REDUCTION BEHAVIOUR OF THE AKANVAARA CHROMITES OF NORTHERN FINLAND

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ABSTRACT

The Akanvaara intrusion (surface area 50-55 km^2) in Savukoski, Northern Finland, hosts 23 distinct monocumulate layers of small euhedral chromite crystals enclosed in a silicate matrix. These chromitite layers have been divided into four groups; UC (upper chromitite), ULC (uppermost lower chromitite) LC (lower chromitite) and LLC (lowermost lower chromitite). The driving force for investigating the Akanvaara chromites and their reduction behaviour originated from their very low MgO content and relatively low Al_2O_3 *content, giving them a unique quality which based on thermodynamics should facilitate the reduction. Another interesting feature is the high amount of* V_2O_3 *present especially in the upper chromitite. The chromites included in this study are from the UC and ULC layers (24.9 and 22.7 per cent* Cr_2O_3 *respectively). To obtain a better understanding of the reduction behaviour of Akanvaara samples in comparison to MgO-bearing chromitites, Kemi chromite from the ferrochrome works in Tornio, Finland, was included in the study as a reference sample.*

The reduction experiments were isothermal in a temperature range of 1000-1400°C in CO atmosphere. Experiments were also conducted with coke addition in pellets and briquettes in $CO/Ar/H_2$ *atmospheres. The results of the reduction experiments complemented with microanalytical research indicate that the Akanvaara chromites do reduce to a higher degree than the Kemi chromite. Although the aim was to characterize the mechanisms of reduction focusing on gas-solid reactions, the nature and amount of the gangue minerals was such that a considerable amount of slag phase was formed, which affected the reduction mechanisms extensively. The structural features together with low MgO and high FeO content in both Akanvaara chromites are important factors resulting in better reducibility than in the Kemi chromite.*

1. INTRODUCTION

The reduction behaviour of chromites has been studied on several occasions at various temperatures and in various atmospheres, with various reductants, with and without the effect of fluxes and for synthetic as well as natural chromites [1-12]. The main goals have usually been characterisation of the kinetics and mechanisms of reduction in order to understand and improve the behaviour of the chromites in industrial processes. Most ferrochrome is produced at present using submerged-arc furnaces followed by the separate processes necessary for stainless steel production. Oxidizing steel belt sintering before reduction combined with preheating and subsequent melting in closed-top submerged-arc are process combinations developed by Outokumpu and implemented into other facilities abroad as well. Although submerged-arc techniques will most likely dominate ferrochrome production for decades to come, other possibilities such as direct production of stainless steel have been and continue to be investigated in order to minimize the costs of the energy intensive production.

Most of the world's ferrochrome production is concentrated in the countries with deposits of chromium. The Kemi chromite mine in Finland is the major source of chromium in Europe with some 70 million tons of ore containing 26 per cent Cr_2O_3 and estimated additional reserves of 144 Mt [13]. The Kemi intrusion and the Akanvaara intrusion in Savukoski, Northern Finland, belong to the same group of cratonic mafic layered intrusions with ages from 2.5 to 2.4 Ga. These types of intrusions are highly prospective worldwide. The exceptional chemical composition of Akanvaara chromites, practically devoid of MgO, high in FeO and fairly low in Al_2O_3 suggests a better reactability in metallurgical practices. This provides an interesting context in which to develop alternative methods of ferrochrome or direct stainless steel production. A preliminary study has been made of the reduction of Akanvaara UC chromite in CO/CO_2 atmospheres [14] and the results justified a further study with another Akanvaara chromite (ULC) and a reference material, Kemi chromite in order to compare the behaviour of low-MgO Akanvaara chromites with the MgO-bearing Kemi chromite.

2. GEOLOGICAL SETTING

The Akanvaara layered intrusion belongs to a group of layered intrusions (2.5 to 2.44 Ga) in the Fennoscandian Shield in Northern Europe. A block-faulted monocline dipping SE, it has a known surface area of ca. 50 km^2. The rocks underwent amphibolite facies regional metamorphism during which the original cumulates suffered hydration and recrystallisation to a variable degree. The chromitites of the Akanvaara intrusion have been divided into four groups; UC (upper chromitite), ULC (uppermost lower chromitite) LC (lower chromitite) and LLC (lowermost lower chromitite) of which the most interesting are the V-enriched chromite of the upper chromitite and the layers in the basal part of the intrusion. The ULC layer is of a fair grade (22.7 wt. per cent Cr_2O_3) and is amenable to flotation concentration. The mineral resource for the UC layer have been estimated to be 18.1 million metric tons with 22.8 per cent Cr_2O_3, 0.4 per cent V and 0.912 g/t total Platinum Group Elements. The UC layer is geologically, mineralogically and compositionally very uniform [13].

The Kemi intrusion belongs to the same group of Early Proterozoic layered intrusions as the Akanvaara intrusion. Its lower part is composed of peridotitic and pyroxenitic cumulates and chromitite layers. A continuous chromitite layer which varies in thickness from a few millimeters to as much as 90 m in the central part can be traced for the entire 15 km of the intrusion. The mafic minerals of the lower and upper parts of the intrusion are completely altered to chlorite, serpentine, talc, amphiboles and carbonates [15]. The average grade of the ore is 26.6 per cent Cr_2O_3 with a Cr/Fe ratio of 1.53. The ore reserves are estimated at 144 Mt.

3. CHARACTERISATION OF THE SAMPLES

3.1 Properties of the Concentrates and Preparation of the Pellets

Ore samples were crushed and processed by the Technical Research Centre of Finland (VTT), where the preliminary tests on flotation concentration of the ULC chromite had been carried out yielding encouraging results. The analytical results, determined by the XRF (X-Ray Fluorescence) method at VTT, are given in Table 1. The Kemi sample which includes carbonates (dolomite, magnesite) has a column for CO_2 content. The parameters for grinding, concentrate yields and contents as well as standards of purity are given in Table 2 [16].

Table 1. Chemical compositions of the ore samples [16].

Sample	**Cr_2O_3 %**	**V_2O_3 %**	**CO_2 %**	**SiO_2 %**	**Al_2O_3 %**	**FeO %**	**MgO %**	**CaO %**
UC	24.9	0.67	-	15.2	11.6	31.4	4.3	2.1
ULC	22.7	0.14	-	14.4	15.2	28.3	13.4	-
Kemi	25.1	-	7.2 (∗)	21.1	8.1	15.6	24.2	1.1

Table 2. Grinding times, fineness of the samples, concentrations of Cr_2O_3 and V_2O_3 in the concentrates and standards of purity [16].

Sample	**Grinding**		**Concentrate yield %**		**Concentrate contents / Std of Purity**		
	Time/min	**Fineness /%-90μm**	**Cr_2O_3**	**V_2O_3**	**Cr_2O_3 %**	**V_2O_3%**	**%**
UC	20	53.3	86.2	82.8	32.2	0.83	75
ULC	20	74.4	84.0	81.5	36.0	0.21	79
Kemi	15	70.0	80.0		39.2		82

The concentrates described in Table 4 were used to prepare pellets (average 10 mm diameter) with a 0.75 wt. per cent bentonite addition and 10 per cent H_2O. Additional grinding was carried out on the UC and Kemi samples, in order to achieve as similar a grain size distribution as possible and minimize the effects of differences in grain size on the reduction experiments. The pellets were dried for 2 h at 100°C after which they were sintered in an oxidizing atmosphere at 1100°C for 47-54 minutes. Compression strengths measured for dried and sintered pellets are given in Table 3. The difference in strength is the most notable in sintered UC samples, which, given the same amount of bentonite in all three samples, indicates the sintering behaviour of UC gangue (biotite, hornblende). Samples with 2 wt. per cent addition of coke in pellets were also prepared by the same procedure at VTT. Coke powder (fineness 73 per cent -36 µm) was mixed with the concentrate and pelletised with 0,75 wt. per cent bentonite. The compression strengths of these pellets are also given in Table 3. This small coke addition almost doubled the strength of the sintered UC pellets while the effect on ULC and Kemi samples was the opposite. Samples with 15 wt. per cent coke addition were also prepared by the Research Center of Rautaruukki in Raahe, Finland.

Table 3. Compression strengths of pellets [16].

	Dried sample N/cm^2	Sintered sample N/cm^2	Dried sample with small coke add. N/cm^2	Sintered sample with small coke add. N/cm^2
UC	10.0	274.8	12.0	556.0
ULC	15.5	150.4	17.1	39.8
Kemi	12.7	92.0	19.1	22.4

3.2 Properties of the Chromites

XRF analyses of the concentrates [16] and SEM/EDS (Scanning Electron Microscope/Energy Dispersive Spectrometer) analyses of chromites and sintered chromites are given in Table 4. The amount of ferric iron is calculated according to Droop (1987). The Akanvaara chromites have lower Cr_2O_3 and higher iron oxide content than the Kemi chromite. The UC chromite has practically no MgO, while the MgO of the concentrate presented in Table 4 is incorporated in the gangue. Other specific features of the Akanvaara chromites are their higher ZnO and the higher V_2O_3 content of the UC chromite in particular. The Akanvaara chromites also have a lower Al_2O_3 content than the Kemi chromite.

Table 4. Chemical compositions of the concentrates and chromites.

	Akanvaara UC			**Akanvaara ULC**			**Kemi**		
Wt.-%	**Concentrate**	**Chromites**	**Sintered chrom.**	**Concentrate**	**Chromites**	**Sintered chrom.**	**Concentrate**	**Chromites**	**Sintered chrom.**
MgO	2.3	0.0	0.7	5.2	0.5	1.9	12.3	8.9	11.6
Al2O3	9.5	12.0	10.7	10.7	12.7	11.9	12.2	14.5	14.8
TiO2	2.7	1.1	1.2	0.8	0.6	0.5	0.5	0.5	0.3
V2O3	0.8	1.4	1.4	0.2	0.2	0.1	0.1	0.0	0.0
Cr2O3	31.8	37.9	39.8	36.5	43.9	44.7	42.1	49.5	50.5
MnO	0.9	1.6	1.8	1.0	1.6	3.6	0.3	0.4	0.2
FeO	35.2	35.1	41.3	36.0	31.6	32.6	25.9	20.5	20.8
Fe2O3		10.3			7.8			5.3	
ZnO	0.5	1.0	1.1	0.5	0.9	3.0	0.0		
SiO2	9.0			4.9			3.2		
Total		100.4	97.9		99.7	98.2		99.7	98.2

The ULC and Kemi chromite grains resemble each other structurally, while the UC chromite possesses a lot of silicate inclusions and its structure seems to be cataclastic. This is also obvious from the standard of purity of the concentrates (Table 2), which is the lowest for UC concentrate. All chromitites differ in their gangue mineralogy that of the UC being composed mainly of hornblende and biotite, ULC having almost entirely chlorite as its gangue, while the Kemi ore is of the talc-carbonate type as reported by VTT but also includes some chlorite as detected by XRD (X-Ray Diffraction) and SEM/EDS analyses.

4. REDUCTION EXPERIMENTS

4.1 Experimental Setup

The reduction experiments (isothermal, temperature range 1000-1400°C) were conducted in a vertical furnace incorporating a balance which recorded the weight of the sample automatically at approximately 5 second intervals. The samples were dried in 110°C before the experiments, and also stabilized in the TG furnace before the runs. After the runs the samples were cooled in an Ar flow. The atmosphere consisting of CO and/or H_2 and Ar was controlled by means of a mass flow gauge. The experiments, each of 3 hours' duration, were carried out on one pellet at a time, which was placed in a Pt or Mo basket. The degree of reduction (R%) was calculated according to the change in weight of the sample and the stoichiometric amount of removable oxygen in the chromite, Equation 1 [14].

$$R\% = \frac{W_0 - W_t}{(W_0 \cdot \frac{M_O}{M_{FeCr_2O_4}})} \cdot 100 \qquad (1)$$

where W_0 = initial weight of the pellet
W_t = weight of the pellet at time t during the experiment
M_O = molar mass of oxygen in chromite (64 g/mol)
$M_{FeCr2O4}$ = molar mass of chromite (224 g/mol)

4.2 Results of the Experiments

The reduction behaviour of the chromite pellets without a coke addition in 100 per cent CO atmosphere within a temperature range 1000-1400°C is presented in Figures 1, 3 and 4. The basic behaviour of the chromites appears to be similar in all three samples, a lot of the weight being lost during the first few minutes of the experiments. This indicates loss of oxygen from the surfaces of the grains in chemical reactions by which the ferric and subsequent ferrous iron is eventually reduced to the metallic state. Reduction with CO is said to be of a mixed type, being controlled by the chemical reaction itself, internal diffusion through the product layer in the chromite grain, pore diffusion within the pellet and gas phase mass transfer [4]. At later stages of the experiments, the reduction reactions appear to be diffusion controlled. For graphite-chromite composite pellets the early stages of reduction have been found to be governed by nucleation and chemical reaction while gas/solid diffusion is most likely the rate controlling in the late stages [1,7].

Despite general similarities in reduction behaviour, all the chromites have individual features that are manifested in the extent of the reduction at different temperatures. The degrees of reduction achieved by the Akanvaara chromite pellets with CO gas are markedly higher than those of Kemi pellets at almost all temperatures of the experiments as seen in Figures 1, 3 and 4. The Akanvaara chromite pellets achieved reduction degrees of 37-40 per cent at their highest, while the Kemi chromite pellets achieved only 28 per cent. The degrees of reduction for the Kemi chromite pellets are actually higher than in other experiments conducted on pellets from the same source under similar conditions [4,5].

Although UC chromite usually has the highest degrees of reduction in CO atmospheres, it reaches surprisingly low degrees of reduction at 1400°C, only 35 per cent which is the same as that achieved already at 1100°C. This behaviour is clear evidence of the importance of gangue behaviour during the experiments, as revealed in a microanalytical study. The degrees of reduction achieved for the samples originally prepared with small coke addition (2 wt. per cent) were lower in all temperatures for UC chromite than without any coke addition, Figure 2, which underlines the importance of the amount of ferric iron for the reduction reactions as discovered also in [2,11]. According to the XRD analyses of the sintered samples, all three chromites possess a hexagonal eskolaite-type structure after sintering in oxidizing atmosphere. This behaviour was not detected in the XRD patterns of the pellets containing a small amount of coke. Although the structural features after sintering were similar in all three chromites both with and without an addition of coke, there was no observed effect on the behaviour of the ULC and Kemi chromite during the reduction experiments, as the pellets of these reduced to the same degree or even slightly better with a small coke addition depending on the temperature of the experiment. This difference in reduction behaviour is probably due to the higher amount of iron in the UC samples as well as the structure of the chromite. It may also be partly explained by the more extensive melting of the UC gangue minerals during sintering, which enhanced the compression strengths of the pellets (Table 3).

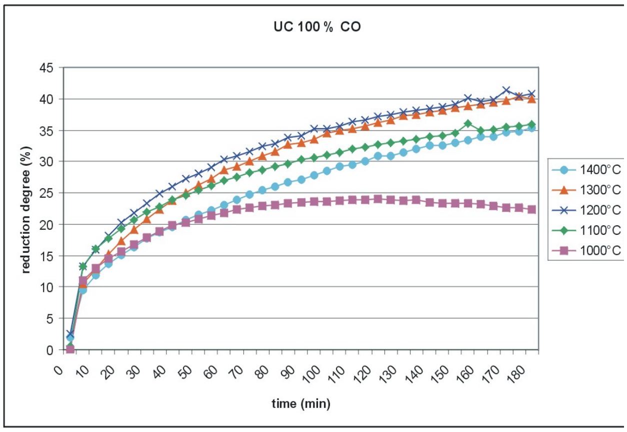

Figure 1. Reduction of sintered UC chromite pellets in a 100 % CO atm. at temperatures of 1000-1400°C.

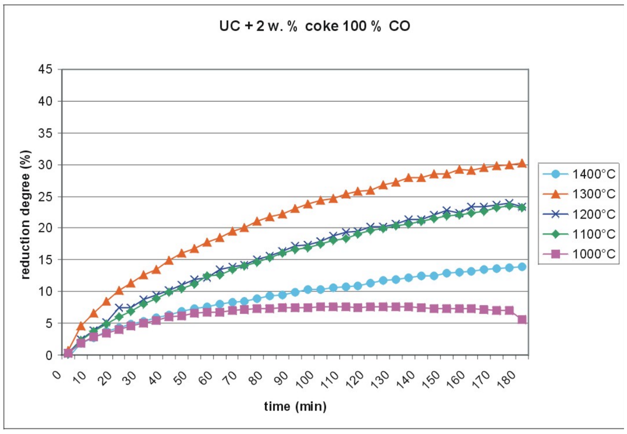

Figure 2. Reduction of sintered UC chromite pellets with originally 2 wt. per cent addition of coke. In a 100 % CO atm. at temperatures of 1000-1400°C.

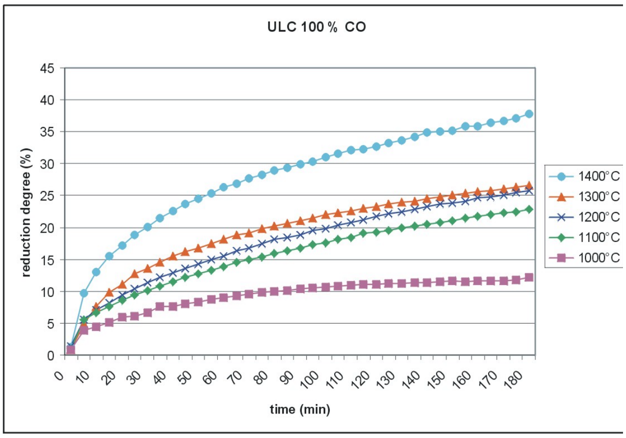

Figure 3. Reduction of sintered ULC chromite pellets in a 100 % CO atm. at temperatures of 1000-1400°C.

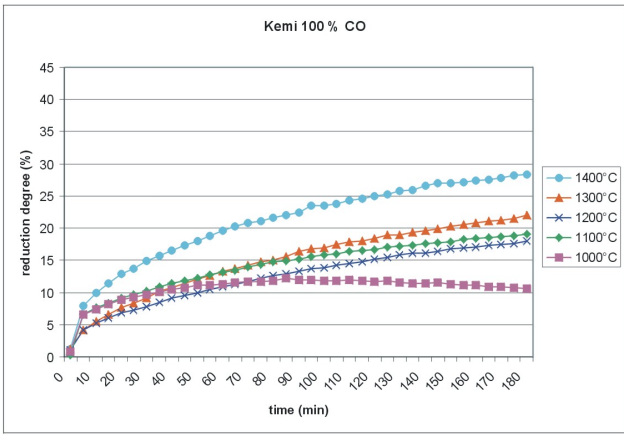

Figure 4. Reduction of sintered Kemi chromite pellets in a 100 % CO atm. at temperatures of 1000-1400°C.

The UC and Kemi samples with a 15 per cent addition of coke were pelletised and briquetted whereas only briquettes were prepared from the ULC samples. These samples were studied at 1400°C in atmospheres with mixtures of either 95 per cent Ar with 5 per cent H_2 or 95 per cent CO with 5 per cent H_2. The UC pellet and briquette achieved 100 per cent reduction in the Ar/H_2 mixture but only 88 per cent reduction in the CO/H_2 atmosphere, while the Kemi pellet also achieved 100 per cent reduction in the Ar/H_2 atmosphere but the briquette only 75 per cent for and the pellet only 82 per cent in the CO/H_2 atmosphere. Surprisingly, the ULC briquettes achieved a reduction as low as 50 per cent in the Ar/H_2 atmosphere. After the experiments the samples were cut into two pieces for the XRD runs and the preparation of polished sections for SEM/EDS analysis.

5. MECHANISMS OF REDUCTION

The reduction mechanisms were characterized according to the compositional and structural features observed by SEM/EDS (Jeol JSM-6400) and XRD (Siemens D5000, Cu Kα). All the microanalytical research was carried out at the Institute of Electron Optics, University of Oulu. The differences in chromite structures and chemical compositions between the three samples resulted in different observed mechanisms of reduction. These differences were most obvious between the UC and Kemi chromite, while the behaviour of the ULC chromite was more similar to that of the Kemi sample. The UC chromites reduced very evenly throughout the grains (Figures 5-6) with metal precipitates forming in the grains and on their edges. One important factor which appears to facilitate reduction is the formation of iron-containing exsolutions during sintering especially in the UC samples. These exsolutions are reduced very easily during the experiments, causing the chromite structure to disintegrate and creating a greater surface area on which the reactions could occur. Small addition of coke to the pellets prevented the iron from oxidizing to a ferric state and the formation of these exsolutions to such an extent.

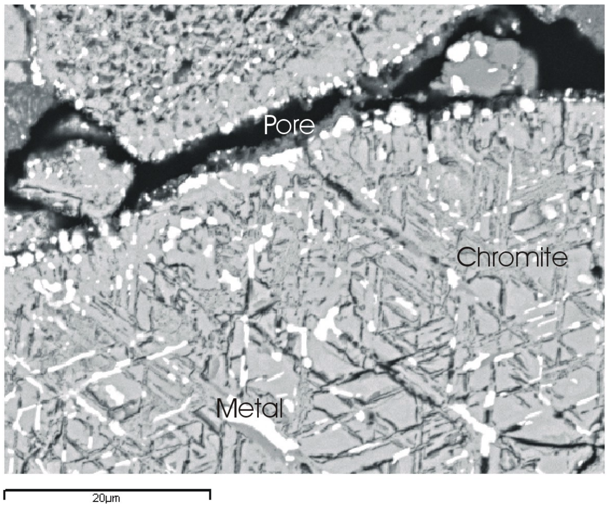

Figure 5. Reduction mechanisms of the UC chromite at 1000°C in a 100% CO atm.

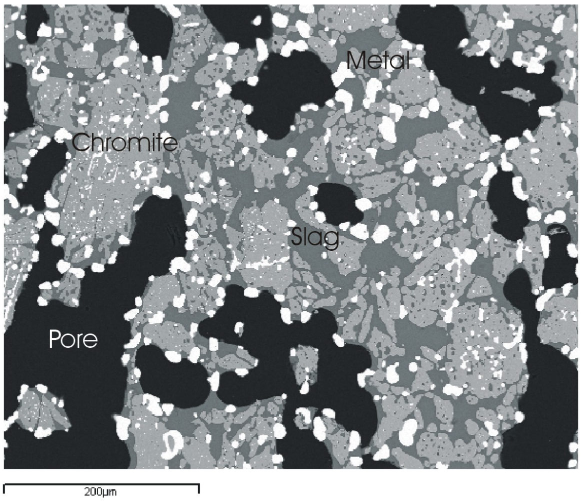

Figure 6. Outer zone structure of the UC pellet at 1400°C in a 100% CO atm.

As is well known from several experiments performed on chromite pellets, their reduction with CO gas proceeds from the exterior into the interior, so that chromite grains in different parts of the pellet experience different reduction conditions which are also affected by the reaction products (CO_2) as reduction proceeds [4,5,11]. Chromite grains are known to exhibit zonation in carbothermic reduction due to the diffusion of cations up to certain degrees of reduction, after which the shrinking core of almost original composition disappears [3,7,8,9]. Similar zonation was observed here particularly clearly in the ULC and Kemi chromites, Figures 7-8. The smaller grains in the pellets did not show observable zonation, whereas the larger grains in the ULC and Kemi samples were distinctively zonal up to a temperature of 1300°C. At 1400°C Kemi chromite in particular appeared to include a lot of small metal precipitates also in the cores of the grains.

This zonation (Figures 7-8) is mainly due to the diffusion of iron towards the boundaries of the grains. The original compositions of the chromites in the core were preserved presumably including the ferric iron, while the iron content of the diffusion zones was low and other components seemed to be enriched at the expence of iron (Table 5). It is assumed that most of the iron in the diffusion zone is ferrous. The driving force for the diffusion of ferrous iron towards the boundaries is the concentration gradient between the surface, where it is reduced to a metallic state, and the core. The border between the core and the outer zone is quite sharp indicating the presence of a chemical reaction boundary. This reaction boundary has been attributed to the reactions with ferric iron which is reduced from an octahedral site in the chromite lattice to ferrous iron at a tetrahedral site by inward-diffusing Cr^{2+} [3,7,9,10]. According to the results of the analyses and in view of the existence of the eskolaite-corundum phases, it is assumed that most of the chromium in the spinel lattice remains trivalent. Chromium diffuses inwards balancing the structure in which the octahedral sites become available after the reduction of Fe^{3+}. Aluminium contents of the chromites in all the samples remained fairly constant at all temperatures of the experiments (Table 5) except the samples with a 15 wt. per cent coke addition.

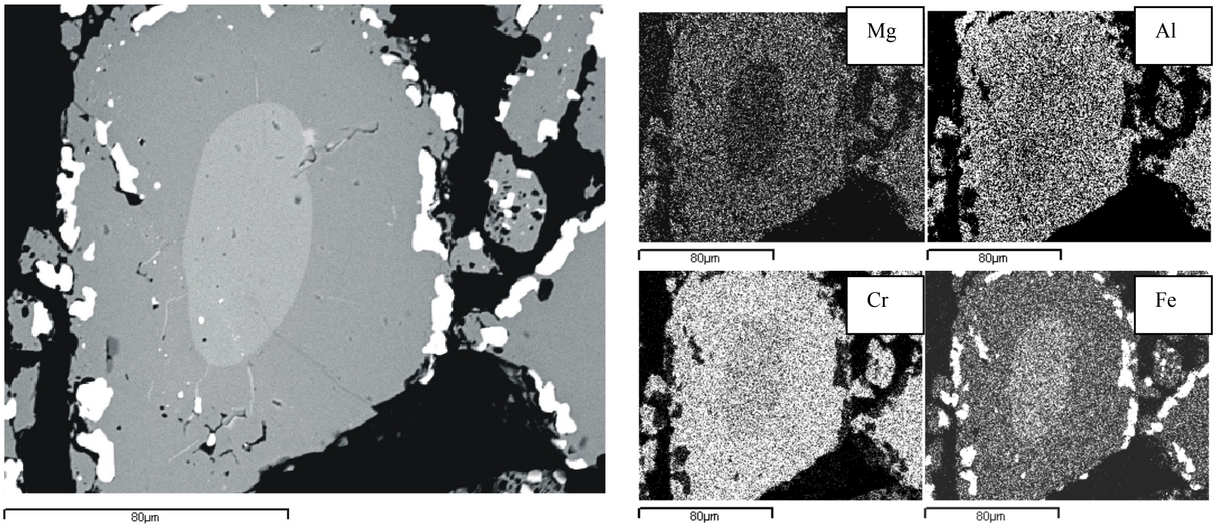

Figure 7. Zonation and X-ray maps of the ULC chromite at 1300°C in a 100% CO atm. (with small addition of coke).

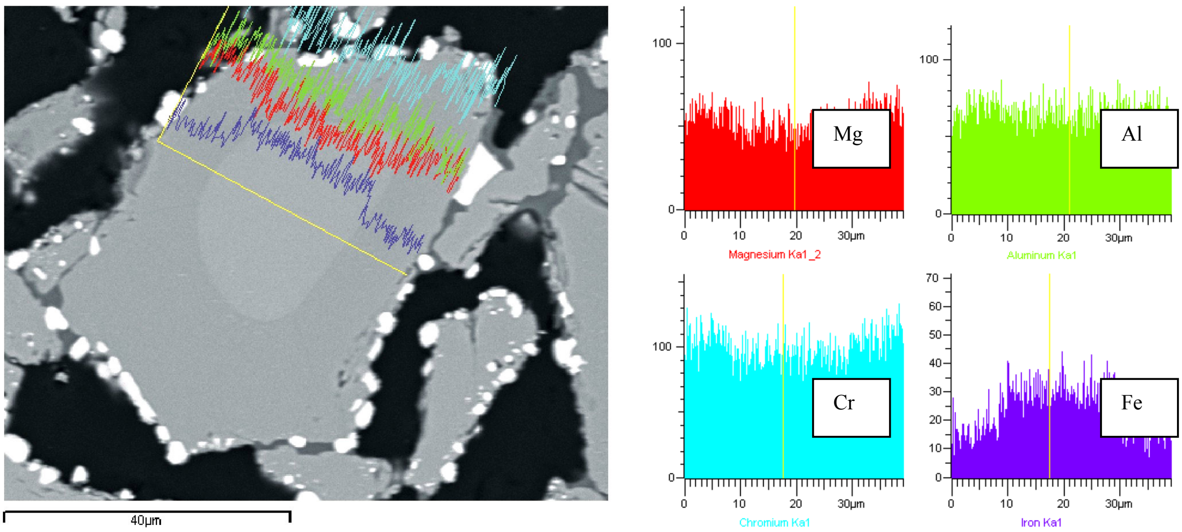

Figure 8. Zonation and line spectra of Kemi chromite at 1300°C in a 100% CO atm.

Table 5. Chemical compositions of the UC and ULC chromites. Analyses apply to the outer and inner parts of the pellet and the zonated chromites in the ULC samples (o.z. = outer zone of the grain).

	Akanvaara UC						**Akanvaara ULC**							
T°C	**1200°C**		**1300°C**		**1400°C**		**1300°C**						**1400°C**	
Pellet zone	Outer	Inner	Outer	Inner	Outer	Inner	Outer			Inner			Outer	Inner
Wt.-%								o.z.	core		o.z.	core		
MgO	11.7	1.0	11.2	5.8	9.2	2.9	6.0	4.6	1.5	4.8	4.6	2.8	8.5	5.5
Al2O3	12.0	10.1	13.5	11.2	13.6	11.6	15.4	14.8	12.5	15.2	14.0	12.2	16.8	14.8
TiO2	1.7	1.3	2.4	3.2	2.0	2.7	1.1	0.7	0.6	1.0	1.0	0.6	0.6	1.2
V2O3	1.2	1.0	1.4	1.4	1.5	1.1	0.3	0.1	0.2	0.2	0.0	0.1	0.3	0.2
Cr2O3	60.4	39.9	59.1	56.2	61.1	52.0	55.8	54.0	44.8	52.8	53.0	44.4	60.0	56.6
MnO	5.9	0.5	5.7	3.1	4.3	0.5	2.0	1.9	1.5	1.8	1.9	1.8	2.7	2.0
FeO	6.6	42.6	5.8	17.7	8.3	28.4	18.2	22.6	36.4	23.0	24.4	36.5	9.4	17.4

The gangue minerals in UC pellets show quite extensive melting already at 1200°C increasing the differences in reduction between their outer and inner parts, although the structure of the pellet still appears to show open porosity. At temperatures of 1300°C and 1400°C the resulting slag phase blocks this open porosity (Figure 6) and prevents the gases from diffusing into the interior of the pellet, so that degrees of reduction achieved are only 40 and 35 per cent, respectively (Figure 1). Although the edges of the pellets show extensive reduction in terms of the amount and composition of the metal precipitates and the disintegration and dissolution of chromites in the slag phase, the interior parts are prevented from undergoing similar reduction.

The formation of a silicate melt affected the mechanisms not only by altering the porosity of the pellet, but also by reacting with chromite relicts dissolving the chromites and donating divalent Mg cations to the defective spinel structure. An increase in Mg in the chromites can already be seen at the lowest temperatures, but this occurs more extensively at the temperatures involved in silicate melt formation, Table 5. Originally MgO-poor chromites take up the divalent Mg cations to fill the tetrahedral sites in spinel structure so that eventually the chromite relicts in the perimeter of the UC pellets have as high as 11-12 per cent MgO at 1200-1300°C. Counter-diffusion of magnesium from the silicates and silicate melt is evident from the analyses which show increased MgO content in both Akanvaara chromites.

The dissolution of the UC chromites into the slag begins extensively at a temperature 1300°C as seen in the analyses of the slag phase, Table 6. The melt formed in the UC samples representing originally MgO-bearing silicates eventually does not contain any MgO, corresponding to an anorthitic composition with a considerable amount of dissolved Cr_2O_3, on average 11 per cent in the outer zone of the pellet at 1400°C. The analyses of the melts from the inner and outer zones of the pellets are given in Table 6 to highlight the differences between the two, and the same table also presents the results for the ULC slag, which formed from 1300°C upwards. The composition of the UC melt particularly showed a clear variation in composition at 1300°C, which seemed to homogenize at 1400°C. The amount of dissolved chromium in the ULC slag is almost twice as much as in the UC slag, on average 21 per cent in the outer zone of the pellet at 1400°C. The decrease in the other components of the slag is considered proportional to the increase in Cr_2O_3. The behaviour of gangue minerals in the Kemi pellets differed from that in the Akanvaara samples involving partly melted slag at the highest temperatures together with enstatite, forsterite and periclase. As in the Akanvaara samples, the MgO content of the slag next to the chromite was low.

Table 6. Chemical compositions of the silicate slags in UC and ULC chromite pellets.

	Akanvaara UC						**Akanvaara ULC**					
	1200°C		**1300°C**		**1400°C**		**1300°C**				**1400°C**	
Wt.-%	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Inner zone	Outer zone	Outer zone	Inner zone	Inner zone	Outer zone	Inner zone
MgO	0.0	0.0	0.0	0.0	2.1	0.5	1.0	0.0	2.9	0.0	3.0	1.6
Al2O3	28.7	28.3	20.4	16.3	21.4	19.5	16.6	0.2	14.3	0.0	20.7	19.6
SiO2	50.8	51.1	50.7	50.3	45.9	47.7	61.9	94.6	61.5	93.3	47.9	53.3
K2O	2.5	2.8	3.1	2.9	1.2	2.5	0.5	0.0	0.4	0.0	0.0	0.0
CaO	14.1	13.9	10.2	12.6	10.2	13.5	2.6	0.0	4.8	0.0	0.7	0.8
TiO2	0.5	1.0	2.7	5.4	3.8	6.5	2.9	0.1	1.3	0.0	1.3	2.2
Cr2O3	1.0	0.8	7.3	3.2	11.2	2.4	6.6	1.1	1.6	1.3	20.8	14.0
MnO	0.0	0.0	0.8	0.5	1.2	0.4	0.1	0.0	1.2	0.0	0.5	0.1
FeO	1.1	1.5	0.5	1.6	1.3	3.8	2.6	0.5	8.5	0.7	1.4	3.0

Another feature that was most prominent in the Akanvaara chromite pellets was the formation of an eskolaite-corundum-solid solution series (Cr_2O_3-Al_2O_3) first in the form of distinct areas on the borders of the chromite grains and eventually as individual crystals especially in the perimeter of the pellets at temperatures of 1300-1400°C, Figures 9-10. The existence of this solid solution indicates that the conditions for further reduction of Cr^{3+} from the spinel lattice are not as strong as the tendency to form the hexagonal structure, which was also detected in the XRD patterns of the samples usually with reduction degrees exceeding 30 per cent. The chemical composition of this phase is very uniform at all temperatures, but differences exist between the samples with a higher TiO_2 and V_2O_3 content in the UC eskolaite-corundum and in turn a higher Al_2O_3 content in the ULC samples. The solid solution was detected also in the Kemi pellets at temperatures 1100-1300°C by SEM/EDS.

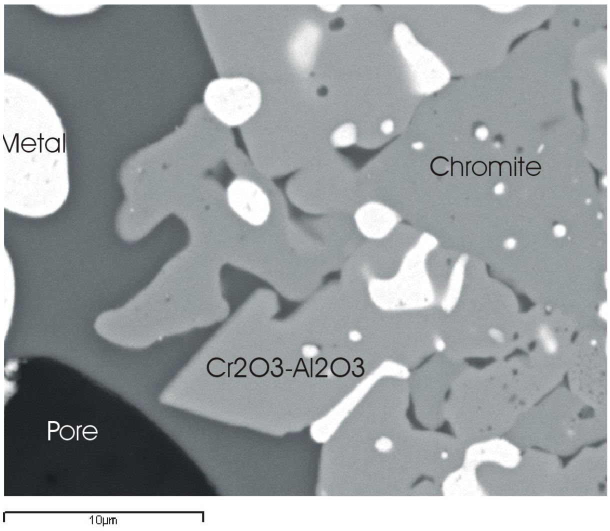

Figure 9. Detailed picture demonstrating the existence of Cr_2O_3-Al_2O_3 crystals on the edges of the UC chromite relict reduced at 1300°C in 100 % CO atm.

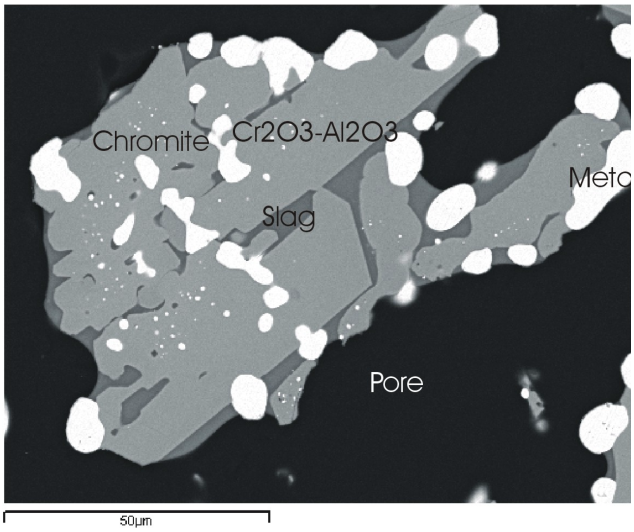

Figure 10. The existence of Cr_2O_3-Al_2O_3 solid solution in the ULC pellet reduced at 1400°C in a 100 % CO atm.

A small amount of Cr^{3+} is already reduced to the metallic state at temperatures of 1000°C in CO atmosphere according to the analyses of metal precipitates, which have an increasing Cr-content in the perimeter of the pellets at increasing temperatures, while those of interior parts remain fairly low, especially after melt formation (Table 7). Iron and chromium were the only components in the precipitates in Akanvaara samples. The amount of metal is considerably less in the interior parts at higher temperatures than at lower temperatures, particularly in the case of the UC samples. The analyses of metal from pellets with a small coke addition correlated with the degrees of reduction in above described manner.

Table 7. Compositions of the metal precipitates in chromite pellets at temperatures of 1000-1400°C.

	1000°C	**1100°C**		**1200°C**		**1300°C**		**1400°C**	
Wt. %	**Outer zone**	**Outer zone**	**Inner zone**	**Outer zone**	**Inner zone**	**Outer zone**	**Inner zone**	**Outer zone**	**Inner zone**
Cr UC	1.5	3.3	4.2	5.3	2.5	11.5	2.6	7.4	2.2
ULC	4.8	4.5	6.3	4.5	3.6	4.6	3.2	8.7	4.3
Kemi	6.2	5.8	6.2	7.2	5.7	7.5	4.8	13.1	4.7
Fe UC	98.3	95.6	96.3	94.2	97.9	86.5	95.7	93.0	98.1
ULC	94.4	94.8	92.0	95.5	95.1	95.6	97.2	90.1	94.6
Kemi	93.2	95.0	92.5	93.1	96.2	93.3	95.5	88.1	96.5

The UC samples with a 15 per cent addition of coke had experienced thorough melting at 1400°C leading to the formation of large accumulations of a carbide-containing metal in the pellets and briquettes, a feature unique to the UC samples. The reactions occurred during the first 15 minutes of the experiments, most of the reactions happening during the first minute, after which there was no significant change in the recorded weight. The existence of metal-carbide accumulations are presented in Figure 11. The role of vanadium in previous experiments with CO gas did not appear to be significant for the reduction reactions, but with an addition of coke vanadium participates in the reactions that take place in the melt existing eventually in carbides. All the phases previously discovered, even a small quantity of chromite relicts and significant amounts of silicate melt and eskolaite-corundum solid solution series were detected in the high coke addition UC samples by SEM/EDS (Figure 12). According to the XRD patterns, it was difficult to identify the peaks for carbides, which were in the form of inclusions in the metal, since they overlapped with the peaks for metal. Calculated from the chemical analyses, the carbides correspond mainly to $(Cr,Fe)_{23}C_6$ and $(Cr,Fe)_7C_3$.

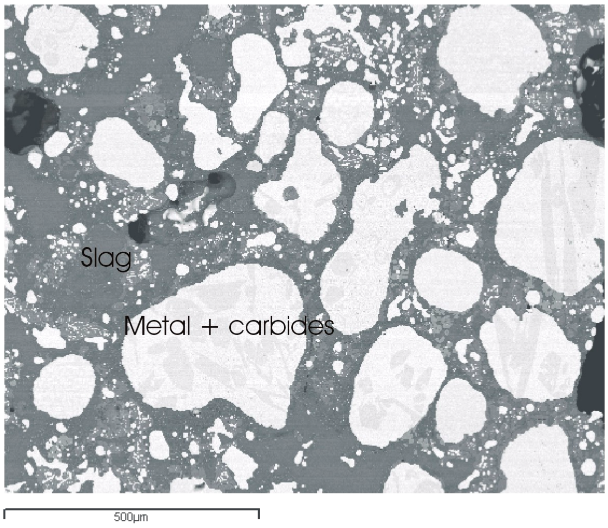

Figure 11. Large carbide-containing metal accumulations surrounded by silicate melt in UC pellets with a 15 % coke addition reduced in a Ar/H_2 atm. at 1400°C.

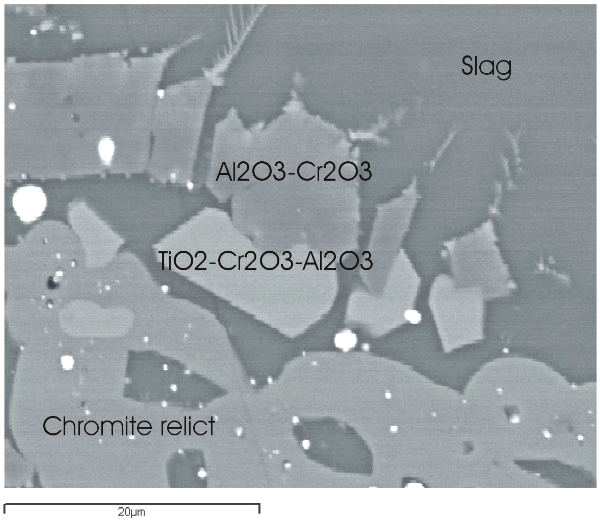

Figure 12. The existence of chromite relicts, Al_2O_3-Cr_2O_3-TiO_2-phases and silicate melt in UC pellets with a 15 % coke addition in reduced in a Ar/H_2 atm. at 1400°C.

Only one experiment was carried out on a ULC briquette with a 15 wt. per cent addition of coke. The degree of reduction remained surprisingly low, only 50 per cent, and although metallization was extensive, quite large chromite relicts survived throughout the experiment. The amount of chromium in the metal was 40 per cent on average, and no carbides were detected in the briquette.

6. DISCUSSION

The mechanisms of reduction of the chromite pellets in CO atmosphere were found to be similar to those described for carbothermic reduction of graphite-chromite composite pellets. The basic behaviour of the chromites appears to be similar in all three samples in view of the form of the reduction curves, a lot of the weight being lost during the first few minutes of the experiments. This indicates loss of oxygen from the surfaces of the grains in chemical reactions by which mainly the ferric and subsequent ferrous iron is eventually reduced to the metallic state. According to the analyses of metal precipitates, a small amount of Cr^{3+} is also reduced to the metallic state already at temperatures of 1000°C. At later stages of the experiments, the reduction reactions appear to be diffusion controlled. Oxidizing sintering of the pellets was found to have a significant effect on the reduction kinetics particularly in the case of UC chromite.

The zonation of chromites during reduction due to the diffusion of iron was detected especially in the ULC and Kemi samples. The interface between the inner and outer zones appears to be a sharp topochemical interface. The eskolaite-corundum solid solution (Cr_2O_3-Al_2O_3) existed in the form of distinct areas on the borders of chromite grains and eventually as individual crystals particularly at and above 1300°C in the Akanvaara samples. The existence of this phase as well as the extent of reduction would seem to correlate well with the Akanvaara chromites and is effected mainly by the formation of a silicate slag phase. The compositions of the relicts of chromites in all three samples eventually approached the spinel composition at higher degrees of reduction with a 15 wt. per cent coke addition in samples.

The natural addition of silica together with other components in the gangue was found to have a negative effect on reduction with CO. The formation of silicate slag modified the pore structure of the pellet and also donated Mg^{2+} from the melt to the spinel structure in which tetrahedral sites were available after the reduction of iron. In addition, the dissolution of chromite to the slag was notable in both Akanvaara samples. On the other hand, the formation of slag in samples with a 15 wt. per cent addition of coke appeared to facilitate the reduction in UC samples in which large accumulates of metal containg (Cr,Fe) carbides were formed.

The results suggest that the Akanvaara chromites, especially the UC chromite do reduce to a higher degree with CO gas at the same or even lower temperatures than the Kemi chromite. The UC chromite has a lot of silicate inclusions and chromites possess a catalastic structure, which provides a large surface area on which reduction reactions can occur. These features together with the lower MgO and higher FeO content of both Akanvaara chromites are important factors resulting in better reducibility compared with the Kemi chromite. The high vanadium content of the UC chromite seemed to play the most important role in the samples containing a 15 wt. per cent addition of coke in which the vanadium existed together with chromium and iron in carbides. The behaviour of the UC samples in these experiments is also the highly promising one with regard to the possibilities for using Akanvaara chromites in the production of chromium alloys.

7. ACKNOWLEDGEMENTS

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