnesium-chromium oxide spinel mineral, and can generally be written as $(Fe,Mg)(Fe,Cr,Al)_2O_4$. Depending on the chromite source, magnesium may occur in variable amounts, and aluminium and iron may partially substitute for chromium. Alternatively, it can be defined as a combination of Fe_3O_4, $FeCr_2O_4$, $MgCr_2O_4$, $MgAl_2O_4$ and

$(Cr,Al)_2O_3$. These compounds form a complicated spinel structural solid solution. It is commonly associated with olivine, magnetite, and serpentine.

In general, the current experimental evidence suggests that the reduction of chromite with carbon monoxide is possible, but the presence of solid carbon is essential to convert the formed CO_2 gas back to CO through the Boudouard reaction. Otherwise, reduction of chromium oxide is practically ceased in a short period of time. The reaction procedure could be described as follows:

1. diffusion of CO gas to the chromite surface and further inside the pellet (or lumpy ore) through the pores;
2. cation diffusion to the reaction sites in the chromite particles;
3. reduction of iron oxides in iron chromite from Fe^{3+} to Fe^{2+} and from Fe^{2+} to metallic Fe;
4. nucleation of metallic iron in the cracks or at the surface of the chromite particles;
5. reduction of chromium oxides from Cr^{3+} to Cr^{2+} and from Cr^{2+} to metallic Cr;
6. dissolution of metallic chromium into metallic iron and outward diffusion of CO_2



Closely packed Loosely packed

Figure 10: EDS analyses from lumpy ore samples reduced with CO; closely packed with coke (left) and loosely packed (right), respectively.

In parallel to the chemical reactions, structure changes are taking place due to sintering and poreformation. Figure 11 illustrates the schematic diagram of chromite reduction with CO gas in the packed bed. FeCr alloy is formed during the solid state reduction with CO gas. A rim of residual spinel with the major composition of MgCr2O4 and MgAl2O4 remains on the outer ring of the chromite particles. The reduction extent decreases toward the inner core of the chromite lump. The chromite spinel structure is maintained at lower tempera-

tures, and certain sintering occurs due to the melting of gangue minerals within the chromite with increasing temperature.

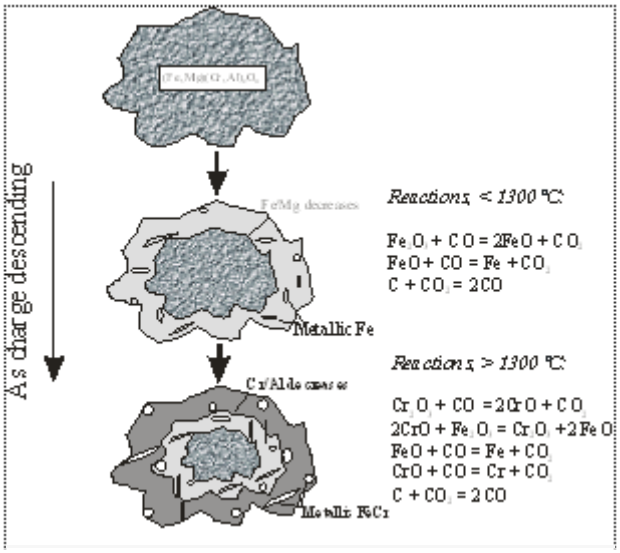


Figure 11: Schematic illustration of chromite reduction in the packed bed zone of SAF

In general, the reduction of chromite is favoured by a higher temperature. Under similar experimental conditions, reduction of a chromite pellet is easier and faster than reduction of a chromite lump due to the more porous structure of the pellet. Reduction proceeds from the surface to the inner part of the chromite. Metal beads formed first during reduction are almost pure iron at temperatures below 1300°C in accordance with the thermodynamic calculations [5], but gradually the chromium content increases starting from the outer surface [4]. As the reduction proceeds the Fe/Mg and Cr/Al ratios in the reacted layer of the chromite particles decrease towards the surface, as indicated in Figure 4.

In the packed bed zone of the furnace, if the maximum temperature is 1200 °C as estimated by Ringdalen [3], it is most probable that only the iron oxides are reduced. The average retention time in the burden was estimated to be about 12~24 hours depending on furnace size, where only a small part of the reduction takes place due to the lower temperatures. Contrary to the low extent of gas-solid reaction as mentioned above, the chromite particles are present in various stages of alteration as reported by Wedepohl and Barcza [2]. In the upper part of the furnace, the reduced metal globules are rich in Fe and containing very little Cr. When proceeding downwards in the region near the electrode, the Cr/Fe ratio in the metallic phase increases. In general, the blebs within the partially reacted chromite particles consist of Fe-rich phases. This is in agreement with the present observation and the mechanism described in Figure 11.

According to the microstructure analysis the reduction reaction moves from the edge of the particles towards the centre, indicating that it is a diffusion-controlled reaction. Preferential reduction along cracks in the particles also supports this suggestion, as generally observed in the present study. The initial reducing agent is coke in contact with the chromite particles. Once the first metallic phase is formed, carbides may also form through the carbon diffusion into metallic phases at sintering temperatures. During the charge descending and temperature rising, the gangue materials will be sintered and melted, and react with the flux and form slag in the furnace. Such slag formation may on one hand hinder the CO gas diffusion and further its reaction with the chromium oxides in the chromite, and on the other hand promote the dissolution of the reduced or partially reacted chromite into the slag, which has been discussed in the previous publication [15]. In addition, the metal beads formed at the location close to coke contain a certain percentage of silicon, which proves that the silica in the chromite ore is reduced to a certain degree even in the packed bed zone.

6. SUMMARY AND CONCLUSIONS

In the packed bed zone of the Submerged Arc Furnace, chromite is reduced with CO gas in the solid state, where most of the iron oxides in the chromite are reduced. With charge descending and temperature increasing in the furnace, chromium will be reduced from the chromite and dissolved into the formed iron metal

phase. In the present study, the structural changes of the partially reduced chromite samples, i.e. solid-state reduction of industrial pellets and lumpy ore with carbon monoxide in the absence or presence of coke particles, were examined with a scanning electron microscope with an EDS analyser. In general, under similar experimental conditions, the reduction of the chromite pellet is easier and faster due to its more porous structure than the reduction of the lumpy chromite. Reduction proceeds from the surface to the inner part of the chromite material. Metal beads formed first during reduction are almost pure iron, but gradually the chromium content increases starting from the outer surface, which confirms the results from previous researchers [8 – 14].

In the experiments with industrial pellets, if the reaction proceeds long enough (16 hours at 1500°C), metallic beads grow larger and their Cr content increases, especially in the outer region of the pellet. In the highly reduced region, two separate alloy phases were observed in single metal beads, i.e. iron-based and chromium-based Fe-Cr alloys. For the reduction of lumpy ore, the lumpy ore packed with coke has a higher reduction rate than that reduced only by CO gas. This reveals that the presence of carbon for instant Boudouard reaction is essential for efficient chromite reduction.

Although the smelting and coke bed regions contribute to the most part of the overall chromite reduction, the gas-solid reaction in the packed bed plays also important roles in the production process. The process aims at high chromium recovery and low energy consumption. Higher share of the solid state reduction of chromite in the packed bed zone can promote the total reduction rate and thus improve Cr recovery. In order to be able to optimize the furnace operation it is important to know the different stages and mechanisms of the reduction process as well as the burden distribution and location of different reaction zones in the furnace.

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REFERENCES

[1] K. Yamagishi, K. Endo, and J. Sada, A comprehensive analysis of the furnace interior for high-carbon ferrochromium. Proceedings of the first International Congress on Ferro-Alloys, Edited by H. Glen, South African Institute of Mining and Metallurgy, Johannesburg, South Africa, April 22-26, 1974, 143 – 148.

[2] Wedepohl and N. A. Barcza, The “dig-out” of a ferrochromium furnace. Spec. Publ. Geol. Soc. S. Afr., 7 (1983), 351-363.

[3] E. Ringdalen and J. Eilertsen, Excavation of a 54 MVA HC-ferrochromium furnace. Proceedings of the ninth International Ferroalloy Congress and the Manganese 2001 Health Issues Symposium, Quebec City, Canada, June 3-6, 2001, 166 – 173.

[4] M. Kekkonen, Y. Xiao and L. Holappa, Kinetic study on solid state reduction of chromite pellets. Proceedings of INFACON 7, Trondheim, Norway, June, 1995, pp.351 - 360.

[5] Y. Xiao and L. Holappa, Kinetic modelling on solid state reduction of chromite pellet with CO, Proceedings of INFACON 8, Beijing, China, June 7 – 10, 1998, pp.135 -140.

[6] Y. Xiao, M. Reuter, and L. Holappa, Reduction of Chromite Pellet with CO, Proceedings of the ninth International Ferroalloys Congress and the Manganese 2001 Health Issues Symposium, Quebec City, Canada, June 3 – 6, 2001, pp.147 – 156.

[7] M. Kekkonen, A. Syynimaa, L. Holappa and P. Niemelä, Kinetic study on solid state reduction of chromite pellets and lumpy ores. Proceedings of INFACON 8, Beijing, China, June 7 – 10, 1998, pp. 141 – 146.

[8] W. J. Rankin, The reduction of chromites by graphite and carbon monoxide. Archiv. fur Eienhuttenewes Vol. 50, No. 9, 1979, pp. 373-378.

[9] W. J. Rankin, The composition and structure of chromite during reduction with carbon. Trans.Inst. Min. Met. C88, 1979, pp. 107-113

[10] O. Soykan, R.H. Eric and R.P. King, Kinetics of the reduction of Bushveld complex chromite ore at 1416 °C. Metallurgical Transactions B, Vol. 22B, December, 1991, pp. 801 – 810.

[11] C.P.J. van Vuuren, J.J. Bodenstein, M. Sciarone and P. Kestens, The reduction of synthetic iron chromite in the presence of various metal oxides – a thermo-analytical study. Proceedings of INFACON 6, Cape Town, South Africa, 1992, South African Institute of Mining and Metallurgy, Johannesburg, Vol.1, pp. 51 – 55.
[12] M.J. Niayesh and R.J. Dippenaar, The solid-state reduction of chromite. Proceedings of INFACON 6, Cape Town, South Africa, 1992, South African Institute of Mining and Metallurgy, Johannesburg, Vol.1, pp. 57 – 63.
[13] D. Neuschütz, Kinetic aspects of chromite ore reduction with coal at 1200 to 1550 °C. Proceedings of INFACON 6, Cape Town, South Africa, 1992, South African Institute of Mining and Metallurgy, Johannesburg, Vol.1, pp. 65 – 70.
[14] H.G. Vazarlis and A. Lekatou, Pelletising-sintering, prereduction, and smelting of Greek chromite ores and concentrates, Ironmaking and Steelmaking, vol.20, 1993, No.1, pp.42-52.
[15] Y. Xiao, Y. Yang and L. E. K. Holappa, Tracking chromium behaviour in submerged arc furnace for ferrochrome production, to be published in the Proceedings of the Sohn International Symposium on Advanced Processing of Metals and Materials: Principles, Technologies and Industrial Practice, 27 – 31 August 2006, San Diego, California, USA.
[16] Y. Xiao, C. Schuffeneger, M. Reuter, L. Holappa and T. Seppälä, Solid state reduction of chromite with CO. Proceedings of the tenth INFACON, Cape Town, South Africa, February 1 – 4, 2004, pp. 26 – 35.