SOLID STATE REDUCTION OF CHROMITE WITH CO

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ABSTRACT

Reaction kinetics of solid-state reduction of chromite pellets (laboratory made and industrial) and lumpy ore was investigated by the thermogravimetric analysis (TGA) technique. Carbon monoxide was used as the reducing agent, with the presence of graphite in proximity to chromite. The experiments were carried out at both rising temperature and constant temperature in the range of 1450 - 1550°C. Scanning electron microscopy was employed to observe and analyse the structure and composition changes of the chromite samples. For the lab-made chromite pellets, the effects of particle size and bentonite addition on the reduction behaviour were studied. The pellet with smaller particle size gave a higher reduction rate. Bentonite addition had slightly negative effect on the reduction rate. When reducing industrial pellets, temperature and CO flow rate had positive influence on the reduction rate. Reduction of lumpy ore took place slower than reduction of a pellet. In all samples, chromite reduction proceeded longer in the outer part of the sample than in the centre part. The porosity of the chromite samples was determined before and after the experiments. The porosity of lumpy chromite increased significantly during the reduction. However, the porosity of lab-made chromite pellet decreases due to sintering effect. The reaction mechanism is discussed on the basis of experimental results and earlier investigations.

1. INTRODUCTION

Production of high carbon ferrochromium from chromite concentrates follows the steps of pelletising, sintering and smelting in the submerged arc furnace. Because of the large temperature gradient in the submerged arc furnace, quite different reduction mechanism exists in different reaction zones. As a prerequisite to analyse the EAF furnace, and further to simulate the reduction progress within the furnace charge, it is essential to understand the reaction mechanism of the chromite with CO gas within the furnace.

Due to the variation of the chromite composition, different ore types may behave in different ways and thus have different reaction mechanism. In previous studies reaction kinetics of solid-state carbothermal and CO gas reduction of industrial chromite pellets have been investigated [1]. The unreacted core model was applied to discuss 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 [2,3]. Reviewing the literature, several works were reported on chromite reduction with carbon [1, 4-9], but only a few studies on chromite reduction with CO [4, 7, 9]. There are some disagreement regarding the proposed reduction mechanism. Therefore, a systematic study is needed, in order to understand the reaction mechanism of chromite with CO.

As a continuation of the previous work, the main objectives of the present paper are to investigate the effects of temperature, chromite particle size in a pellet, bentonite addition and CO flow rate on the chromite reduction. In addition, this work sought to evaluate and compare the differences between the reduction of lab-made pellets, sintered industrial pellets and chromite lumpy ore. The reaction mechanism is discussed based on the microstructure analysis and observations. These experimental results will be applied to validate the kinetic reaction model [3], and to provide fundamental basis of process modelling in the submerged arc furnace for the production of ferrochromium.

2. EXPERIMENTAL

2.1 Chromite samples

Three types of chromite samples were investigated in this work: lab-made pellets, industrial pellets and chromite lumpy ore. Chromite concentrate used for pelletising, industrial pellets, lumpy ore and coke were provided by AvestaPolarit Chrome Oy, Finland.

The chemical composition of Kemi chromite differs from sample to sample. An average composition for the concentrate is used in this work and is listed in Table 1. Chromite concentrate was sieved into different size categories, weighed and homogeneously mixed with about 1.5 wt% of bentonite as it was found that the minimum quantity required to keep the pellets mechanically strong was around 1wt%. A certain amount of water was added into the mixture prior to preparation of the pellets in the laboratory.

Table 1. Chemical analysis of Kemi chromite concentrate.

Components	Cr_2O_3	SiO_2	Fe_2O_3	FeO	MgO	Al_2O_3	K_2O	CaO	TiO_2	V_2O_5	MnO	NiO	C(tot)	Volatiles
wt%	44.1	2.8	5.58	19.3	10.7	13.3	0.1	0.4	0.48	0.18	0.34	0.13	0.54	2.4

In an industrial furnace the pellets should be mechanically strong, any fracture of the pellets would decrease the charge permeability and increase the recycling load. The minimum amount of water needed for pelletising increases with decreasing the particle size. The spherical lab-made pellets were 20 mm in diameter in average and weighed ca. 10g. They were first dried at 105 °C for 20 hours. From the weight changes it was realised that despite the long drying time, some water still remained inside the pellets. Usually, the pellet, which was made of smaller particle sizes, had higher free surface area but resulted in lower pellet porosity. However, the more water was added for pelletising, the higher porosity was formed in the pellet due to water evaporation. According to the measurements, the porosity of the unreacted lab-made pellets was on average 40.1% for L1 and 40.7% for L2. Table 2 shows the characteristic data for the lab-made pellets.

Table 2. Chromite Pellets prepared in laboratory scale.

Samples	**Particle Size category, μm**	**Chromite, g**	**Bentonite, g**	**H_2O, g**	**Raw pellet, g**	**Dried Pellet, g**
L1	35	10.002	0.149	1.920	11.830	10.042
L2	85	10.003	0.150	1.711	11.531	9.977
H1	35	10.001	0.149	1.911	11.818	9.985
J1	35	10.002	0.148	1.900	11.750	9.966
J2	85	10.003	0.147	1.713	11.525	9.926
X2	85	10.000	0.151	1.699	11.476	9.912
X4	220	10.001	0.152	1.271	10.970	9.773
X5	50	10.001	0.154	1.885	11.531	9.890
X-bent.	85	10.000	0.300	1.718	11.615	9.985

The microstructure of the pellets was observed by a Scanning Electron Microscope (SEM), and the chemical composition of the chromite particles was analysed with an EDS Analyser. Figures 1 and 2 demonstrate backscatter images showing the microstructure of the pellets with average particle size of 35 μm and 85 μm, respectively. SEM took the photographs at the middle of the pellet radius. It can be seen that the concentrate consists roughly of two types of minerals: chromite spinel seen as light grey particles, and a darker phase of gangue silicate minerals. The average stoichiometric compositions of these two minerals are listed in Table 3. The FeO and Fe_2O_3 were calculated based on the chemical analysis of the concentrate.

Table 3. Compositions of chromite minerals calculated based on the EDS analysis.

Comp., wt%	**Cr_2O_3**	**FeO**	**Fe_2O_3**	**SiO_2**	**MgO**	**Al_2O_3**	**TiO_2**
Light grey	67.2	15.8	5.08	0	3.04	8.48	0.34
Dark grey	10.4	2.18	0.70	55.2	24.5	7.02	0

As samples of industrial pellets, a few identical pellets with 12 mm in diameter were selected. The average weight of the selected industrial pellets was 3.45 g. The lumpy ore sample was prepared by shaping and polishing into a sphere 20 mm in diameter and 14.96 g in weight.

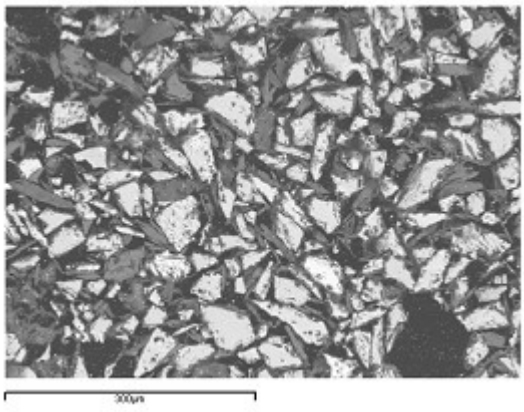


Figure 1. Microstructure of unreacted chromite pellet with average particle size of 35 μm.

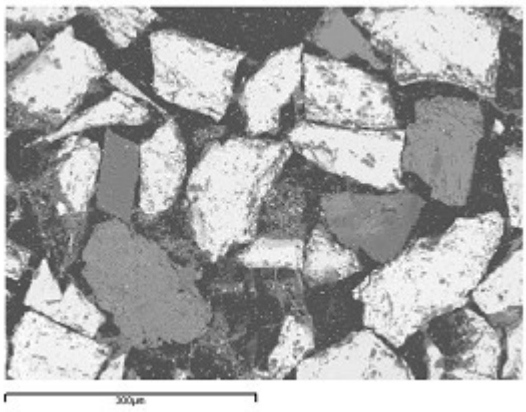


Figure 2. Microstructure of unreacted chromite pellet with average particle size of 85 μm.

2.2 Experimental set-up and procedure

The reduction experiments were carried out in a vertical tube furnace by thermo gravimetric analysis (TGA). A graphite tube with no contact to the sample was installed near to the chromite sample, so that the carbon dioxide formed during the chromite reduction could be reduced back to carbon monoxide to maintain a strongly reducing atmosphere. The equipment layout is illustrated in Figure 3.

The chromite sample was placed on an alumina supporting tube, and introduced to the furnace at room temperature. A Pt/Pt-Rh10 thermocouple was located just above the chromite sample. The supporting tube was fixed onto the balance located under the furnace. A stream of nitrogen gas was supplied with 1.5 l/min to flush the furnace, to eliminate the volatiles from the sample, and to maintain an inert atmosphere. The furnace was heated up with controlled temperature profile. Reduction started with the introduction of CO gas of 99.9% purity. The weight change of the pellet during the experiment was measured every 6th second. After an experiment, nitrogen gas was supplied to protect the sample from oxidation during cooling down.

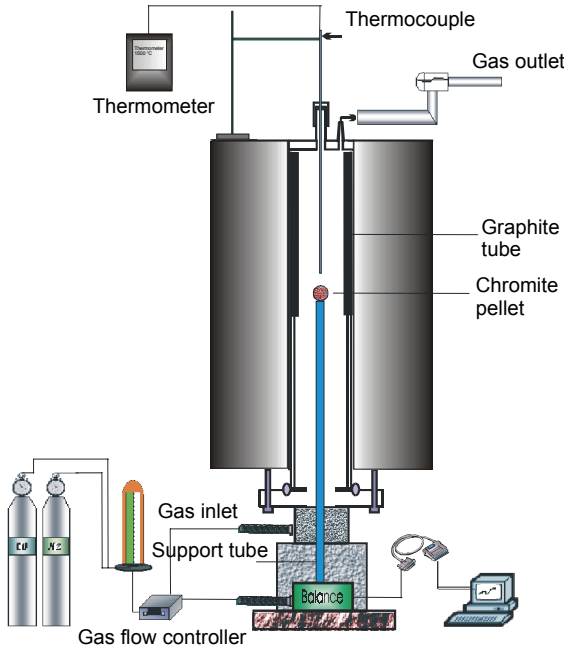


Figure 3. Experimental Set-Up.

The reduced chromite pellet was cut through its cross section. Half of the sample was prepared for microstructure examination with scanning electron microscope. The rest of the sample was used for porosity analysis with mercury intrusion.

3. RESULTS AND DISCUSSION

For a chromite pellet reduced with CO gas, the degree of reduction is defined as the percentage of oxygen removed from total removable oxygen in chromite, and is expressed as follows:

$$R(t) = \frac{W_0 - W_t - W_{volatiles}}{W_O^{reducible}} \quad (1)$$

where W_0 is the weight of the dried sample in the beginning of the reduction, W_t is the weight of the sample at time t during the reduction, $W_{volatiles}$ are the weight loss due to volatiles; $W_O^{reducible}$ is the total initial reducible oxygen theoretically calculated from oxygen in iron and chromium oxides based on the chromite composition. For sintered industrial pellets, 76% of iron exists in trivalent state [2], therefore the amount of reducible oxygen in the industrial pellet is higher than that in the lab-made pellets.

3.1 Lab-made pellets

Two temperature profiles were used for the reduction of lab-made pellets: rising temperature and constant temperature. Under rising temperature condition, carbon monoxide as reducing gas was supplied after a temperature of 450°C was attained. Reduction trials at rising temperature can simulate the behaviour of a single pellet as the charge descends in the submerged arc furnace. For the reduction at constant temperature, carbon monoxide was brought in only after the desired temperature was reached.

3.1.1 Reduction under rising temperature

Effects of temperature and chromite particle size on the reduction rate were investigated. The pellets were reduced first at rising temperature and then at 1450°C or 1500°C with CO flow rate of 2 l/min. To eliminate the influence of volatile components of the pellet, the results were calibrated against the weight loss curve of an identical pellet in nitrogen atmosphere. Examples of reduction curves are shown in Figure 4. It can be seen that during the temperature rise, the effect of particle size on the reduction rate was negligible. During the period when temperature had reached its constant value, higher temperature led to higher reduction rate, as well as the pellet with smaller particle size resulted in higher reduction degree.

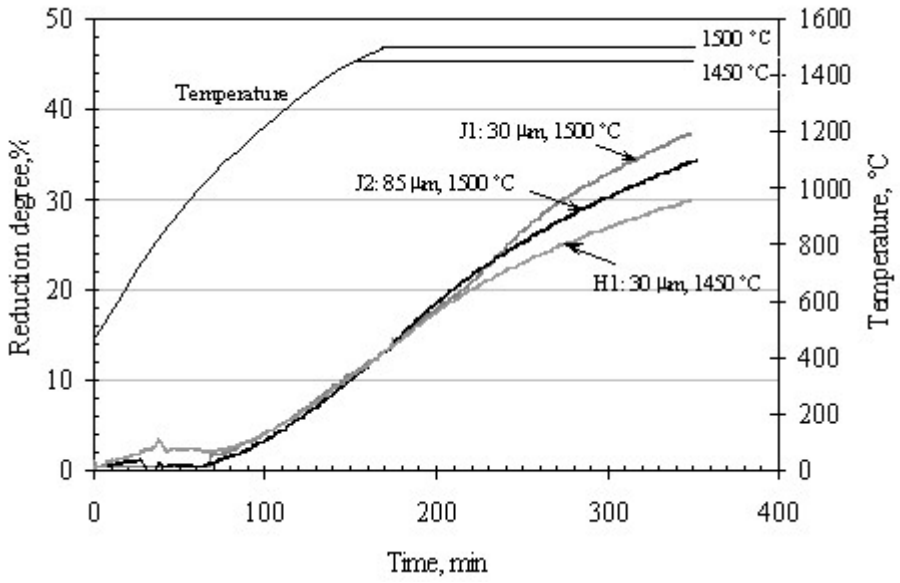


Figure 4. Reduction of lab-made chromite pellets under rising temperature conditions.

Figure 5 shows the microstructure changes through the pellet cross-section. It can be observed that the reduction occurred through out the pellet. A dense metallic rim is not found around the chromite particles. The metal beads (white colour) are bigger in the surface zone of the pellet. The gangue minerals (dark grey) were sintered and melted around the partially reduced chromite particles (light grey). The dark regions are void. According to the analysis on the metal beads, the reduced chromium concentration increased toward the surface. Certain metallization is also observed inside the chromite particles. The porosity of the pellet decreases as a result of sintering and reduction. According to the mercury intrusion analysis, the open porosity for the pellet with particle size of 30 µm decreased from 40.1% before the experiment to 19.4% after the reaction, respectively. For the pellet with particle size of 85 µm, the open porosity decreased from 40.7 to 28.6 %.

3.1.2 Reduction under constant temperature

The effects of chromite particle size and bentonite addition on the reduction behaviour were studied at constant temperature. Three pellets with different particle size and a pellet with double amount of bentonite addition were reduced with carbon monoxide at 1500 ºC. The sample was heated up in nitrogen atmosphere, and carbon monoxide was supplied when the furnace reached the working temperature.

The results are illustrated in Figure 6. Particle size of chromite in the pellets seems to have quite a strong effect on the reduction rate. Decreasing the particle size increases the internal surface area thus increasing the interfacial area for reduction reactions. Higher amount of bentonite addition results in a stronger pellet, but slightly decreases the pellet reducibility (- 2.5% in reduction degree). This could be associated with the increased sintering tendency with the additional bentonite, which may decrease the effective diffusion coefficient of CO towards the pellet centre.

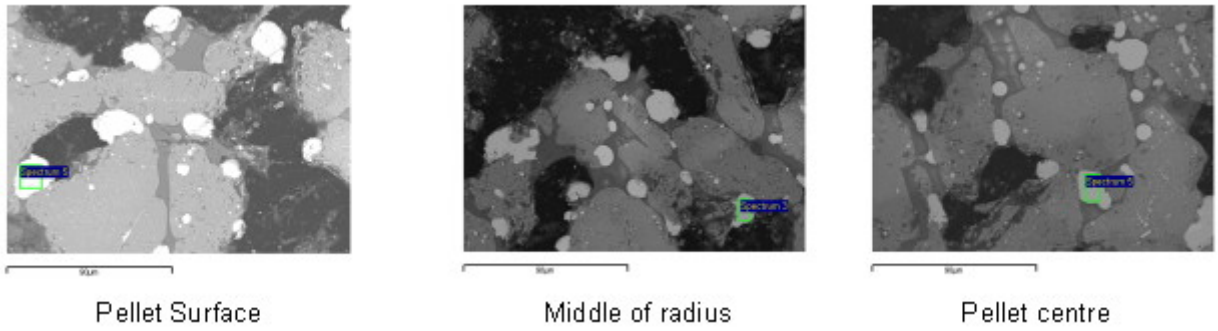


Figure 5. Chromite pellet (J2) reduced with CO under rising temperature conditions white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void.

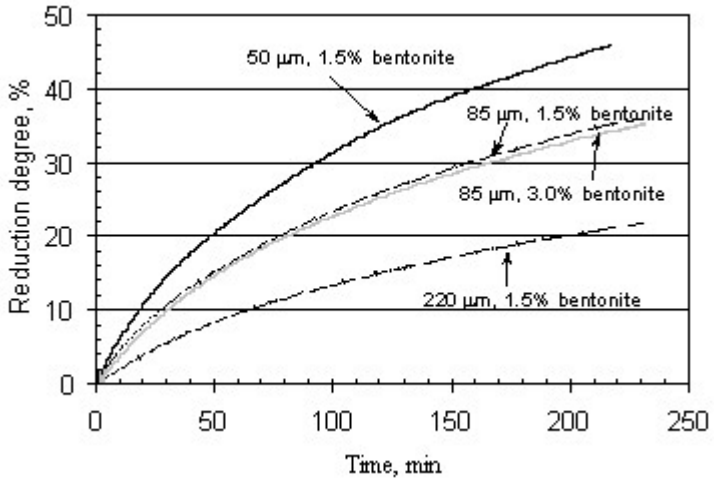


Figure 6. Effect of particle size and bentonite on the reduction rate at 1500 °C.

Figure 7 demonstrates the composition changes in the formed metal phase through the pellet cross section. Each point in the figure is an average value of six selected metal beads. In the centre area of the pellet iron content is over 95 wt% in the metal beads, i.e. mainly iron oxides are reduced. The reduction degree at the outer part of the pellet is higher than that in the inner part of the pellet, especially for the pellet with smaller particle size of 50 µm. The effect of particle size on the reduction degree is clearly displayed in the outer region of the pellet, the larger the chromite particle, the lower the chromium concentration in the agglomerated metal beads, thus the lower the reduction extent in that region. The relative decreased iron concentration as the reduction proceeds is due to the dissolution of chromium metal. The absolute amount of reduced iron increases, which is exposed from the growing metal beads in both size and amount. Figure 8 depicts the correlation of iron and chromium contents in all measured metal beads. It shows that concentration of iron decreases with increasing chromium concentration. The total of iron and chromium reaches 98.5wt% in average, the rest of 1.5wt% contains other reduced alloying elements mainly Si and Ni.

The preferential reduction of iron over chromium is consistent with the thermodynamic calculation, which was discussed in a previous work [3]. The metal beads are distributed mostly at the surface of the chromite particles, as shown in Figure 9.

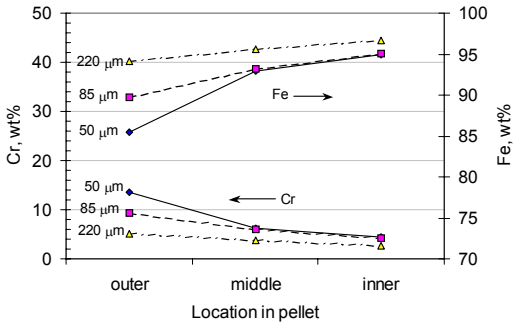


Figure 7: Iron and chromium contents in metal phase

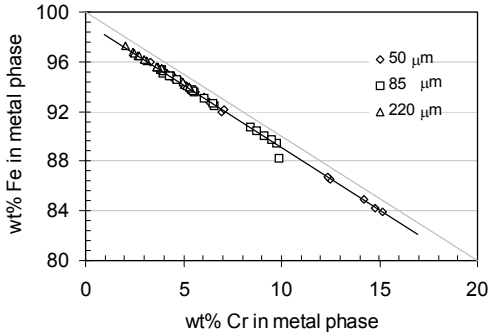
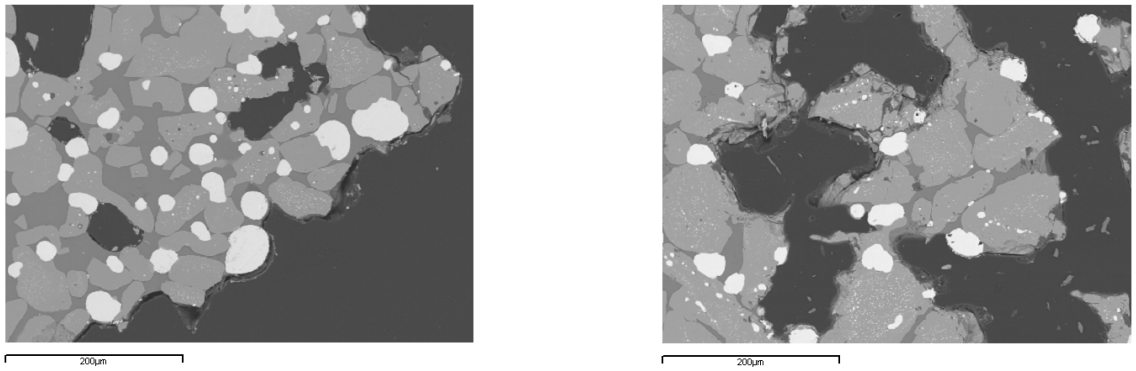


Figure 8: Correlation of iron and chromium contents in metal phase



Average particle size: 50 µm

Average particle size : 85 µm

Figure 9: Surface structure of two chromite pellets reduced with CO at 1500°C for four hours
white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void

3.2 Industrial pellets

The influence of temperature and flow rate of carbon monoxide on reduction behaviour of sintered industrial pellets was experimentally studied. The results of three selected industrial pellets are shown in Figure 10. When increasing temperature from 1500 °C to 1550 ºC, reduction rate increased with temperature. If increasing CO flow rate from 2.0 l/min to 4.5 l/min, the reduction rate increased during the initial period of the reaction, i.e. when the reduction degree was less than about 25%. In the later stage the influence of flow rate slowed down. Thus an increase in the CO flow rate did not affect the final reduction degree.

To understand the entire reduction behaviour, one long time experiment was conducted. An industrial pellet was reacted with CO at the flow rate of 2.0 l/min at 1500 °C for 16 hours. Figures 11 and 12 exhibit the microstructure of the reduced industrial pellets under different conditions. More metal was formed for 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 in average, and chromium based alloy – a dark colour phase with composition of 84.9 wt%Cr and 13.6 wt%Fe. Iron and chromium contents in the metal beads are represented in Figure 13. The reduction degree increased significantly toward the pellet surface.

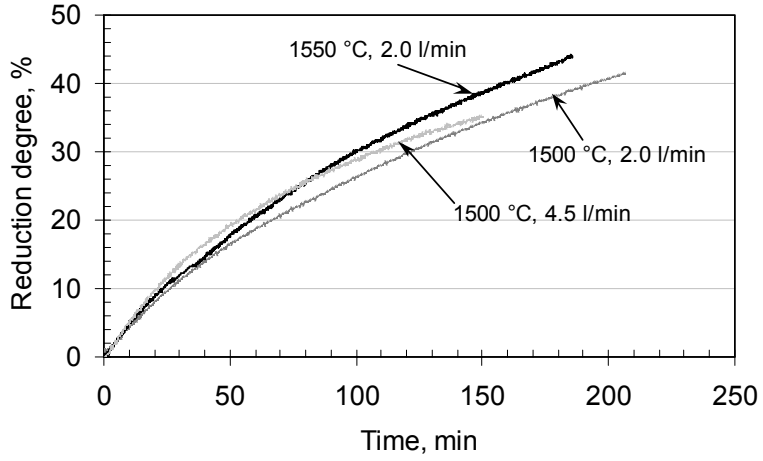


Figure 10. Effect of temperature and CO flow rate on the reduction of industrial pellets.

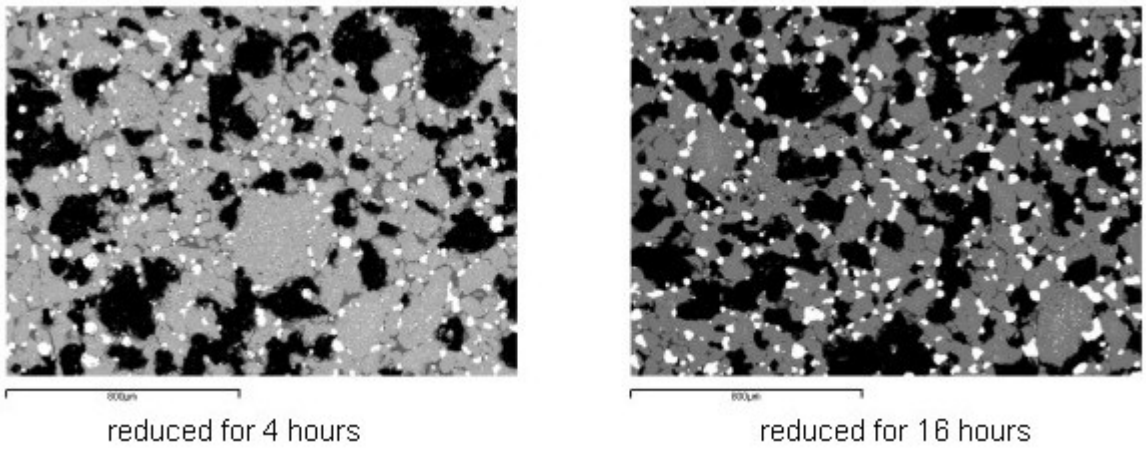


Figure 11. Microstructure of inner part of two industrial pellets reduced at 1500°C with CO
White: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark void.

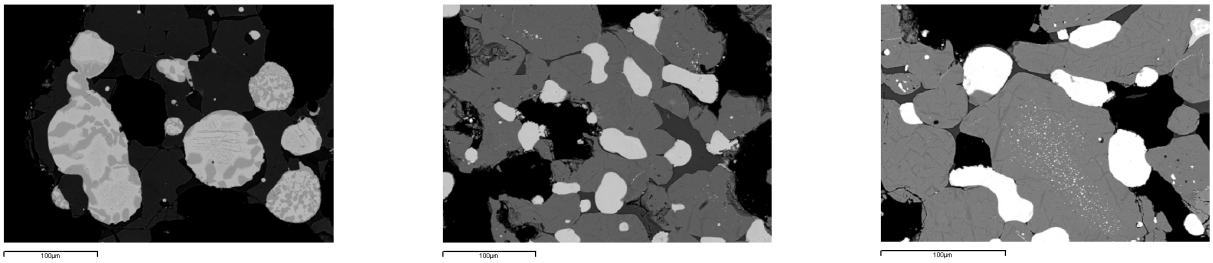


Figure 12: Microstructure of industrial pellet reduced at 1500°C with CO for 16 hours
white: metal phase; light grey: partially reduced chromite; dark grey: sintered gangue minerals; dark: void
Metal phase in surface area: light colour with 23.0 wt%Cr and 75.7 wt%Fe,
and dark colour with of 84.9 wt%Cr and 13.6 wt%Fe

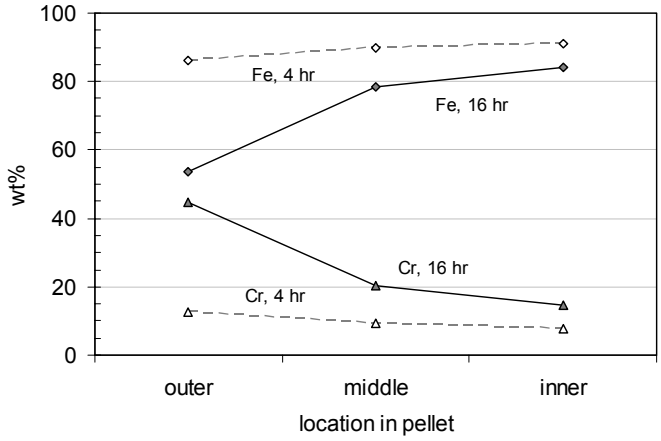


Figure 13. Iron and chromium contents in metal phase in industrial pellets reduced at 1500 °C with CO for 4 and 16 hours, respectively.

3.3 Lumpy ore

A spherical chromite lumpy ore was reduced with carbon monoxide at 1500 ºC. In addition, 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 and distributed on the wall of the crucible to maintain a homogeneous reducing atmosphere around the reacting sample. The reduction degree is expressed in Figure 14. It can be seen that the lumpy ore contacted with solid carbon (coke) is reduced much faster. This agrees with the previous results that the reduction rate of chromite particle mixed with solid carbon is much faster than with CO [1].

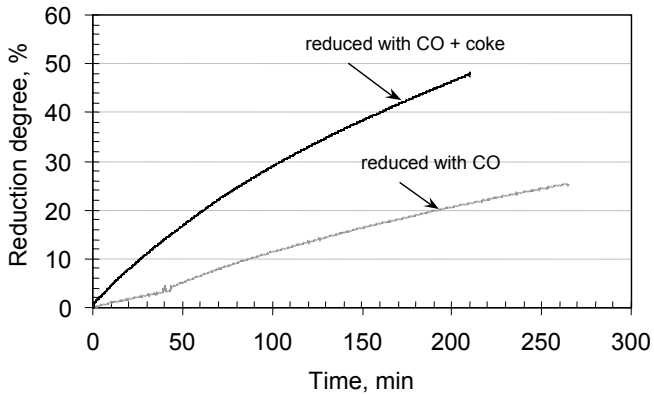


Figure 14. Reduction of chromite lumpy ore with CO or with CO and coke at 1500°C.

Figure 15 describes the composition changes in the formed metal phase through the cross section of the chromite samples. For the chromite lumpy ore reduced with carbon monoxide, mainly iron oxides were reduced, less than 1.5 wt% Cr was alloyed in the metal phase. Two reduced lumpy samples from the packed bed experiment were selected and analysed. The presence of coke promoted Cr reduction and the highest reduction degree was obtained for the lumpy ore closely packed with coke.

A photograph of reduced chromite lumpy ore is shown in Figure 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. According to the mercury intrusion analysis, the apparent density of the lumpy ore increased from 3.5 to 3.9 g/cm^3, and the porosity increased from 1.7% to 8.1%. Figure 17 illustrated the difference of cumulative pore volumes of chromite lumpy ore before and after the reduction. It can be seen the total pore volume for unreacted lumpy ore was 5 mm^3/g while the reacted lumpy ore had an increased total pore volume of 23 mm^3/g. This difference is mainly caused by the increased large pores of 50 – 100 μm and small pores of 3 – 100 nm.

In general, the present 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 by the Boudouard reaction. Otherwise, reduction of chromium oxide is practically ceased. The reaction procedure could be the following: diffusion of CO gas to the chromite surface and further inside the pellet (or lumpy ore) through the pores; cation diffusion to the reaction sites in the chromite particles; reduction of iron oxides in iron chromite from Fe^{3+} to Fe^{2+} and from Fe^{2+} to metallic Fe; nucleation of metallic iron in the cracks or at the surface of the chromite particles; reduction of chromium oxides from Cr^{3+} to Cr^{2+} and from Cr^{2+} to metallic Cr; dissolution of metallic chromium into metallic iron and outward diffusion of CO_2. Parallel to chemical reactions structure changes are taking place due to sintering and pore formation. The detailed reaction mechanism will be discussed in a separate publication.

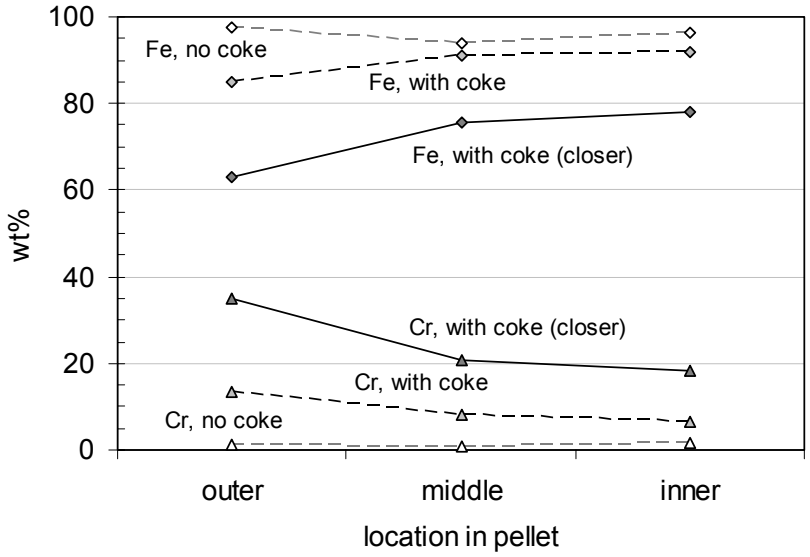


Figure 15. Iron and chromium contents in metal phase of lumpy ore samples reduced with CO without coke and with coke packed in two different locations, respectively.

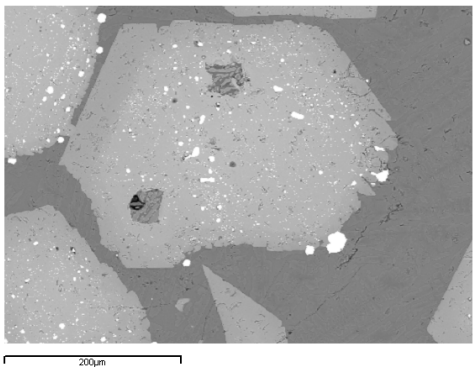


Figure 16: Reduced lumpy ore with CO

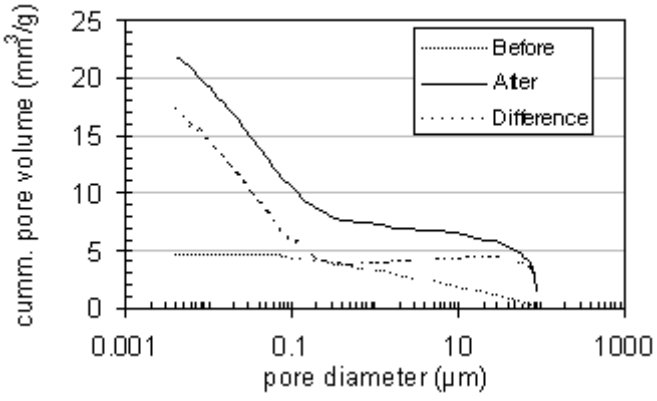


Figure 17: Porosity analysis on chromite lumpy ore before and after reduction with CO with mercury intrusion

4. CONCLUSIONS

Kinetics of solid-state reduction of lab-made pellets, industrial pellets and lumpy ore with carbon monoxide were investigated by thermo gravimetric analysis in the temperature range of 1450-1550°C. Scanning microscope with EDS analyser as well as a porosity analysing technique were used to examine the structural changes of the partially reduced chromite samples.

In general, the reduction of Kemi chromite is favoured by higher temperature. Under similar experimental conditions, the reduction of chromite pellet is easier and faster than lumpy chromite due to the more porous structure. Reduction proceeds from the surface to the inner part of the chromite samples. Metal beads formed first during reduction are almost pure iron, but gradually the chromium content increases starting from the outer surface.

In the experiments with lab-made pellets prepared from certain sieve fractions of ground concentrate, decreasing chromite particle size increased reduction rate. Bentonite used as a binder for pelletising slightly lowered the reduction rate when its content rose from 1.5 to 3.0 wt%.

In the experiments with industrial pellets, increased CO gas flow rate had a positive effect on the reduction rate in the initial stage of the reduction. In the case that the reaction proceeds long enough (16h at 1500°C), metallic beads grow large and 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 FeCr alloys.

For the reduction of lumpy ore, the lumpy packed with coke has a higher reduction rate than that reduced only with CO gas. This reveals that the presence of carbon for Boudouard reaction is essential for efficient chromite reduction.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] 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.
[2] Y. Xiao and L. Holappa, Kinetic modelling on solid state reduction of chromite pellet with CO, Proceedings of 8th International Ferroalloys Congress, June, Beijing, 1998, pp.135 -140.
[3] 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, June 3 – 6, 2001, Quebec City, Canada, pp.147 – 156.
[4] 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.
[5] 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.
[6] 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, S. Africa, Vol.1, Johannesburg, 1992, pp. 51 – 55.
[7] M.J. Niayesh and R.J. Dippenaar, The solid-state reduction of chromite. Proceedings of INFACON 6, Cape Town, S. Africa, Vol.1, Johannesburg, 1992, pp. 57 – 63.
[8] D. Neuschütz, Kinetic aspects of chromite ore reduction with coal at 1200 to 1550°C. Proceedings of INFACON 6, Cape Town, S. Africa, Vol.1, Johannesburg, 1992, pp. 65 – 70.
[9] H.G. Vazarlis and A. Lekatou, Pelletising-sintering, prereduction, and smelting of Greek chromite ores and concentrates, Ironmaking and Steelmaking, 1993, vol.20, No.1, pp.42-52.