Kinetic Study on Solid State Reduction of Chromite Pellets and Lumpy Ores

Marko KEKKONEN*, Ari SYYNIMAA*, Lauri HOLAPPA*, and Pekka NIEMELA**

*Laboratory of Metallurgy, Helsinki University of Technology
P.O. Box 6200, FIN-02015 HUT, Finland
**Outokumpu Chrome Oy., FIN-95400 Tornio, Finland

Abstract

The kinetics of solid state CO reduction of chromite pellets and lumpy ores were studied by thermogravimetric analysis (TGA) in the temperature range 1420-1595°C. Optical and scanning electron microscopy as well as microanalysis were used to obtain information on the structural changes of the partly reduced samples. Generally, the reduction rate increased with the temperature. In the case of lumpy ores, at the highest temperature the kinetic conditions changed due to partial melting of the surface and thus the reduction degree remained lower. In the case of sintered pellets, the effect of surface melting was not so remarkable even at the highest temperature and the reduction rate further increased. Optical photographs and microanalysis showed that the reduction degree was higher in the outer zone of the samples. In addition the reduction of sintered pellets with rising temperature was studied. Results showed that the reduction rate increased rapidly when the temperature reached about 1000°C and the final reduction degree was almost the same as it was in constant temperature experiment at 1520°C.

Introduction

High-carbon ferrochromium which is the central alloying material used in the production of stainless and high-alloy ferritic steels is nowadays mainly produced in submerged-arc furnaces. The process has been intensively developed during the years. Some recent developments to improve the efficiency of submerged-arc furnaces include closed top operations with utilisation of off-gas energy, computerised control to optimise power inputs, pelletised and pre-oxidised fines feed and optimising slag composition for maximum chromium recovery [1]. Despite the improvements in submerged arc furnace operations, there is still need to reduce the energy consumption and to improve the chromium yield in the process. In electric submerged-arc process, quite different reduction mechanisms exist in different reaction zones, due to large temperature gradient.

Knowing the reaction mechanisms in each zone can provide a guidance for improving the reduction efficiency, getting better chromium yield and thus decreasing the energy consumption. The kinetics and mechanisms of solid state reduction of carbon free and carbon containing chromite raw pellets under Ar and CO atmospheres have been investigated earlier by the authors [2]. Now in the present paper the solid state CO reduction of sintered chromite pellets and lumpy ores at 1420°C, 1520°C and 1595°C as well as reduction of chromite pellets with rising temperature has been studied.

Experimental method

Materials

Two different types of lumpy ores and one type of sintered pellet of Kemi chromite were investigated at constant temperature experiments. Experiments with rising temperature were performed by using sintered pellets. The compositions of the samples are shown in Table 1.

Table 1. Chemical compositions of the lumpy ores and sintered pellet, wt-%.

Sample	Cr_2O_3	Fe_{tot}	SiO_2	Al_2O_3	MgO	CaO	TiO_2	V	Mn	Ni
lumpy ore 1	39.9	14.1	7.8	14.9	13.4	0.7	0.55	0.10	0.23	0.10
lumpy ore 2	35.7	14.1	12.1	11.1	17.7	0.2	0.35	0.09	0.17	0.12
pellet	43.3	19.3	4.2	13.1	10.7	0.5	0.51	0.13	0.27	0.10

Method and procedure

Number of experiments were carried out by the thermogravimetric analysis (TGA), where samples were heated under CO atmosphere at different temperatures. The experimental apparatus is illustrated in Fig.1.

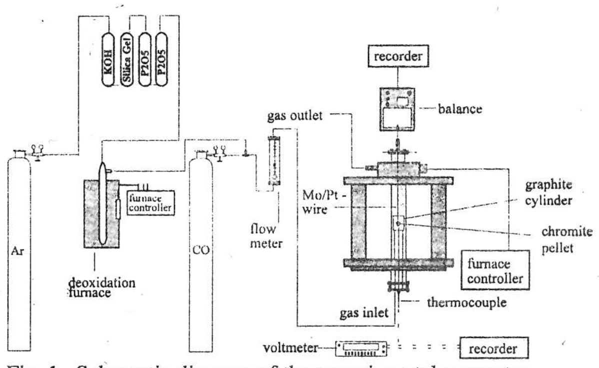


Fig. 1. Schematic diagram of the experimental apparatus.

Reduction experiments with sintered pellets and lumpy ores were carried out at 1420, 1520 and 1595°C. In a typical test the furnace was heated up under Ar-atmosphere, the sample was first put in the upper part of the furnace, where the temperature (500~700°C) was low enough to avoid the reduction, but high enough to remove moisture.

When the furnace reached the desired temperature, the sample was slowly put down to the constant temperature zone in the centre of the furnace and the atmosphere was changed to CO. A PtRh30-PtRh6 thermocouple was installed just below the sample to record the temperature of the reaction zone. In the experiments, graphite cylinder with no contact to the sample was used to maintain a high reducing atmosphere outside the sample. The weight loss of the sample was continuously recorded during the experiment. In the experiments with rising temperature, the pellet was put down when the temperature was 700°C, then the used temperature programme involved a constant-rate increase (2.5°C/min.) from 700°C to 1520°C, followed by 2 hours at 1520°C.

Experimental results

Reduction degree

The reduction degree was calculated from the equation:

$$\text{Reduction degree, \%} = X = (W_0 - W_t) * 100 / W_{ox} \qquad (1)$$

where

W_0 = weight of the sample at the beginning of reduction after the moisture removal

W_t = observed weight of the sample at time t during the reduction

W_{ox} = amount of total initial removable oxygen (only the chromium and iron oxides were regarded as reducible components)

Figures 2, 3 and 4 show he reduction degree curves of lumpy ore 1, lumpy ore 2 and sintered pellet at 1420, 1520 and 1595°C under CO atmosphere, respectively. Fig. 5 shows two experiments of the reduction of sintered pellets with rising temperature.

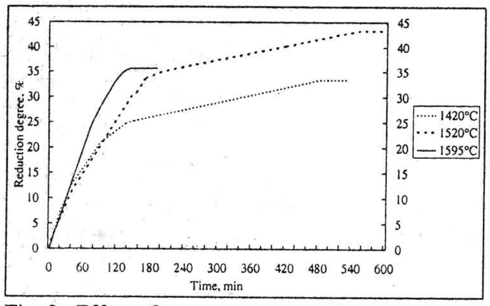


Fig. 2. Effect of temperature on reduction of chromite lumpy ore 1 under CO.

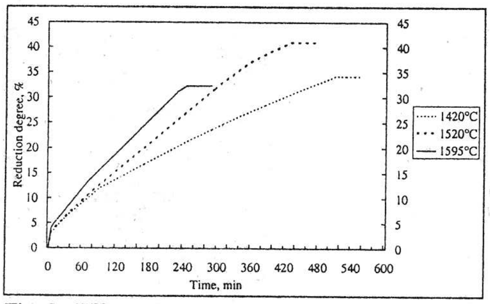


Fig. 3. Effect of temperature on reduction of chromite lumpy ore 2 under CO.

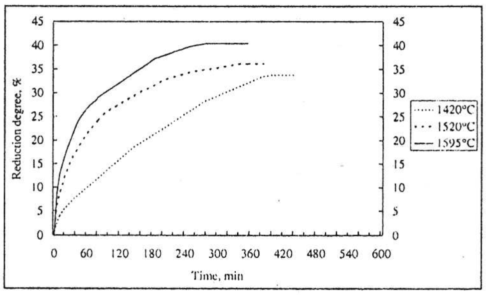


Fig. 4. Effect of temperature on reduction of sintered pellet under CO.

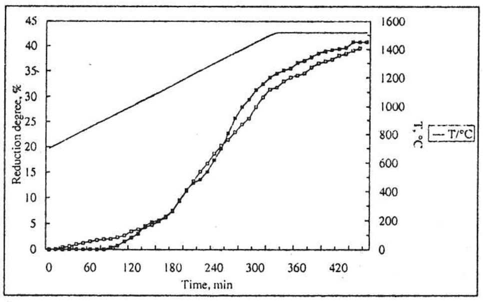


Fig. 5. Reduction of two sintered pellets with rising temperature.

From Figs. 2 and 3 it can be seen that the effect of temperature on the reduction rate was not very prominent for both types of lumpy ores. When the temperature increased from 1420 to 1520°C, the reduction degree increased. When further increasing the temperature to 1595°C reduction started with high rate but then ceased when the samples started to melt which almost stopped the reaction and the final reduction degree remained lower than at lower temperature experiments.

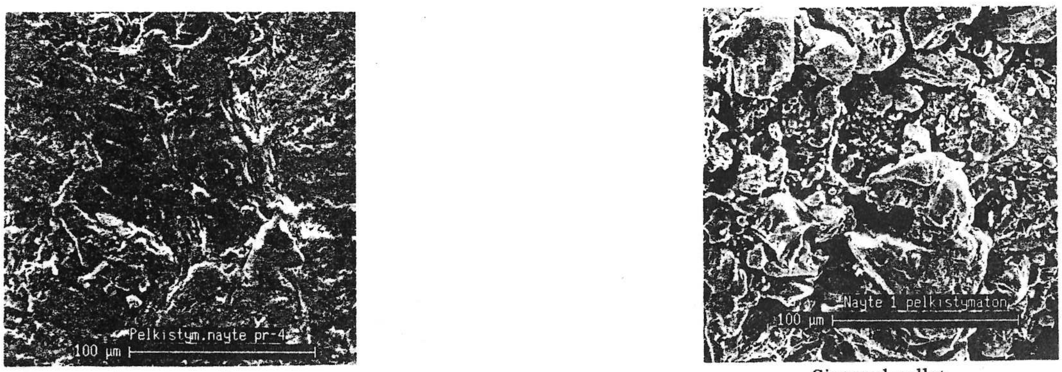
In the case of sintered pellet (Fig. 4) the reduction rate increased when increasing the temperature from 1420 to 1520°C and further to the temperature 1595°C.

From Fig. 5 we can see that the reduction rate increases rapidly in both experiments when the temperature reached about 1000°C and the final reduction degree is almost the same as it was in constant temperature experiment at 1520°C (Fig. 4).

SEM - photographs

Photographs were taken from the surface of the chromite samples by scanning electron microscope to obtain information on the changes of the surface structure at different temperatures. Fig. 6 shows the surface of the non-reduced samples and Figs. 7, 8 and 9 the surface of lumpy ore 1, lumpy ore 2 and sintered pellet reduced at different temperatures, respectively. Round particles in the reduced samples are metal droplets.

As Figs. 6-9 show the surface structure changes quite much with temperature. When increasing the temperature the surface of the samples starts to melt and the size of the metal droplets increases.

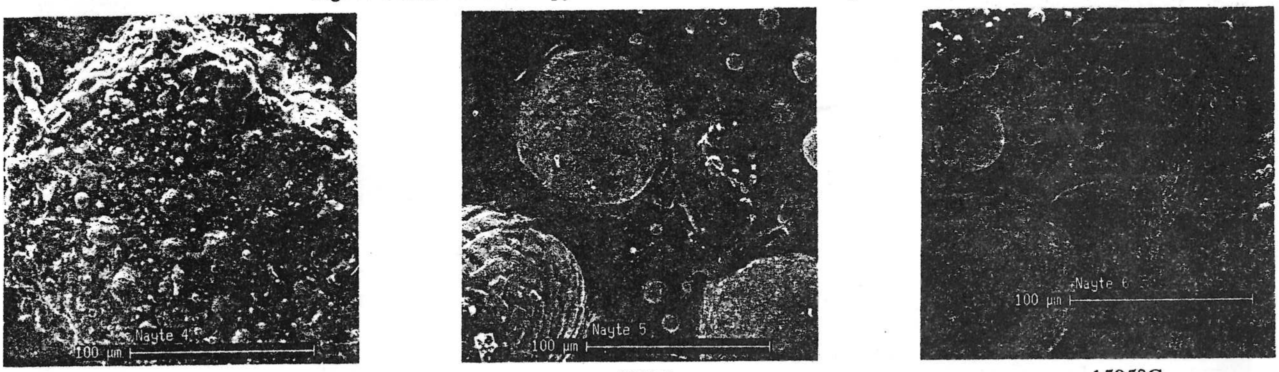


Lumpy ore 2 Sintered pellet

Fig. 6. Surface of the non-reduced samples.

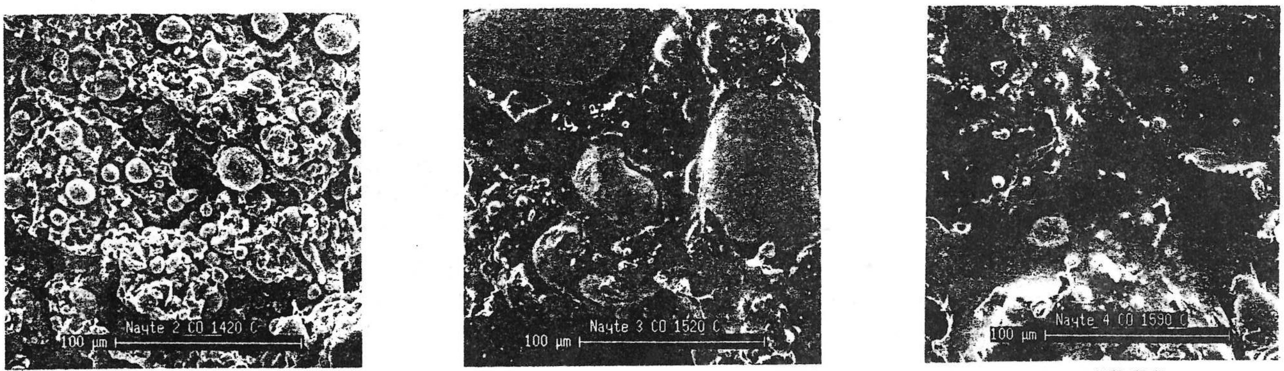
1420°C 1520 °C 1595°C

Fig. 7. Surface of the lumpy ore 1 reduced at different temperatures.



1420°C 1520°C 1595°C

Fig. 8. Surface of the lumpy ore 2 reduced at different temperatures.



1420°C 1520°C 1595°C

Fig. 9. Surface of the sintered pellet reduced at different temperatures.

Optical photographs

Optical photographs were taken on cross-sections of the lumpy ores and sintered pellets reduced under different temperatures to obtain information on the structural changes of the samples. Selected photographs from the outer and the inner part of the chromite samples are shown in Figs. 10-12. Different phases are marked in Fig. 10 (c).

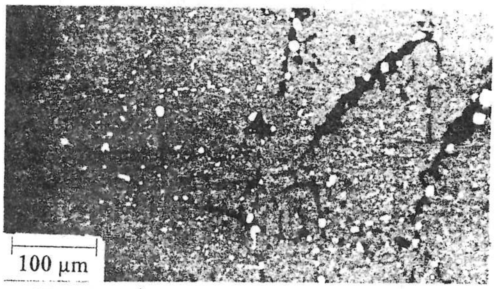


Fig. 10 (a) Lumpy ore 1, 1420°C, outer part.

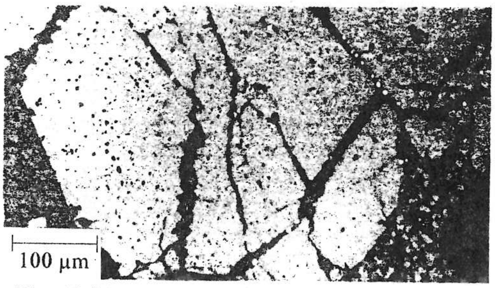


Fig. 10 (b) Lumpy ore 1, 1420°C, inner part.

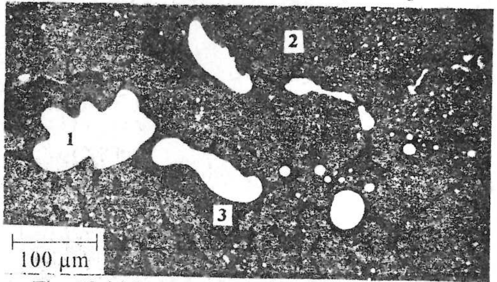


Fig. 10 (c) Lumpy ore 1, 1520°C, outer part. (1=metal, 2=chromite, 3=silicate).

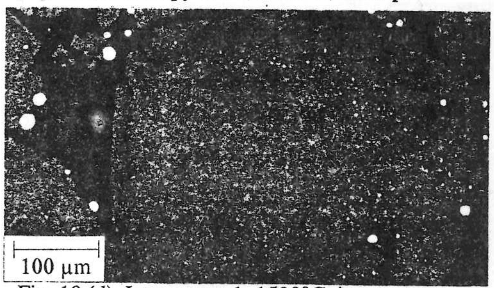


Fig. 10 (d) Lumpy ore 1, 1520°C, inner part.

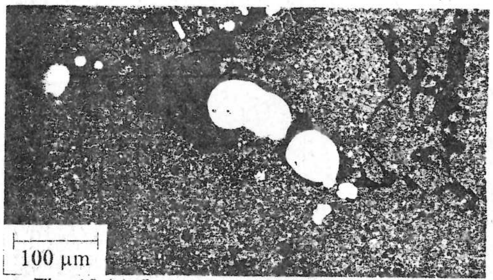


Fig. 10 (e) Lumpy ore 1, 1595°C, outer part.

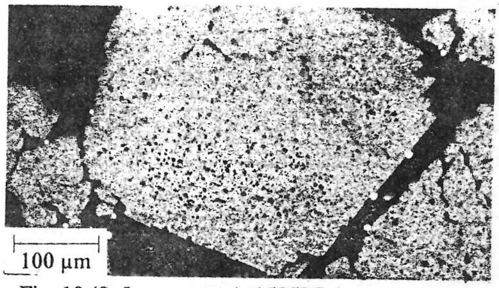


Fig. 10 (f) Lumpy ore 1, 1595°C, inner part

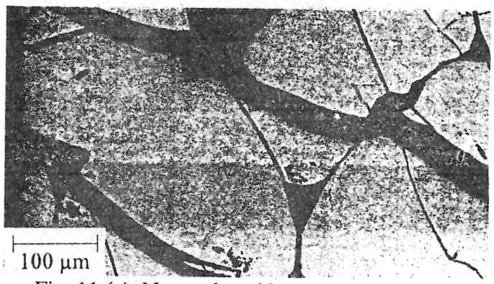


Fig. 11 (a) Non-reduced lumpy ore 2, outer part.

Fig. 11 (b) Non-reduced lumpy ore 2, inner part.

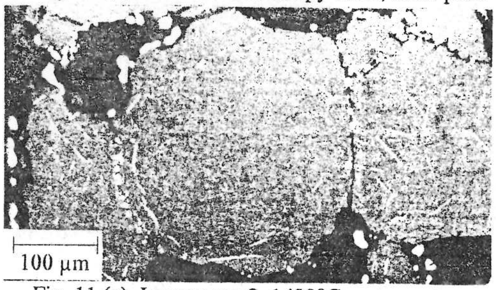


Fig. 11 (c) Lumpy ore 2, 1420°C, outer part.

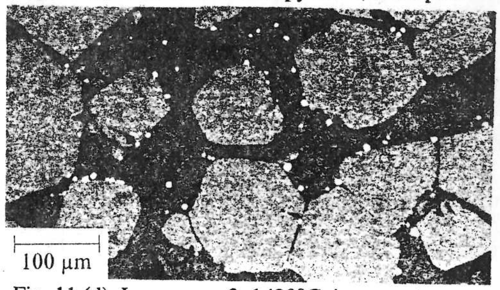


Fig. 11 (d) Lumpy ore 2, 1420°C, inner part.

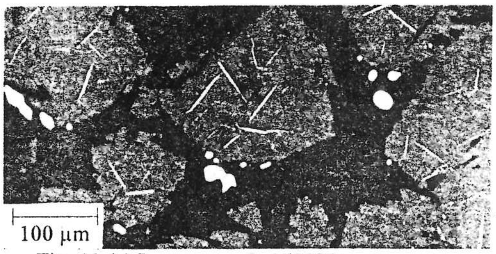


Fig. 11 (e) Lumpy ore 2, 1520°C, outer part.

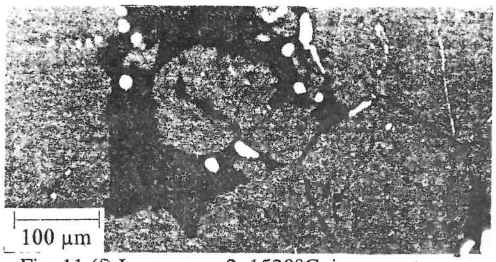


Fig. 11 (f) Lumpy ore 2, 1520°C, inner part.

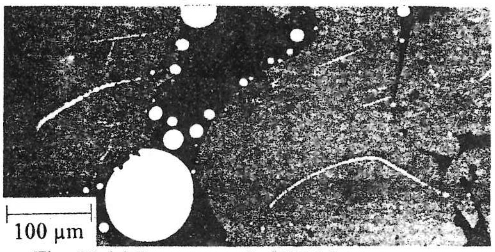


Fig. 11 (g) Lumpy ore 2, 1595°C, outer part.

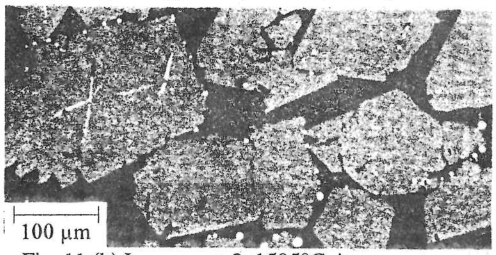


Fig. 11 (h) Lumpy ore 2, 1595°C, inner part.

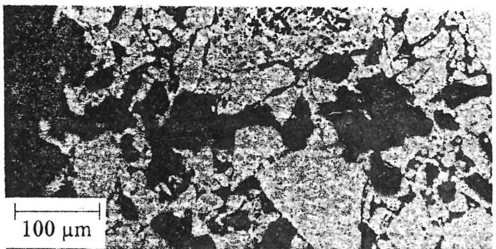


Fig. 12 (a) Non-reduced sintered pellet, outer part.

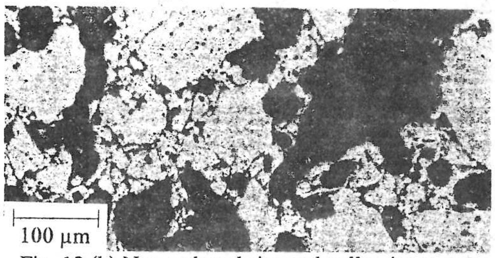


Fig. 12 (b) Non-reduced sintered pellet, inner part.

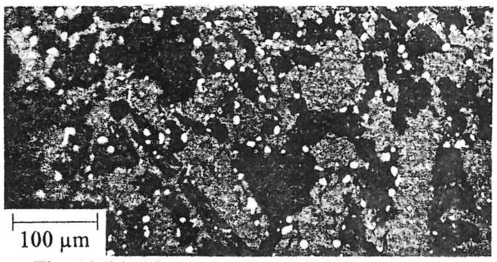


Fig. 12 (c) Sintered pellet, 1420°C, outer part.

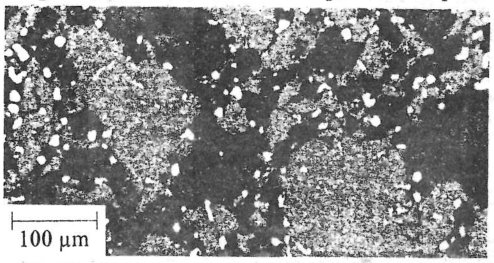


Fig. 12 (d) Sintered pellet, 1420°C, inner part.

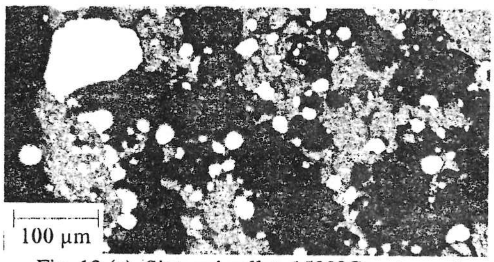


Fig. 12 (e) Sintered pellet, 1520°C, outer part.

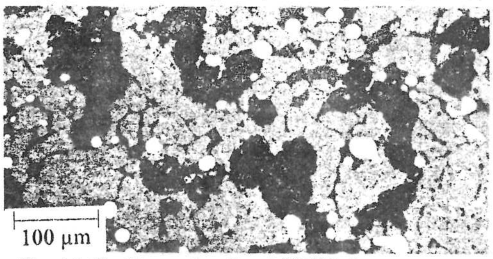


Fig. 12 (f) Sintered pellet, 1520°C, inner part.

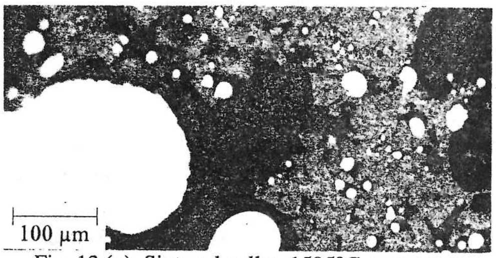


Fig. 12 (g) Sintered pellet, 1595°C, outer part.

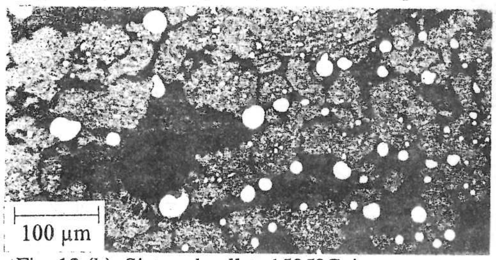


Fig. 12 (h) Sintered pellet, 1595°C, inner part.

Figs. 10-12 show that the reduction degree is higher at the outer than at the inner parts of the samples. One can also see for example from the Fig. 10d that chromite particles have two distinct zones - inner zone, rich in iron, and outer zone, where iron content is much lower. Analysis of the different zones of chromite particle in Fig. 10d is shown in Table 11.

Microanalysis

In order to scrutinize the reduced chromite samples, they were divided into three zones; the outer zone, the middle zone and the inner zone, which have been analysed respectively. Selected analysis of metallic particles in different zones of the lumpy ore samples are shown in Tables 2-7 and of the sintered pellets in Tables 8-10.

Table 2. Metal particles, chromite lumpy ore 1 reduced under CO at 1420°C.

ZONE	Fe	Cr	Al	Si	Mg	K	Ca	Ni
outer	95.0	3.0	0	0	0	0	0	1.5
middle	92.6	1.7	0	0	0	0	0	5.2
inner	87.1	1.2	0	0	0.1	0	0	11.3

Table 3. Metal particles, chromite lumpy ore 1 reduced under CO at 1520°C.

ZONE	Fe	Cr	Al	Si	Mg	K	Ca	Ni
outer	94.0	5.1	0	0	0	0	0	0.6
middle	95.7	1.0	0	0	0	0	0	3.1
inner	96.0	0.9	0	0	0	0	0	2.8

Table 4. Metal particles, chromite lumpy ore 1 reduced under CO at 1595°C.

ZONE	Fe	Cr	Al	Si	Mg	K	Ca	Ni
outer	93.9	2.2	0	0	0	0	0	2.4
middle	89.6	2.3	0	0	0	0	0	7.8
inner	90.1	3.2	0	0	0	0	0	6.3

Table 5. Metal particles, chromite lumpy ore 2 reduced under CO at 1420°C.

ZONE	Fe	Cr	Al	Si	Mg	K	Ca	Ni
outer	83.9	14.3	0.2	0.1	0.2	0	0	1.0
middle	93.3	1.9	0	0.1	0.1	0	0	4.4
inner	92.3	2.2	0	0.1	0.1	0	0	5.0

Table 6. Metal particles, chromite lumpy ore 2 reduced under CO at 1520°C.

ZONE	Fe	Cr	Al	Si	Mg	K	Ca	Ni
outer	94.2	4.7	0	0.1	0.1	0	0	0.8
middle	97.0	1.2	0	0	0	0	0	1.4
inner	95.4	1.9	0	0.1	0.1	0	0	2.3

Table 7. Metal particles, chromite lumpy ore 2 reduced under CO at 1595°C.

ZONE	Fe	Cr	Al	Si	Mg	K	Ca	Ni
outer	91.7	5.4	0	0.1	0	0	0	2.5
middle	91.0	4.2	0	0.1	0	0	0	4.4
inner	90.8	2.2	0	0.1	0	0	0	6.6

Table 8. Metal particles, sintered pellet reduced under CO at 1420°C.

ZONE	Fe	Cr	Al	Si	Mg	Ni	S
outer	92.6	6.8	0	0	0	0	0
middle	93.1	6.2	0	0	0	0.7	0
inner	94.1	5.2	0	0	0	0.6	0

Table 9. Metal particles, sintered pellet reduced under CO at 1520°C.

ZONE	Fe	Cr	Al	Si	Mg	Ni	S
outer	69.9	29.5	0	0	0	0.5	0
middle	89.1	10.2	0	0	0	0.6	0
inner	94.9	4.4	0	0	0	0.5	0

Table 10. Metal particles, sintered pellet reduced under CO at 1595°C.

ZONE	Fe	Cr	Al	Si	Mg	Ni	S
outer	61.1	38.2	0	0.4	0	0.5	0
middle	87.4	11.9	0	0.1	0	0.5	0
inner	94.3	5.2	0	0	0	0.5	0

Table 11. Chromite particle, lumpy ore 1, inner part of the sample, T=1520°C.

ZONE	Fe	Cr	Al	Si	Mg	Ti	O
inner	16.9	35.3	7.5	0.1	5.4	0.4	34.2
outer	11.0	30.6	12.7	0.2	8.6	0.3	36.3

From Tables 2-10 it can be seen that reduction degree is bigger in the outer zone of the samples and in the case of sintered pellets it increases with temperature. The chromium content of metallic particles is higher in sintered pellets than in lumpy ores. As can be seen from the Table 11 chromite particles have two zones - inner zone, rich in iron, and outer zone, where the iron content is lower. From the Fig. 13 we can see that in the case of sintered pellets Fe-content of the metallic particles decreases and Cr-content increases in the outer zone of the samples when the temperature increases.

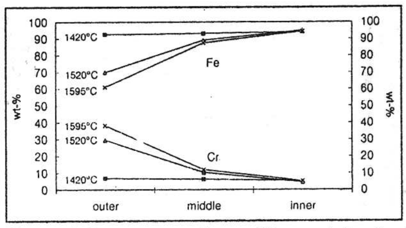


Fig. 13. Fe- and Cr-content of metallic particles in difrerent zones and temperatures in the case of sintered pellets.

Conclusions

The kinetics of solid state CO reduction of sintered chromite pellets and lumpy ores were studied by thermogravimetric analysis (TGA) in the temperature range 1420-1595°C. The investigations indicated that in the case of sintered pellets the reduction degree increased with the temperature. In the case of lumpy ores the reduction degree increased when increasing the temperature from 1420°C to 1520°C, but at the highest temperature 1595°C the kinetic conditions changed due to partial melting of the surface and thus the final reduction degree remained lower. The reduction rate of the lumpy ore 2 was much slower than reduction rate of the lumpy ore 1. Lumpy ore 2 was a serpentine based ore which sometimes has been observed to reduce slower than other ores.

Optical and scanning electron microscopy as well as microanalysis were used to obtain information on the structural changes of the partly reduced samples. Optical photographs and microanalysis showed that the reduction degree is higher in the outer zone of the samples and reduction proceeded further in the outer and inner zone of the sintered pellets than in the case of lumpy ores, because pellets are more porous than lumpy ores and thus CO-gas can penetrate easier inside through the pores. Also the size of chromite grains in the pellets is smaller than in lumpy ores.

The reduction experiments of sintered pellets with rising tempara-ture showed that the reduction rate increased rapidly when the temperature reached about 1000°C and the final reduction degree was almost the same as it was in constant temperature experiment at 1520°C.

Acknowledgements

The authors gratefully acknowledge Outokumpu Research Oy for opical and microanalytical investigations.

References

1. D. D. Slatter, "Technological trends in chromium unit production and supply", Proceedings of INFACON 7, 1995, Trondheim, 249-262.

2. M. Kekkonen, Y. Xiao, and L. Holappa, "Kinetic study on solid state reduction of chromite pellets", Proceedings of INFACON 7, 1995, Trondheim, 351-360.