

Reduction of chromium oxide and ore by methane-containing gas mixtures

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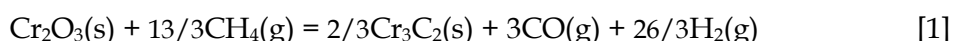
Abstract – The solid-state reduction of pure chromium oxide (Cr₂O₃) and chromium ores by methane-containing gas mixtures was investigated in a fixed-bed laboratory reactor in the temperature range 900–1200°C. Experiments were conducted at the University of New South Wales (UNSW, Australia) and SINTEF (Norway). The extent and rate of chromium oxide/ore reduction were determined by on-line off-gas analysis using a mass spectrometer. Samples at different stages of reduction were examined by SEM and XRD. Reduction of pure chromium oxide in the experimental temperature range was close to completion. The rate and extent of Cr₂O₃ reduction increased with increasing temperature and methane content in the reducing gas. Reduction of Chromtau (Kazakhstan) and Coobina (Western Australia) ores was studied at UNSW, while reduction of Ferbasa Comisa (Brazil) ore was examined at SINTEF. The extent and rate of ores reduction were relatively low; in the temperature-programmed experiments, the extent of reduction upon heating to 1200°C reached 67% for Comisa Ferbasa ore, 47% for Coobina ore, and only 24% for Chromtau ore. The paper discusses ores mineralogy, morphology, and constraints in the reduction of chromium ores by the methane-containing gas.

Keywords: chromium oxide, chromium ore, reduction, methane, carbon activity

INTRODUCTION

Reduction of chromium oxide by methane-containing gas was studied by Read *et al.* (1974), Qayyum and Reeve (1976), Anacleto and Ostrovski (2004), and Khoshandam *et al.* (2006). Chromium oxide is reduced to Cr₃C₂ by methane-containing gas at much lower temperatures than those of carbothermic reduction (Read *et al.*, 1974; Qayyum and Reeve, 1976; Anacleto and Ostrovski, 2004, Khoshandam *et al.*, 2006).

In a study by Anacleto and Ostrovski (2004), conversion of Cr₂O₃ to Cr₃C₂ was close to completion at 910°C. It was suggested that reduction of chromium oxide by methane followed the reaction:



for which $\Delta G^\circ = 1\,097\,519.4 - 989.79T$ (J) (Knacke *et al.*, 1991). Close-to-completion conversion of chromium oxide to carbide at low temperature (925°C) was also observed by Khoshandam *et al.* (2006). Isothermal curves obtained by Anacleto and Ostrovski (2004) and Khoshandam *et al.* (2006) are in a very good agreement, although experimental conditions were different.

This paper presents results of an investigation into the reduction of chromium oxide and chromite ores by methane-containing gas in non-isothermal and isothermal

experiments. The aim of the paper was to establish the degree and rate of reduction of chromite ores of different origin under different conditions, and the feasibility of using natural gas for the reduction of chromium ores.

EXPERIMENTAL

The reduction of chromium ores of different origin was studied using methane-containing gas. Chromtau (Kazakhstan) and Coobina (Western Australia) ores were studied at UNSW; Comisa (Ferbasa, Brasil) ore and pure chromium oxide were examined at SINTEF. The ores compositions are given in Table I. The compositions of Chromtau and Coobina ores were determined using XRF spectrometry at UNSW; the composition of Comisa ore was provided by Ferbasa.

Table I: Compositions of Chromtau (Kazakhstan), Coobina (Australia) and Comisa (Brasil) chromium ores [mass%]

Ore	Cr ₂ O ₃	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	TiO ₂	K ₂ O	BaO
Chromtau	51.9	6.63	10.9	6.87	0.37	20.17	0.15	0.05	1.4
Coobina	38.3	7.3	16.6	18.5	2.88	14.5	0.24	0.12	0.45
Comisa	31.4	14.2	27.4	6.2	0.53	19.7	0.16	n/a	n/a

Synthetic Cr₂O₃ (>98%) with a particle size of <325 µm was supplied by Alfa Aesar. The powder was pelletized with the addition of water. The pellets with particle size 1.2–1.4 mm were hardened at 1000°C (200°C/hour) for 2 hours. Samples of chromium oxide in the reduction experiments were 4 and 10 g.

Samples of Comisa ore (10 g) were also prepared in the form of pellets using the same procedure as for the pure oxide; the particle size was 1.2–1.4 mm. Samples of Chromtau and Coobina ores were dried in a muffle oven at 200°C to remove moisture. The lumps were crushed to less than 1.7 mm using a laboratory cone crusher, and then sieved into five fractions: +1.18–1.7 mm, +0.85–1.18 mm, +0.6–0.85 mm, +0.425–0.6 mm, and +0.3–0.425 mm. A sample mass in the reduction experiments was 2–3 g.

Reduction experiments at UNSW were conducted in a laboratory fixed-bed reactor in a vertical furnace with molybdenum disilicide heating elements. The experimental set up and procedure are described elsewhere (Anacleto and Ostrovski, 2004).

Experiments at SINTEF were also carried out in the vertical electric furnace (up to 1200°C). A schematic diagram of the furnace and experimental set-up are shown in Figure 1. A 10-g sample in the crucible formed an approximately 5-mm-high bed. The CH₄-H₂-Ar gas mixture was introduced to the reaction zone from the bottom of the crucible via an Alsint tube. The gas was distributed through a perforated oxide plate placed on the bottom of the Alsint crucible. The gas contained 10 vol% CH₄, 50 % H₂, and 40 vol% Ar. The gas flow rate was 6 L/min.

The off-gas in experiments at SINTEF was analysed by a GasLab 600 Mass Spectrometer. A PRIMA 600 mass spectrometer (Fisons Instruments, UK) was used for the analysis of the off-gas at UNSW. The oxygen content of the samples before and after reduction at UNSW was analysed with a LECO TC-436 DR instrument (DR stands for dual range; TC, for thermal conductivity). Oxygen in samples in the experiments at SINTEF were analysed by a LECO TCH600 instrument at Elkem Technology, Kristiansand.

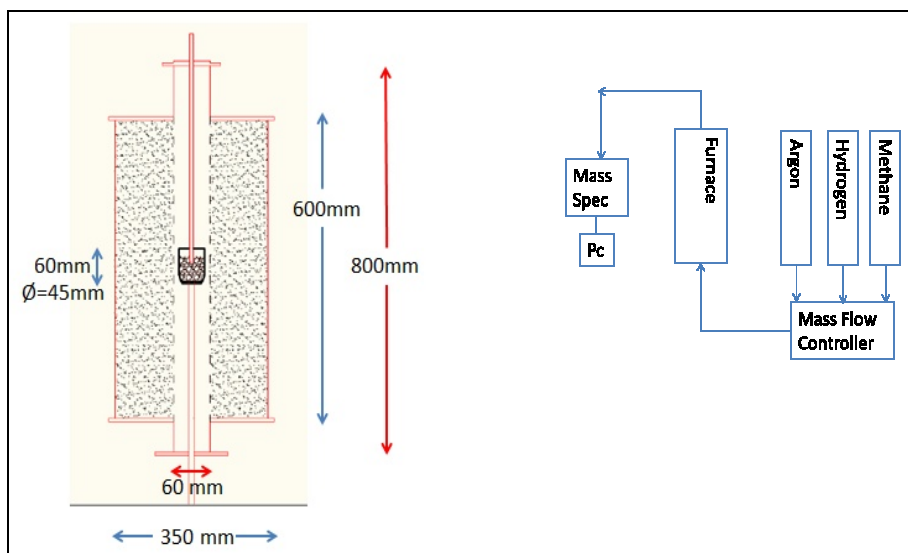


Figure 1: Schematic diagram of the furnace (left) and experimental set-up to study reduction reactions with methane-containing gas at SINTEF

Reduction of chromium oxide/ores was studied in the temperature-programmed experiments (TPE) and isothermal experiments. The heating rate in all TPEs at UNSW and SINTEF was 2°C/min. The tube furnace was flushed with argon. CH₄-H₂-Ar gas in experiments with Cr-ore was introduced at 200°C; reduction experiments with Cr₂O₃ (SINTEF) started at 600°C.

Oxygen removed from the sample in the reduction experiment at UNSW was calculated on the basis of CO and H₂O contents in the exit gas measured on-line by the mass spectrometer. The CO₂ content in the off-gas was negligible. In experiments at SINTEF, only CO concentration in the off-gas was measured on-line. These measurements were sufficient to monitor the extent of reduction of pure chromium oxide, as H₂O was not formed in these experiments. However, in experiments with chromium ore, only final extent of reduction was determined using results of oxygen analysis by LECO instrument.

The extent of reduction was calculated as a ratio of oxygen removed to the total oxygen in iron and chromium oxides in the ore before the reduction.

Phases were identified by XRD, optical and scanning electron microscopy, and electron-probe micro-analysis (EPMA). Standards for the calibration of EPMA were pure (electrolytic) Fe and Cr, SiC for Si and C, Al₂O₃ for Al and O, and MgO for Mg.

RESULTS

Reduction of pure chromium oxide

The heating of Cr₂O₃ under argon had no effect on the chromium oxidation state. Chromium oxide was not reduced by hydrogen under the given experimental conditions. However, Cr₂O₃ was reduced by the CH₄-H₂-Ar gas mixture. Figure 2 presents CO evolution curves in reduction experiments with samples of 4 and 10 g. The reduction of chromium oxide to chromium carbide, Cr₃C₂, started at 780°C in the experiment with 4 g Cr₂O₃, and 810°C in the reduction of a 10-g sample; the conversion of Cr₂O₃ to Cr₃C₂ in experiments with samples of 4 and 10 g was close to completion at 995°C and 1020°C respectively. The degree of reduction of these samples was about 99%; a high degree conversion of Cr₂O₃ to Cr₃C₂ was confirmed by the XRD and oxygen analysis.

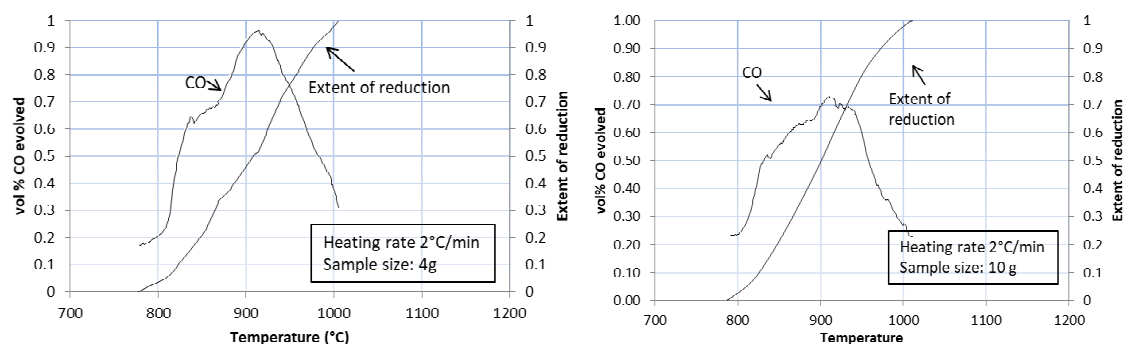


Figure 2: CO evolution in the reduction of pure chromium oxide by CH₄-H₂-Ar gas

Experimental results on the reduction of pure chromium oxide obtained at SINTEF are in a good agreement with data obtained at UNSW, although conversion of Cr₂O₃ to Cr₃C₂ at UNSW was observed at lower temperatures: it started at 770°C and was close to completion at 910°C (Anacleto and Ostrovski, 2004). The difference in the experimental data can be explained by the difference in the sample mass (2–3 g in experiments at UNSW) and experimental design. Note that the increase in the sample mass increased the reduction temperature.

Characterization of chromium ores

Samples of chromite ore were examined by XRD, optical microscopy, SEM, and EPMA. XRD analysis of Chromtau and Coobina ores revealed that both ores included chromite spinel (Mg,Fe)(Fe,Cr,Al)₂O₄ (magnesio-chromite) with cementing gangue composed of magnesium silicate 2(Mg_{0.91},Fe_{0.09})SiO₂ (forsterite). Coobina chromium ore also contained magnesium aluminium silicate hydroxide, (Mg,Al)₆(Si,Al)₄O₁₀OH₈ (Clinochlore); this phase could be also present in small amounts (below the XRD detection level) in other ores.

Quantitative XRD of Comisa concentrate detected eskolaite, magnesio-chromite, chromite, olivine and a small amount of quartz. Unreduced ores had predominantly a two-phase structure – large chromite spinel grains, and a cementing gangue phase distributed randomly between grains.

The chromite spinel is a solid solution formed between FeO·Cr₂O₃ (chromite), MgO·Cr₂O₃ (magnesio-chromite), MgO·Al₂O₃ (spinel), and FeO·Fe₂O₃ (magnetite). The chemical formula of the spinel in Chromtau and Coobina chromium ores was determined by the EPMA. The mole fraction of each constituent of the chromite spinel and chemical formula of the spinel are listed in Table 2.

Table 2: Composition of chromite spinel in Chromtau and Coobina ores

Ore	Chromite Spinel
Chromtau	0.20 MgO·Al ₂ O ₃ -0.57 MgO·Cr ₂ O ₃ -0.20 FeO·Cr ₂ O ₃ -0.03 FeO·Fe ₂ O ₃ or (Fe _{0.23} Mg _{0.77})O·(Fe _{0.03} Cr _{0.77} Al _{0.20}) ₂ O ₃
Coobina	0.23 MgO·Al ₂ O ₃ -0.28 MgO·Cr ₂ O ₃ -0.43 FeO·Cr ₂ O ₃ -0.06 FeO·Fe ₂ O ₃ or (Fe _{0.49} Mg _{0.51})O·(Fe _{0.06} Cr _{0.71} Al _{0.23}) ₂ O ₃

Comisa ore was the richest in iron and poorest in chromium of the three ores; it contained the highest fraction of chromite. Chromtau chromium ore contained much less chromite and significantly more magnesio-chromite than Coobina and Comisa ores.

Temperature programmed reduction of chromium ores

Iron and chromium oxides in chromium ores were reduced by the CH₄-H₂-Ar gas mixture to ferrochromium carbides. The degree of reduction was calculated as the ratio of oxygen loss to total oxygen in iron oxides presented as Fe₂O₃ and chromium oxide Cr₂O₃. Iron oxides were partially reduced to metallic iron by hydrogen, which was checked in the reduction experiments with Chromtau and Coobina ores using the H₂-Ar gas mixture.

The evolution of H₂O and CO in the reduction of Coobina and Chromtau ores by the CH₄-H₂-Ar gas mixture (10 vol% CH₄ and 40 vol% H₂) and the degree of reduction are shown in Figure 3.

Reduction of iron oxides to metallic iron in the Coobina ore started at approximately 450°C. Evolution of CO was observed from 620°C. Hydrogen partially reduced iron oxide while methane reduced chromium oxides; CH₄ was also involved in the reduction of Fe₂O₃ to Fe and reaction with water. The extent of reduction of Coobina ore after heating to 1200°C reached 47%. Formation of iron-chromium carbide was confirmed by the XRD analysis.

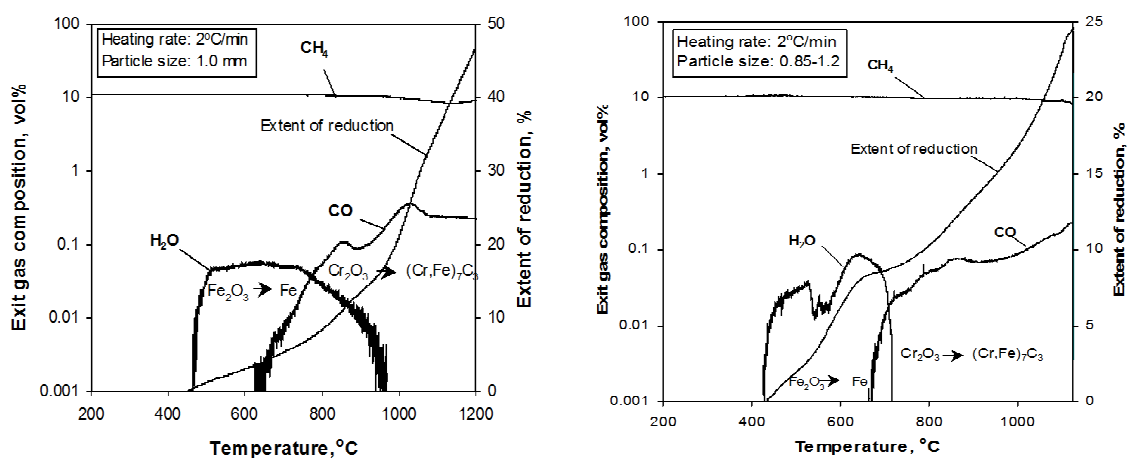


Figure 3: Temperature programmed reduction of Coobina (left) and Chromtau (right) chromium ores with 10 vol% CH₄, 40 vol% H₂, and 50 vol% Ar gas mixtures

The formation of ferrochromium in the reduction of Chromtau ore by the CH₄-H₂-Ar gas mixture started at approximately 650°C (see Figure 3). Reduction of this ore progressed only to 24%. XRD detected ferrochromium carbide and unreduced magnesio-chromite in samples of both ores after reduction.

In the reduction of Comisa ore CO evolution started at 755°C and ended at 940°C. The degree of reduction reached 67%. Complete reduction of 'iron oxides' corresponds to a degree of the ore reduction 45%. However, reduction of 'iron oxides' in Comisa ore was incomplete, as in the reduction of other chromium ores. Quantitative XRD detected 35 mass% ferrochromium carbide in the reduced sample.

Isothermal reduction

Reduction of Chromtau and Coobina ores was also studied in isothermal experiments. The effect of temperature on the reduction of Chromtau and Coobina chromium ores is presented in Figure 4. Experiments were conducted between 1000 and 1200°C, with ore particle size of +0.6-0.85 mm. The reduction rate of both ores increased with temperature, but reduction was far from complete.

The extent of reduction of Chromtau ore at 1200°C was 21% after 60 min of reaction, whereas reduction of Coobina ore at 1200°C reached 42% after 80 min. XRD identified the formation of $(Cr,Fe)_7C_3$ at temperatures in a range studied; reduced Coobina ore contained more carbide than reduced Chromtau ore. The X-ray diffractograms of both ores after reduction also included peaks of $(Fe, Mg)(Cr, Al)_2O_4$ (magnesio-chromite) $(Mg,Fe)_2SiO_4$ (olivine) with approximately 10 mol% FeO was detected in the reduced Chromtau ore.

The effect of methane concentration (in the CH_4 - H_2 -Ar gas mixture) on the reduction of Chromtau ore was examined at 1150°C by varying methane content from 0 to 25 vol% at constant hydrogen content of 50 vol%. At 0 vol% CH_4 , the extent of reduction was only 6.5%. An increase in the methane concentration up to 10% increased the rate and extent of ore reduction, which reached 20% after 40 min of reaction. A further increase in the methane content above 10% decreased slightly the rate and extent of reduction.

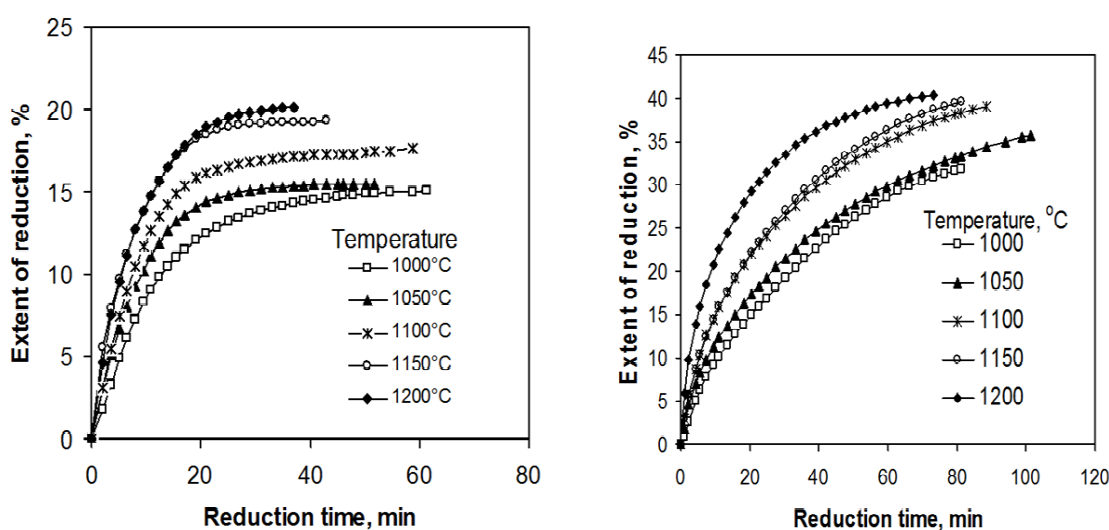


Figure 4: Reduction of Chromtau (left) and Coobina chromium ores by a gas mixture of 10 vol% CH_4 , 50 vol% H_2 , and 40 vol% Ar at different temperatures

The effect of particle size in the range 0.35–1.4 mm on the rate and extent of reduction of Chromtau ore was tested with a gas mixture of 10 vol% CH_4 , 50 vol% Ar, and 40 vol% H_2 at 1150°C. The rate and extent of reduction increased slightly with decreasing particle size.

XRD measurements of samples at various stages in the reduction of Coobina chromium ores at 1150°C detected $(Cr,Fe)_7C_3$ (chromium iron carbide) after 5 minutes of reduction. Reflections of $(Cr,Fe)_7C_3$ in the X-ray diffractogram of reduced Chromtau ore were barely distinguishable even after 20 minutes of reduction. This analysis confirmed the greater difficulty of reducing Chromtau ore than Coobina ore.

DISCUSSION

Reduction of chromium oxide by methane proceeds by reaction (1). At appropriate CH_4/H_2 ratios and temperatures, the activity of carbon from the methane can be well above unity relative to graphite, which provides favourable thermodynamic conditions for reduction to occur at relatively low temperatures.

The reduction process starts with adsorption of methane on the active sites of the oxide surface followed by its decomposition. The overall reaction of methane adsorption and cracking can be presented as



C_{ad} is active carbon adsorbed on the solid surface, which provides higher reducibilities and reduction rates than those of carbothermic reduction. Adsorbed carbon is consumed by reduction/carburization reactions.

Methane, however, is thermodynamically unstable at temperatures above 550°C (under standard conditions) and cracks (decomposes to solid carbon and hydrogen) in accordance with reaction (3):



If solid carbon is formed on the sample surface, it blocks access of the reducing gas to metal oxides, and the carbon activity at the oxide surface is decreased to unity, regardless of the high $p\text{CH}_4/(p\text{H}_2)^2$ ratio in the inlet gas. The key factor in the reduction of metal oxides by methane is the high rate of reduction compared with the rate of carbon deposition.

Reduction of Cr_2O_3 to chromium carbide proceeded at high rates at temperatures from 800 to 1150°C, which is close to the reduction temperature predicted by thermodynamics. Carbide formed in the reduction process was identified as Cr_3C_2 .

In the reduction of chromium ores, magnesio chromite ($[\text{Mg,Fe}][\text{Cr,Al}]_2\text{O}_4$) was partially reduced to $(\text{Cr,Fe})_7\text{C}_3$ (chromium iron carbide). The reduction rates of chromium ores increased with temperature in the range 1000–1200°C. The maximum degree of reduction of Chromtau, Coobina and Comesa ores reached in the temperature-programmed experiments were 24, 47 and 67%, respectively. The low degree of reduction of chromium ores by methane can be explained as follows.

First, magnesia in the ore stabilizes the chromium oxide by forming a stable magnesio-chromite spinel ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$). The appearance of partially reduced ore showed that metallization occurred on the surface of the grain and the remaining solid products ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$ and $\text{MgO} \cdot \text{Al}_2\text{O}_3$) formed shells round the unreacted $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, thereby hindering the diffusion of gas to the grain interior.

Secondly, cementing gangue composed of magnesium silicate surrounds the spinel grains and acts as a barrier to gas transfer. Gaseous diffusion was hindered through this gangue layer; the cementing gangue had a retarding effect on reduction.

Finally, slow consumption of adsorbed carbon by the reduction reaction resulted in the deposition and accumulation of solid carbon on the sample surface, which limited access of methane to the surface of the sample and slowed the reduction. This was particularly evident in the reduction of Coobina ore where accumulation of carbon in the sample was observed by the gradual increase in the gas inlet pressure after one hour of reaction. Iron in the ore catalyses methane cracking, which was not a problem in the reduction of pure chromium oxide.

The highest degree of reduction was observed in the reduction of Comisa ore; the final degree of reduction of Coobina ore was higher than that of Chromtau ore. The rate and extent of reduction of chromium ore were strongly affected by the ore chemical composition. Chromtau ore contained much less chromite and significantly more magnesio-chromite than Coobina and Comisa ores. Comisa and Coobina ores also

contained more magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), which was reduced by hydrogen. During reduction of chromium ores, magnetite was initially reduced, followed by chromite and then magnesio-chromite. The reduction of chromites rich in magnesium oxide, such as Chromtau ores, is more difficult than that of chromites rich in iron (Comisa ore) or aluminium (Coobina ore) oxides.

CONCLUSIONS

Chromium oxide (Cr_2O_3) was reduced to chromium carbide (Cr_3C_2) by methane-containing gas in the temperature range 1000–1250°C.

The reducibility of the chromium ore was strongly dependent on the ore composition. The maximum reduction extents of Chromtau, Coobina and Comisa ores in the temperature controlled experiments were 24, 47 and 67%. Similar low degrees of reduction were observed in the isothermal reduction of Chromtau and Coobina ores; at 1200°C they were 21% and 42%, respectively. The low extent and rate of reduction of chromium ores were attributed to the following: (1) magnesia forms a stable magnesio-chromite ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) spinel, which is difficult to reduce owing to the stabilizing effect of MgO; (2) the layer of cementing gangue composed of magnesium silicate surrounding the spinel grains of the ore hindered access of carbon to the reaction interface; (3) iron in the chromium ore catalysed methane cracking and deposition of carbon black, which blocked the gas access to the particle interior.

The reduction of Chromtau chromite ore with a high content of magnesium oxide proceeded at a lower rate and attained a lower degree of reduction than did Comisa and Coobina ores rich in iron oxide.

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