

ON THE SLAG FORMATION AND ITS ROLE IN THE FERROCHROMIUM PRODUCTION

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Abstract

The reduction behaviour of three natural chromite ores at a temperature range between 1273 K and 1873 K was studied. The reduction was by graphite in the presence of silica. The aim of the present investigations was to get a better understanding of the mechanism of the chromite reduction in the submerged-arc furnace and to evaluate the role of the slag formation on the reduction kinetics and the electrode consumption. The composition of the chromite ores and the gangue minerals affect the reduction behaviour and the electrode consumption. To decrease the electrode consumption a careful adjustment of slag composition and prevention of an early slag formation are recommended.

INTRODUCTION

The submerged-arc furnaces dominate the production process of the high-carbon Ferro-chromium. The chromium recovery in the ferro-chromium production is mainly determined by the chromium content of the discard slags. Although many studies have been reported on the reduction mechanism of chromites [1-6], information on the roll of the slag formation and its roll to improving the reduction efficiency and better chromium yield are still incomplete. At the same time it seems that there exists a correlation between the slag formation and the electrode consumption in the process [7-9]. The thermal stress developed in the electrode may produce a number of micro cracks. The temperature gradient in the electrode makes the cracks growing and joining. An early and fluid slag formation in the furnace may contribute to a diffusion of the slag into the cracks where the reduction of the chromite will take place by using carbon from the electrode.

It is generally accepted that the addition of flux and the quick formation of slag may assist smelting. This effect is attributed to a preferable dissolution of chromites in the slag and relatively easy reduction of chromium from slag. It is also suggested that the slag dissolves some of the $\text{MgO} \bullet \text{Al}_2\text{O}_3$ spinel, which is formed as a dens layer around the chromite particles during the reduction reaction. At the same time there is an opinion that most reduction takes place in the solid state and the chromite particles maintain their solid form, but the structure of the ore changes.

From the producers viewpoint it is often claimed that the melting behaviour and the electrode consumption seem to be influenced by the origin of the ores used in the smelting [9].

Anyhow, the different authors suggest the mechanism of chromite ore reduction to be as follows:

Solid state reduction of chromite ore to metal,

Chromite ore dissolves in slag and CrO_x is reduced to metal,

A combination of solid state reduction and dissolution of ore in slag

The reduction rate of 3 different ores has been studied in the present investigation. The aim is to get more information about mechanism and reducibility of different types of chromite ores. This paper briefly gives the results of these investigations and discusses the mechanism of chromite reduction and the roll of the slag formation.

EXPERIMENTAL METHOD

Materials

Three different types of chromite ores from South Africa (SA), Finland (F) and Kazakhstan (K) in size fraction $\leq 0,16$ mm, prepared by crushing and grinding were investigated. Table 1 gives the chemical composition of the investigated chromite ores and table 2 shows the chemical analysis of the gangue existed in the chromite ores. Industrial coke was used as reductant material (table 3) and quartz was added as flux. Argon was of grade 2 and was supplied by Air Liquide Karlskoga. The gas was purified by passing through silica gel and Mg (ClO_4) to remove moisture, and through a column of ascarite to remove CO_2 impurity. The gas was then passed through a column of Cu turnings at 500°C to remove the traces of oxygen impurity before being admitted into the reaction chamber.

Apparatus and procedure

A schematic diagram of the experimental set-up is shown in figure 1. The experimental works were conducted in a graphite resistance furnace. A sintered alumina tube was installed to permit an atmosphere with controlled oxygen potential. The ends of the alumina tube were sealed with alumina sight hearths, nickel-plated aluminium doors and seal plates with O-rings. Alumina crucibles in size of H 40 mm, I.D. 25 mm and O.D. of 28 mm containing the mixtures of chromite ore, coke and flux were placed in the middle of the furnace. The crucible was placed in the furnace at room temperature. The furnace was then evacuated and flushed with argon. The procedure was repeated two times before start. The argon gas entered the furnace from the top at a rate of 2 l/min. The temperature was measured by a thermocouple of Pt-6%Rh/Pt-30/Rh. The temperature programme involved a constant-rate increase of $7^\circ\text{C}/\text{min}$ up to the desired temperature of 1000, 1200, 1400, 1600°C for a time of 1, 15, 30, 60, 120 and 180 minutes.

EXPERIMENTAL RESULTS

Characterisation of the chromite ores

Chromite is an accepted name of chrome spinel, whose chemical formula is $(\text{Mg, Fe})(\text{Cr, Fe, Al})_2\text{O}_4$ and which is a solid solution of five high melting point spinels actually[10]:

Spinel $\text{FeO} \bullet \text{Fe}_2\text{O}_3$ $\text{FeO} \bullet \text{Al}_2\text{O}_3$ $\text{FeO} \bullet \text{Cr}_2\text{O}_3$ $\text{MgO} \bullet \text{Cr}_2\text{O}_3$ $\text{MgO} \bullet \text{Al}_2\text{O}_3$

Melting

point, °C.	1590	1750	1850	2000	2130
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Table 4 gives the standard free energy changes for some spinel formation [11]. Thermodynamically, the presence of different spinels in the structure of chromite will change the reduction behaviour of the chromite ores. The Gibbs free energy of 53 738 kJ/mol makes Fe quite difficult to be reduced from the $\text{FeO} \bullet \text{Al}_2\text{O}_3$ spinel. At the same time the presence of MgO makes Cr difficult to be reduced from the $\text{MgO} \bullet \text{Cr}_2\text{O}_3$ spinel. It must be noted that according to the Gibbs free energy value MgO and Al_2O_3 can form a dense layer of $\text{MgO} \bullet \text{Al}_2\text{O}_3$ spinel.

In order to understand the characteristics of the investigated chromite ores, chemical analysis of ores from South Africa (SA), Finland (F) and Kazakhstan (K) were carried out. See Table 1 and Table 2.

Table 5 gives the chemical analyses of the chromite ores and the chromite spinel investigated.

It is observed that the Kazakhstani ore contains a higher chromium oxide and magnesium oxide compared to the South-African and Finnish chromite ores. At the same time the iron oxide content is higher in the South-African and Finnish chromite compared to the Kazakhstani chromite.

The EDX (Energy Dispersive X-ray Spectrometer) analyses on the different type of chromite ores reveals the presence of different type of gangue with the chemical analyses shown in Table 2.

This observation was supported by the SEM (Scanning Electron Microscope) analyses, which confirm the presence of multicomponent non-metallic phases (Figs. 2-4).

Reduction degree

Assuming that under Argon atmosphere and at the actual experimental temperatures the reaction product is mainly CO, then the reduction degree R was calculated by using the following relation:

$$R = \frac{(W_0 - W_f)}{W_{ox}} * \frac{16}{28} * 100\%,$$

where

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

W_f = weight of the sample after the reduction,

W_{ox} = amount of total initial removable oxygen (Cr_2O_3 and FeO_x were considered as reducible oxides).

Figures 5 and 6 show the reduction degree curves of different chromite ores at 1200° C and 1400°C, respectively. Note that reduction degrees can reach values above 100 % due to the reduction of SiO_2 in the slag.

From Figs 5 and 6 it can be seen that the reduction rates of the SA- ore and F- ore are higher than the reduction rates obtained during the R- ore reduction. According to our mineralogical and SEM investigations of the samples, no slag formation occurred during the reduction of different ores at 1200°C. This means that the reduction reactions occurred in the solid state.

The chromite ores show different reduction rates. The results indicate that the iron oxide contents into the chromite spinel affected the reduction rates. The Kazakhstani chromite spinel has an iron oxide content which is much lower than the Finnish or South African one: 13.8 % compared to 25.0 % and 28.1 % respectively. At the same time it is observed that the reduction rates of the chromite ores rich in chromium oxide and magnesium oxide are lower than that of the chromite ores rich in iron oxide and aluminium oxide. Experimental results indicate that the reduction rates decrease as the MgO/Al_2O_3 ratio of the samples increases.

Formation of slag

The factors that may influence the formation of slag during the ferrochromium production are as follows:

- The character of the chromite ores,
- Chemical composition and amount of the coke and fluxes,
- The furnace parameters and practical operation.

The temperature for the slag formation may be accepted as the temperature when the silica and the gangue of the chromite ores have formed a homogeneous phase, Table 6. It seems that the $\text{MgO}/\text{Al}_2\text{O}_3$ ratio in the slag is one of the most important factors in determining the melting point of the slag at the same SiO_2 content. The use of the South-African and Finnish ores results in an early slag formation of quite high Cr_2O_3 content and low viscosity. The Kazakhstanian ore will results in a slag of high viscosity and lower Cr_2O_3 content. It is claimed by the producers that using the Kazakhstanian ore results in lower electrode consumption compare to the South African and Finnish ores. An explanation of this may be that an early and fluid slag formation may contribute to a diffusion of the slag into the cracks formed in the electrode where the reduction reactions will take place by using carbon from the electrode.

The SEM investigations of the samples show that the formation of slag starts at different temperatures for different chromite types and that the slag chemical analyses vary as the reduction proceeds (Figures 7 and 8). It is observed that the FeO content in the slag is almost negligible. The amount of SiO_2 in the slag is heavily decreased at reduction degrees above 100%, which is due to reduction of SiO_2 . The amount of Al_2O_3 and MgO in the slag increase with reduction degree. The Cr_2O_3 content decreases gradually and should be related to the content of $\text{MgO}+\text{Al}_2\text{O}_3$ in the slag. This is in accordance with Sano et al [11], who measured the saturation concentration of chromium oxide in a quaternary slag at 1600°C . They found that the saturation concentration of Cr_2O_3 in $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}$ ($\text{CaO}/\text{SiO}_2 = 1$) decreases with the increase of the alumina and magnesia contents. It must be noted that the slag formation mechanism was quite different if the mix contains the reductant additions or not. The samples show no dissolution of chromite spinel in the slag when the coke was not added. These observations show that the reduction reaction and the dissolution of chromite spinel in the slag are dependent of each other and that the spinel dissolves when the reduction

reactions occur in the vicinity of the particle. According to Dawson and Edwards [2] a possible explanation of this is that in the absence of the reductant, the melt immediately adjacent to the chromite particle becomes saturated in one component which then recrystallizes at the surface of the grain and stop the dissolution process of the spinel.

The physical and chemical properties of the chromite ores influence the reduction mechanism. Figures 9 and 10 show the typical features of the reduction:

- Extensive reduction when widespread fine particles of metal were observed all over the grain surface during reduction of the ore from Kazakhstan (Fig.9).
- Topochemical reduction when the reduction front moves from the exterior of the grain to the interior part of it of the ores from South Africa and Finland (Fig. 10).

It is accepted by different researchers that the reduction takes place in two stages. In the first one the reduction is considered to take place at the surface of the chromite particle. As a result the particle becomes zoned, consisting of an inner core that maintains the original composition (Fig. 11). The second stage corresponds to the start of the slag formation when the particles are more or less enveloped in the slag and the reaction rate is decreased, as the reductant is not in a direct contact with the chromite particles. In order for the reduction reaction to continue through the slag layer, there must be an interchange of the Mg^{2+} and Al^{3+} cations of the surface unit cells with the Cr^{3+} and Fe^{2+} . Our SEM and EDX investigations confirm the presence of a slag layer rich in alumina and magnesia around the chromite particles.

CONCLUSIONS

The aim of the present study was to get more information about the role of the slag formation and its influence on the mechanism and reducibility of different types of chromite ore by experiments of the measurements of the reduction rates and reduction degree and the microscopic analyses of the slag.

It is concluded that the slag composition changes during the reduction reaction as the chromite particles dissolve into the molten slag. At the same time the alumina and magnesia from the gangue are transferred to molten slag.

During the reduction of the chromite ore the slag properties have a big influence on the reduction rates and electrode consumption. The gradual decrease of the reduction rate during the reduction reaction may be caused by the increase of the alumina and magnesia contents in the slag that increases the slag viscosity. The reduction rate depends on the composition of the molten slag.

In order to reduce the electrode consumption and to increase the reduction rate an early slagging process will be prevented.

ACKNOWLEDGEMENT

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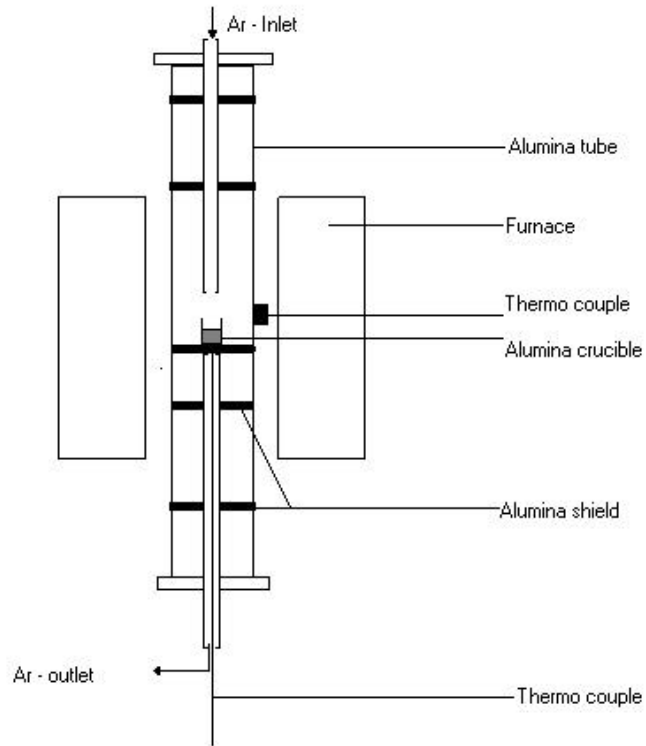


Figure 1. Schematic diagram of the experimental set-up.

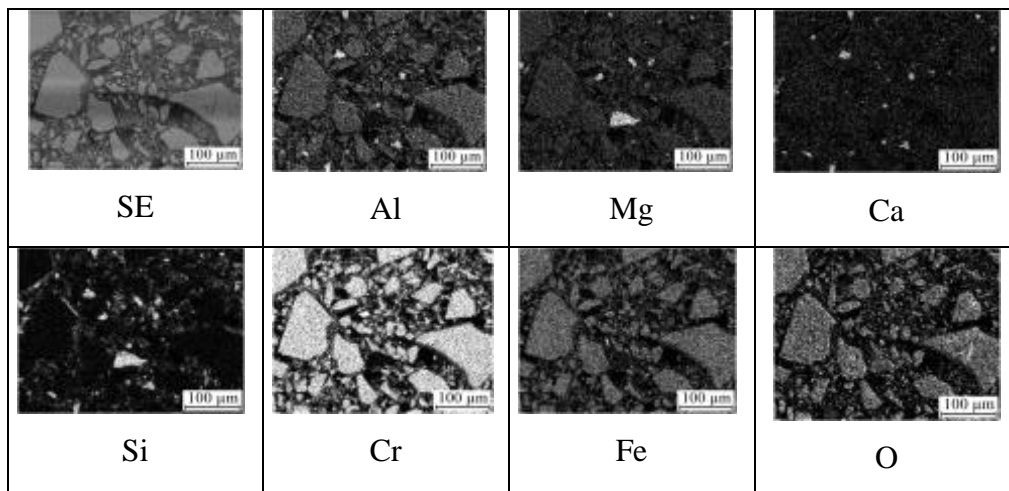


Figure 2. X-ray images for Al, Mg, Ca, Si, Cr, Fe, and O. Crushed South African ore. The presence of two types of gangue is observed.

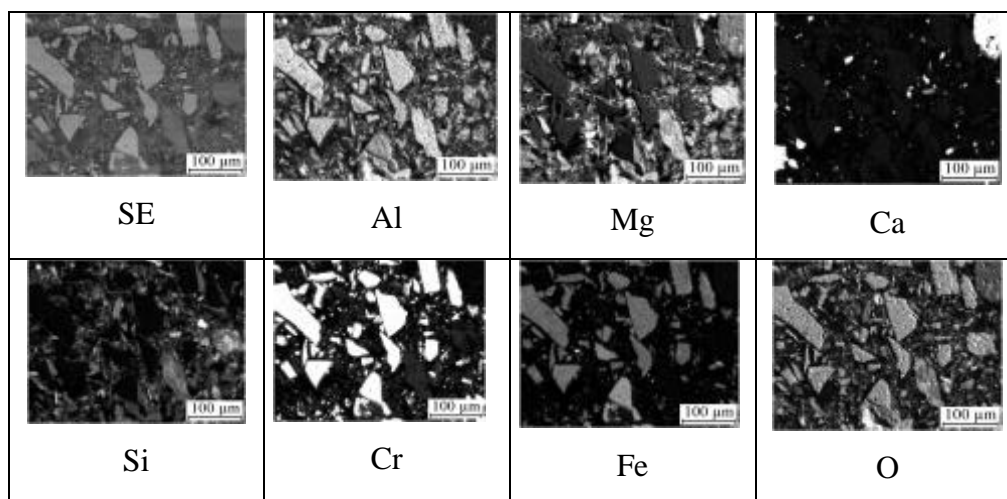


Figure 3. X-ray images for Al, Mg, Ca, Si, Cr, Fe, and O. Crushed Finnish ore. The presence of three types of gangue is observed.

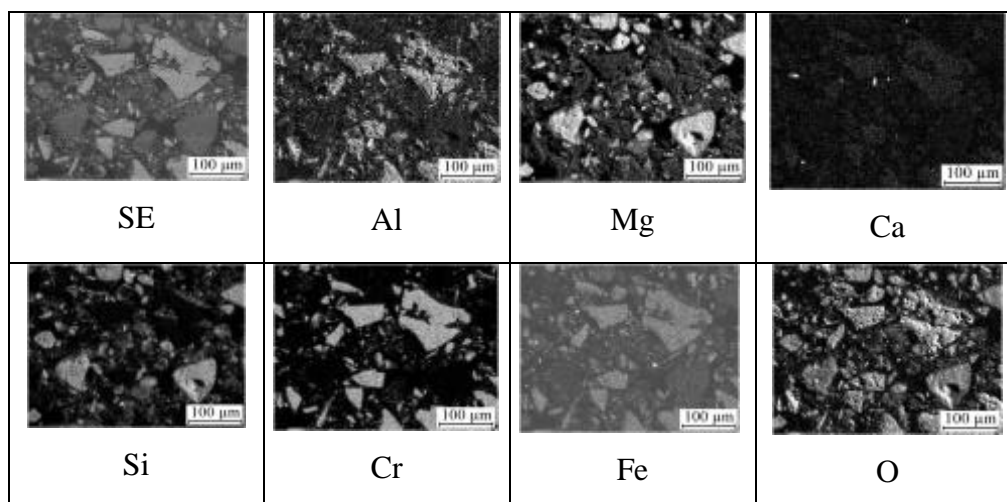


Figure 4. X-ray images for Al, Mg, Ca, Si, Cr, Fe, and O. Crushed Kazakhstani ore. Only one type of gangue is observed.

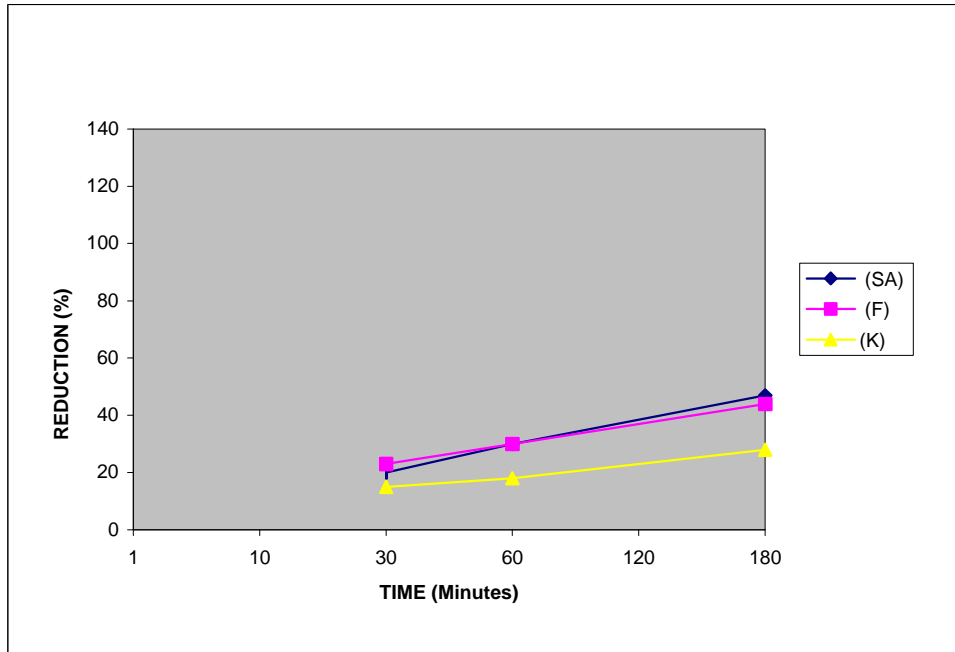


Figure 5. Reduction degree as a function of heating time at 1200 °C (no slag formation). The reduction rate of the SA-ore and the F-ore is fairly similar while the K-ore has a slower reduction rate.

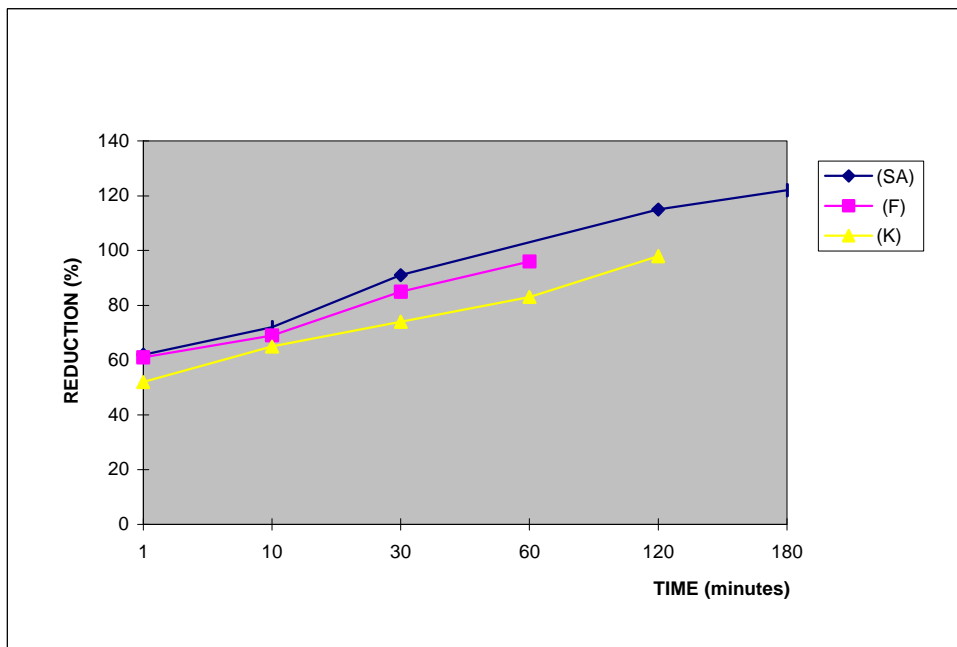


Figure 6. Reduction degree as a function of heating time at 1400 °C (slag formation). The reduction rate of the SA-ore and the F-ore is fairly similar while the K-ore has a slower reduction rate. Reduction degrees above 100% are due to SiO_2 reduction.

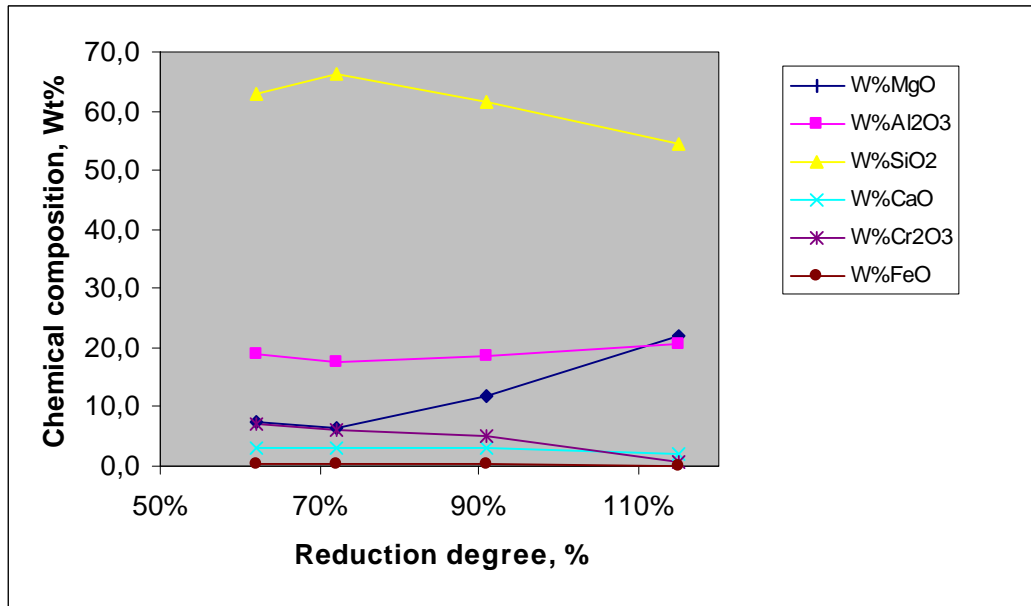


Figure 7. Chemical composition of the slag in samples of SA-ore with quartz and coke reduced at 1400 °C.

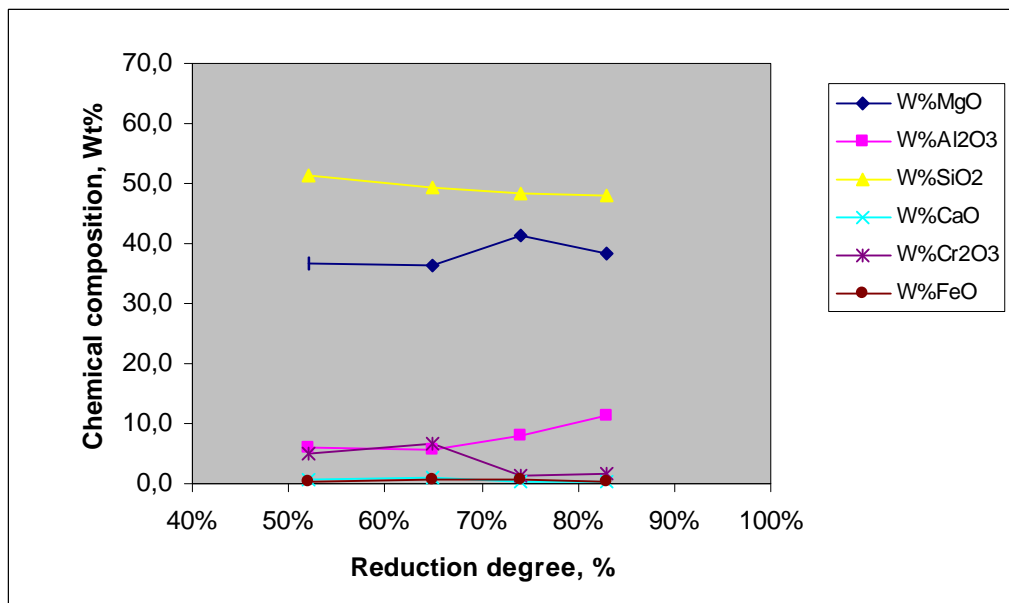


Figure 8. Chemical composition of the slag in samples of K-ore with quartz and coke reduced at 1400 °C.

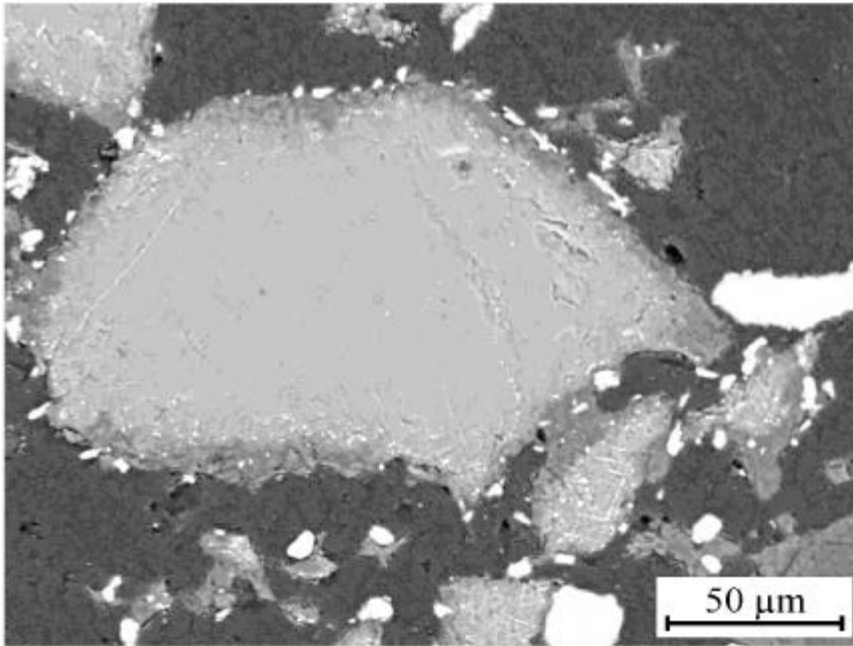


Figure 9. Kazakhstanian ore reduced to 65 % at 1400 °C. Unreacted spinel (light grey) surrounded by slag (grey) and by isolated metal particles (white). Metal is also found in the spinel. Notice that the spinel does not exhibit any depleted zone.

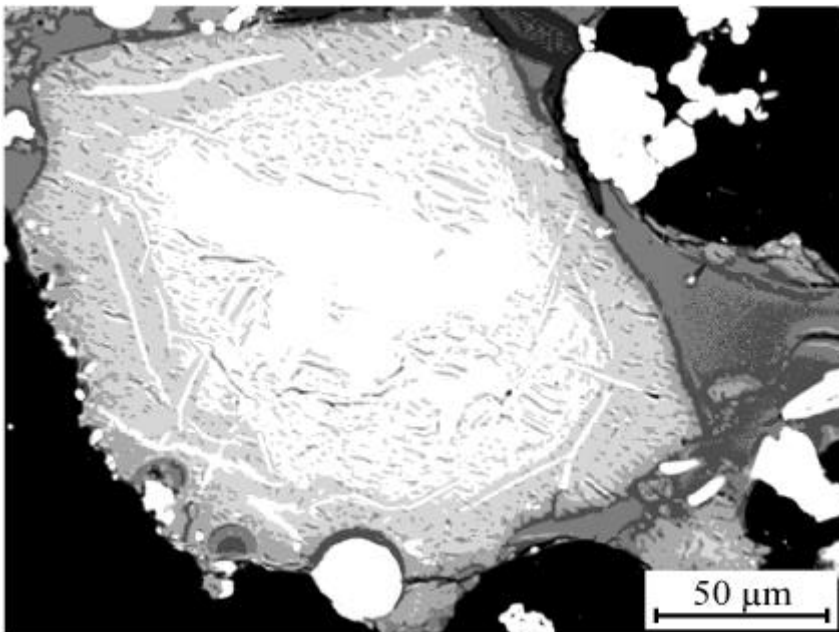


Figure 10. South African ore reduced to 62 % at 1400 °C. Unreacted spinel (light grey) surrounded by a Fe-depleted zone (grey) and by isolated metal particles (white). Metal is also found in the spinel. The dark grey phase is slag.

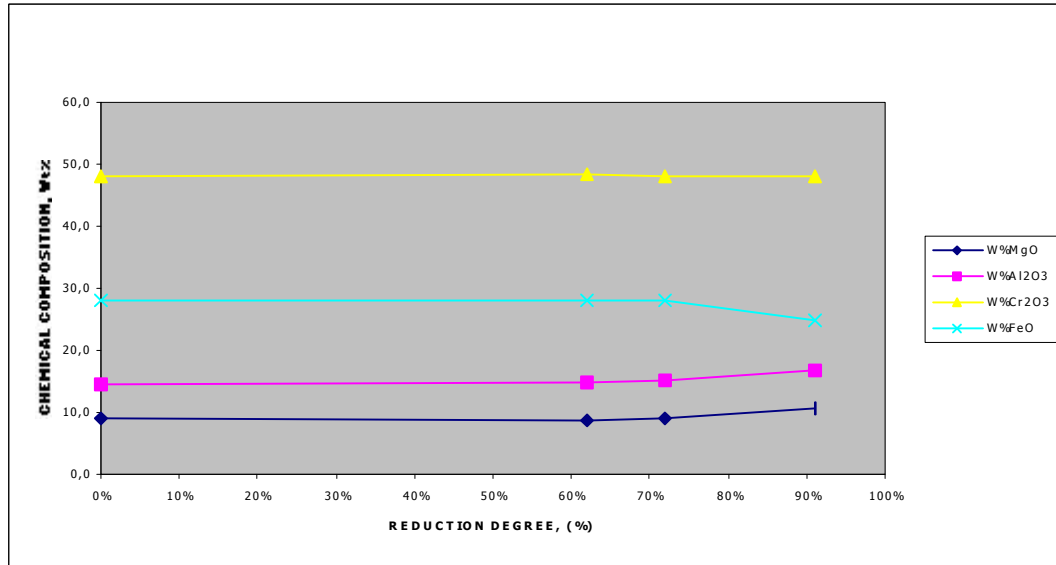


Figure 11. Chemical composition of the inner zone of the chromite spinel in samples of SA-ore, quartz and coke. The composition changes very little with the reduction degree.

Table 1. Chemical composition of the chromite ore (wt%).

Type of ore	Cr ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	MgO	CaO
SA	42,03	23,72	6,26	14,64	11,71	0,52
F	33,60	17,50	11,60	11,70	18,20	1,40
R	44,40	11,50	10,70	6,10	22,70	0,19

Table 2. EDX-analyse of the different kinds of gangue that exist in the investigated chromite ores (wt%).

GANGUE	MgO	Al ₂ O ₃	SiO ₂	CaO	Cr ₂ O ₃	FeO
SA. Type 1	0	26,9	56,3	15,6	1,0	0,5
SA. Type 2	25,4	1,2	61,0	1,2	1,7	9,4
F. Type 1	24,3	0	73,7	0	1,1	0,7
F. Type 2	34,9	0	1,3	58,9	0,8	4,5
F. Type 3	28,8	18,2	44,2	0	6,8	1,9
K.	41,9	0	46,0	0	1,2	10,4

Table 3. Chemical composition of the coke (wt%).

Moisture	11,9
Volatile matter	0,9
Ash	4,5
Fixed C dried sample	94,6
Fixed C undried sample	84,2
S	0,90
P	0,006

Table 4. The standard free energy changes for some spinel formation [11].

FORMATION REACTION	FREE ENERGY FORMULA	FREE ENERGY 1973 (KJ/MOL)	LATTICE CONSTANT (ANGSTROM)
$\text{MgO} + \text{Al}_2\text{O}_3 = \text{MgO} \bullet \text{Al}_2\text{O}_3$	$\Delta G^\circ = -35600 - 2,09T$	- 39724	8,09
$\text{FeO} + \text{Cr}_2\text{O}_3 = \text{FeO} \bullet \text{Cr}_2\text{O}_3$	$\Delta G^\circ = -45144 + 8,36T$	- 28650	8,37
$\text{MgO} + \text{Cr}_2\text{O}_3 = \text{MgO} \bullet \text{Cr}_2\text{O}_3$	$\Delta G^\circ = -42840 + 7,11T$	- 28817	8,32
$\text{FeO} + \text{Al}_2\text{O}_3 = \text{FeO} \bullet \text{Al}_2\text{O}_3$	$\Delta G^\circ = -39710 + 7,11T$	- 53738	8,14

Table 5. Composition of chromite ores and chromite spinel (wt%).

OXIDE	South African		Finnish		Kazakhstanian	
	Ore	Chromite spinel	Ore	Chromite spinel	Ore	Chromite spinel
Cr ₂ O ₃	42,0	48,1	33,6	50,9	44,4	62,2
FeO	23,7	28,1	17,5	25,0	11,5	13,8
SiO ₂	6,3	-	11,6	-	10,7	-
Al ₂ O ₃	14,6	14,7	11,7	14,2	6,1	9,1
MgO	11,7	9,1	18,2	8,5	22,7	14,9
CaO	0,5	-	1,4	-	0,2	-
Cr ₂ O ₃ +MgO	53,7	57,2	51,8	59,4	67,1	77,1
FeO+Al ₂ O ₃	38,3	42,8	29,2	39,2	17,6	28
MgO/Al ₂ O ₃	0,80	0,62	1,55	0,60	3,72	1,64
MgO+ Al ₂ O ₃	26,3	23,8	29,9	22,7	28,8	24,0

Table 6. Temperature for slag formation.

SAMPLE	SLAG FORMATION
SA + quartz + coke	≤ 1350 °C
F + quartz + coke	≤ 1380 °C
K + quartz + coke	1380 - 1400 °C