Reduction of Chromium Oxide by Methane-Containing Gas

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ABSTRACT

The solid state reduction of pure chromium oxide (Cr_2O_3) using methane-containing gas was investigated in a fixed bed laboratory reactor in the temperature range 1000–1250°C. The extent and kinetics of chromium oxide reduction were determined by on-line off-gas analysis using mass-spectrometer. The rate and extent of Cr_2O_3 reduction increased with temperature and methane content in the reducing gas. Hydrogen partial pressure had a slight effect on the reduction rate. The degree of chromium oxide reduction was close to 100% in the temperature range studied. Addition of carbon monoxide to the reducing gas strongly retarded the reduction of Cr_2O_3.

I. INTRODUCTION

In the carbothermic process, reduction of pure chromium oxide with carbon (reaction 1) under standard conditions starts at 1113°C[1].

$$3/2Cr_2O_3 + 13/2C \rightarrow Cr_3C_2 + 9/2CO \quad (1)$$

$$\Delta G^\circ = 1{,}078{,}190 - 777.94\ T,\ (J/mole) \quad (2)$$

At higher reduction temperatures and/or a lower CO partial pressure, carbides such as Cr_7C_3 and $Cr_{23}C_6$ are formed[2-5].

Reduction of Cr_2O_3 with hydrogen or carbon monoxide to metallic chromium requires a much higher temperature.

Reduction of Cr_2O_3 by methane-containing gas is thermodynamically feasible at a lower temperature. Chromium oxide is reduced by methane through the reaction:

$$Cr_2O_3 + 13/3CH_4 = 2/3Cr_3C_2 + 3CO + 26/3H_2 \quad (3)$$

The standard Gibbs free energy of this reaction, calculated using data from Knacke *et al.*[1], is equal to:

$$\Delta G^\circ = 265{,}203 - 238.04\ T\ \ (J/mole) \quad (4)$$

At standard conditions, reaction (3) proceeds spontaneously at temperatures above 841°C, which is much lower than the temperatures required for the carbothermic reduction of chromium oxides. This makes reduction of chromium oxides by methane quite promising.

II. EXPERIMENTAL

Experiments were conducted in a fixed bed reactor assembled in an electric vertical tube furnace. A schematic of the experimental set-up and reactor are shown in Figures 1 and 2, respectively. The reducing gas was introduced to the reactor from the top of the central alumina tube, and exited the reactor through the porous magnesia plug attached to the base of the tube.

The reducing gas mixture was made from 99.995% Ar, 99.999% ultra high purity H_2, 99.5% CO and 99% CH_4. Before being introduced to the reactor, all gases were cleaned for moisture and carbon dioxide using a Hydro Purge 2 purifier (Alltech Associated Ltd. Deerfield, Illinois). The hydrogen gas line had an additional activated charcoal purifier to remove hydrocarbons. Gas flow rates were controlled by Brooks Model 5850E mass flow controllers.

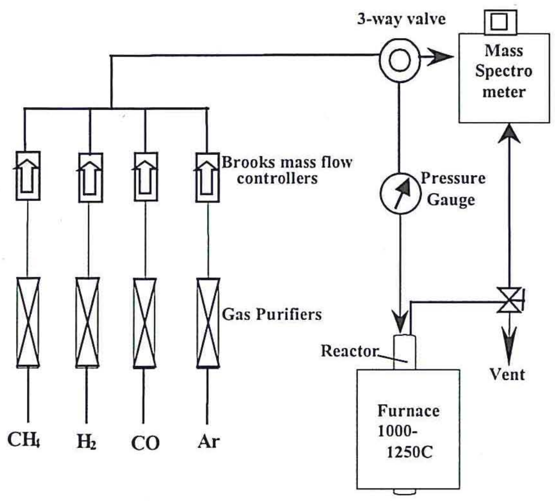

Figure 1 Schematic of the experimental set-up

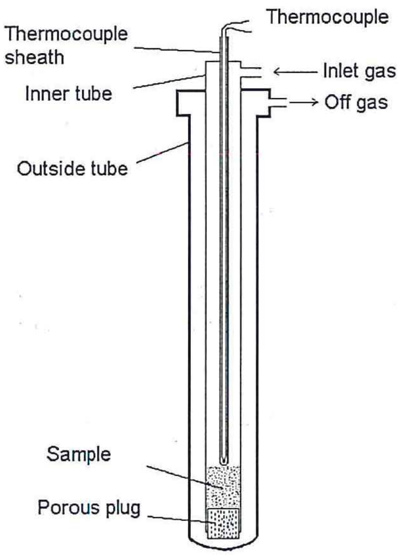

Figure 2 Schematic diagram of the experimental reactor

The exit gas was analysed on-line using a PRIMA 600 mass spectrometer (Fisons Instruments, UK).

Chromium (III) oxide (Cr_2O_3 (98+%, ~50 μm) was supplied by Aldrich Chemical Company. The fine powder blocked the porous magnesia plug and had to be sintered before being used in the reduction experiments. A paste of chromium oxide and water was heated in a muffle furnace at a rate of 200 °C per hour to 1400 °C, and then held for 5 hours. Then it was cooled, crushed, sized, and used in the reduction experiment.

Reduction of chromium oxide was studied in isothermal and non-isothermal temperature programmed experiments. The following experimental procedure was adopted for isothermal reduction:

(a) A 3-gram sample of chromium oxide was placed in the reactor.
(b) The reactor and sample was introduced into the tube, which was sealed and flushed with argon.
(c) The sample was preheated for 5-10 minutes and then brought into the isothermal hot zone. Sample temperature was monitored with a "N" type thermocouple, located in the middle of the reactor.
(d) When a sample reached the experimental temperature, reducing gas was introduced into the reactor from the top at a total flow rate of 1.0 NL/min. Outlet gas was analysed by the mass spectrometer.
(e) The time of exposure of the sample to the reducing gas was varied to achieve different extents of reduction.
(f) The reducing gas was switched to argon and the reactor was quickly pulled up to the lower temperature zone.
(g) Oxygen removed from the sample in the reduction experiment was calculated on the basis of CO and H_2O content in the exit gas. The extent of reduction was determined as a ratio of oxygen loss to total oxygen in the oxide.

The extent of reduction was also calculated on the basis of oxygen content in the reduced sample, which was measured using a LECO TC – 436DR machine.

In the non-isothermal reduction experiments, the sample was heated with a ramping rate of 2°C/min.

Samples reduced to different degrees were subjected to phase analysis using XRD, optical and microprobe analyses. XRD analysis was carried out using a SIEMENS D5000 X-Ray Diffractometer with monochromator and a copper

Kα x-ray source. Scanning range was from 20° to 80° at a speed of 0.6 °/min, with a step of 0.01°.

III. RESULTS

Non-isothermal reduction

Non-isothermal reduction of the sintered chromium oxide was examined under (1) argon atmosphere from 200°C to 1250°C, (2) hydrogen-argon gas mixture from 250°C to 1300°C and (3) methane-hydrogen-argon gas mixture from 250°C to 1200°C. In all cases, the heating rate was 2°C per minute and the chromium oxide size was 850-1180 microns.

Heating of Cr_2O_3 under argon had no effect on the chromium oxidation state. Chromium oxide was not reduced by hydrogen under given experimental condition either. However, Cr_2O_3 was reduced by CH_4-H_2-Ar gas mixture as it is shown in Figure 3. The extent of reduction was calculated on the basis of the CO and H_2O contents in the exit gas, measured by the mass spectrometer.

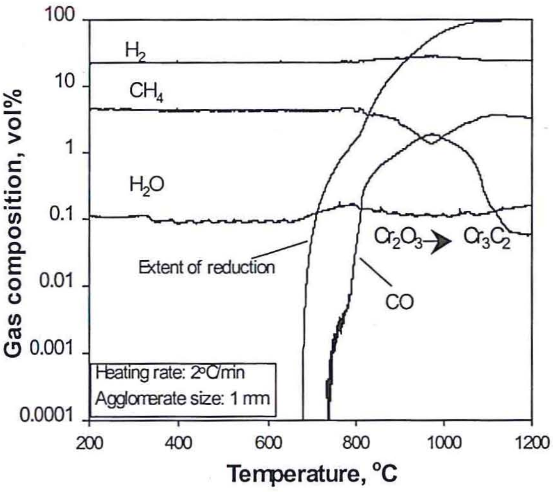

Figure 3 Non-isothermal reduction of pure Cr_2O_3 by 5 vol% methane-25 vol % hydrogen-70 vol % argon mixture.

The reduction of chromium oxide to chromium carbide, Cr_3C_2 started at about 740°C. Cr_2O_3 was completely reduced to Cr_3C_2 at around 1070°C. This was confirmed by the XRD analysis as shown in Figure 4.

Isothermal reduction

Effect of temperature on Cr_2O_3 reduction

Effect of temperature on Cr_2O_3 reduction was studied in the temperature range 1000-1250°C using 10vol% CH_4-50vol%H_2-Ar gas.

Effect of temperature on Cr_2O_3 reduction is illustrated in Figure 5. Reduction of Cr_2O_3 in this temperature interval goes to completion with the rate increasing with temperature. LECO oxygen analysis confirmed that the extent of reduction was 100%.

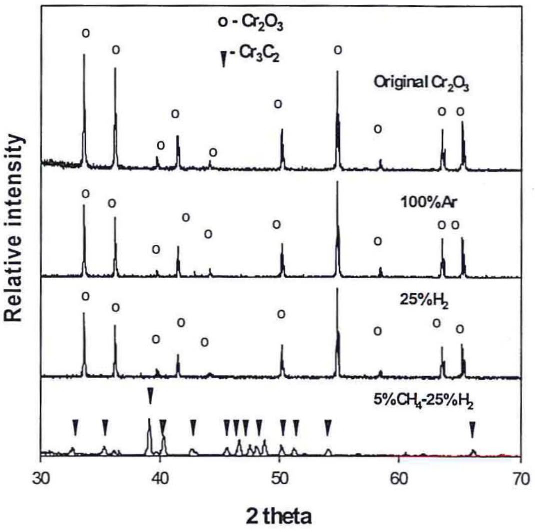

Figure 4 X-ray diffraction patterns of pure Cr_2O_3 before and after non-isothermal reduction in different gas mixtures up to 1200 °C

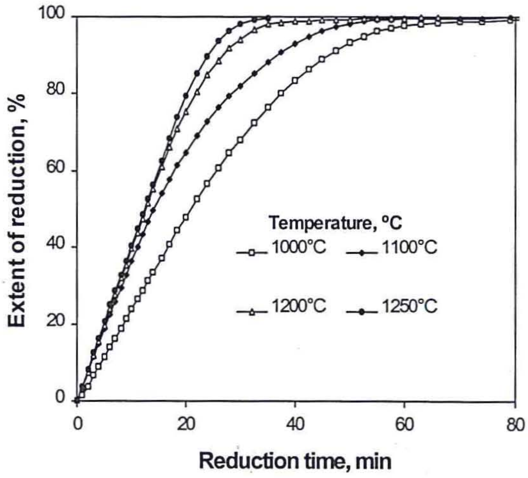

Figure 5 Reduction of Cr_2O_3 by methane-hydrogen-argon gas mixture (10 vol% CH_4-50 vol% H_2- 40 vol% Ar) at different temperatures

Effect of gas composition

Reduction of chromium oxide was studied at different gas compositions by varying the proportion of CH_4, and H_2in the gas mixture and adding CO to the reducing gas. The effect of methane on the rate of chromium oxide reduction was examined at 1150°C by varying the methane content from 0 to 30 vol%, while the hydrogen content was maintained at 50 vol %. The extent of reduction versus time is plotted in Figure 6. The rate of reduction increased with the methane content in the gas.

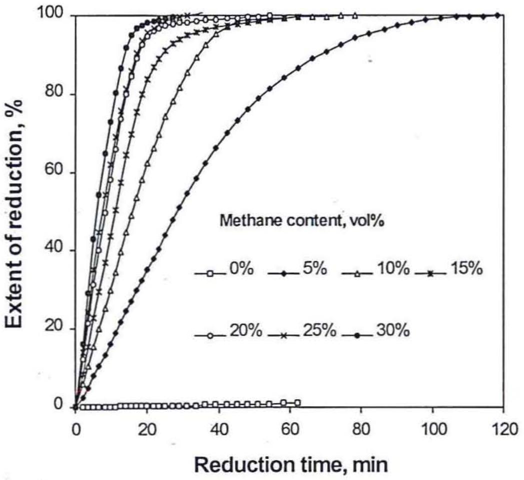

Figure 6 Reduction of Cr_2O_3 by methane containing gas mixture with different methane content at 1150°C (H_2 content was kept at 50 vol %)

The effect of hydrogen content in the gas mixture on the rate of pure chromium oxide reduction was examined at 1150 °C by varying the hydrogen content from 0 to 60 vol%, while the methane content was maintained at 15 vol %. The extent of reduction versus time is shown in Figure 7. The rate of Cr_2O_3 reduction increased slightly with increasing hydrogen concentration in the reducing gas.

The effect of addition of carbon monoxide to the inlet gas mixture on the rate of pure chromium oxide reduction was examined at 1000°C by varying the CO content from 0 to 10 vol% at constant methane and hydrogen contents of 15 vol % and 50 vol %, respectively. In these experiments, the off gas composition was initially analysed in the reactor without the Cr_2O_3 sample to determine the CO background level. CO measured in reduction experiments was the sum of CO formed as a result of reduction and the background CO.

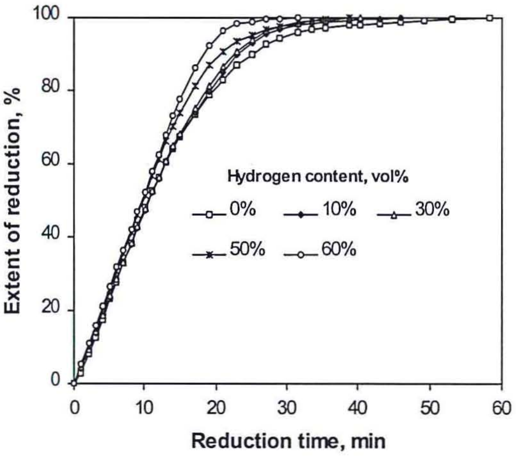

Figure 7 Reduction of Cr_2O_3 by methane containing gas mixture with different hydrogen concentration at 1150°C (CH_4 content was constant at 15 vol%)

The extent of reduction versus time at different carbon monoxide concentrations is shown in Figure 8. Carbon monoxide in the inlet gas had a strong retarding effect on the rate of reduction and limited the extent of reduction. The degree of reduction by the gas containing 10 vol% CO was less than 50 % after more than 3 hours of reduction. The retarding effect of CO increased with decreasing temperature.

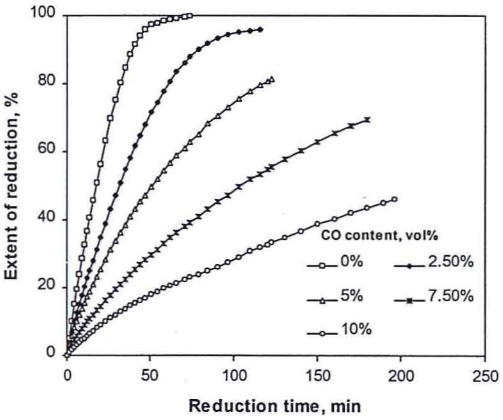

Figure 8 Effect of CO content on the reduction of Cr_2O_3 by methane-hydrogen-argon mixture (15 vol% CH_4-50 vol% H_2) at 1000°C

Effect of particle size

The effect of the chromium oxide particle size on the rate and extent of reduction was examined at 1100°C using reducing gas containing 10 vol% CH_4, 40 vol% H_2, balance Ar. Fig. 9 shows the extent of reduction of samples with a particle size in the range of 425 to 1180µm. There is no significant difference in the reduction curves for samples with different particle size.

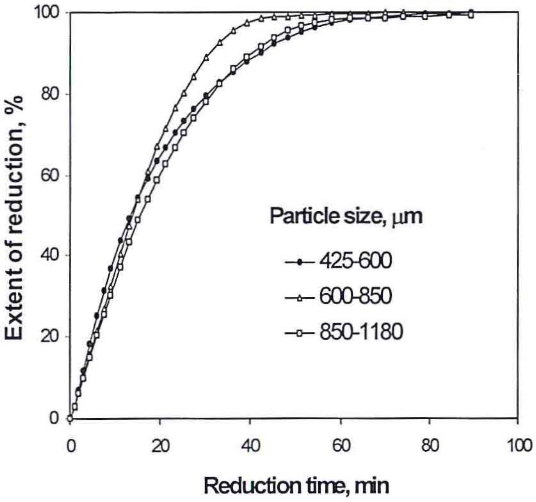

Figure 9. Reduction of samples of Cr_2O_3 with different particle sizes at 1100°C using gas containing 10 vol% methane, 50 vol% hydrogen and 40 vol% argon

XRD analysis

X-ray diffraction patterns of samples at various stages of reduction of pure Cr_2O_3 at 1050 and 1150°C are displayed in Figs 10 and 11, respectively.

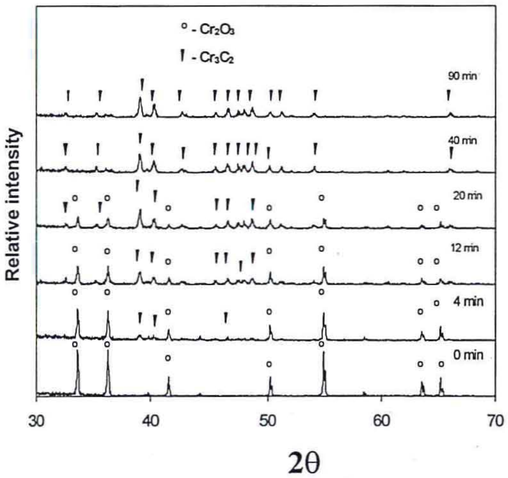

Figure 10 X-ray diffraction patterns at various stages of reduction of pure Cr_2O_3 by 15vol% CH_4-50vol% H_2-35vol% Ar, at 1050 °C.

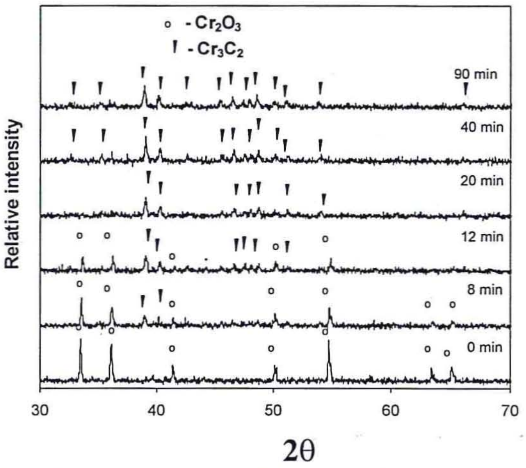

Figure 11 X-ray diffraction patterns at various stages of reduction of pure Cr_2O_3 by 15vol% CH_4-50vol% H_2-35vol% Ar, at 1150 °C.

Formation of chromium carbide, which was identified as Cr_3C_2, was completed after 40 minutes at 1050 °C, and after 20 minutes at 1150 °C.

Morphology of Chromium Oxide and Carbide

Samples of Cr_2O_3 reduced at 1150°C were subjected to optical and SEM analyses. Figure 12 presents microphotographs of partly reduced chromium oxide after 20 min reduction.

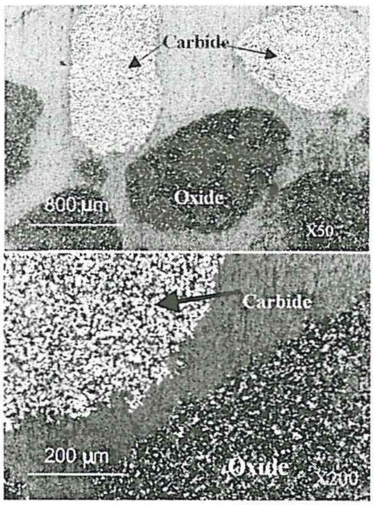

Figure 12 Optical micrographs of partly reduced chromium carbide

The size of the chromium carbide particles is larger than that of the unreduced original chromium oxide particles. This indicates coarsening of the carbide particles during the reduction process. Figure 13 shows the SEM image of the chromium carbide at higher magnification (x500).

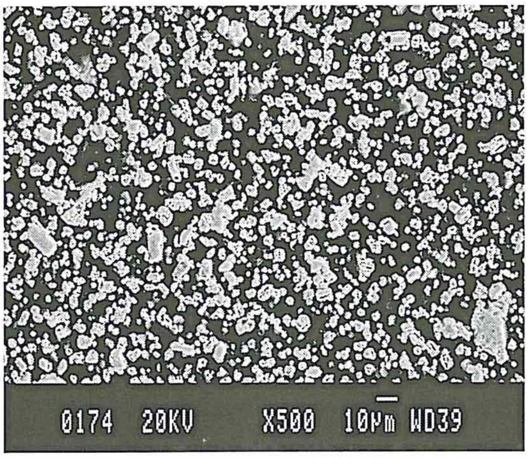

Figure 13 SEM image of chromium carbide

IV. DISCUSSION

Reaction products

Non-isothermal tests showed that chromium oxide is not reduced by hydrogen-argon gas mixture at temperatures up to 1300°C, although Chu and Rahmel[6] reported that Cr_2O_3 could be reduced by hydrogen above 1300°C. Even at these high temperatures, the extent of reduction is very low, and water should be continuously removed from the reaction zone.

In the reduction of chromium oxide by methane containing gas, the reduction of Cr_2O_3 to chromium carbide proceeds with the formation of CO by reaction (3). However, it does not exclude water formation by reaction (5) followed by reaction (6) of water vapour with methane:

$$3Cr_2O_3 + 4CH_4 + H_2 = 2Cr_3C_2 + 9H_2O \quad (5)$$

$$CH_4 + H_2O = CO + 3H_2 \quad (6)$$

The reduction of Cr_2O_3 to Cr_3C_2 starts at about 740°C, as shown in Figure 5. The reduction proceeds with a high rate above 800°C, which is close to the reduction temperature predicted by thermodynamic calculation. This result is in agreement with Read *et al.*[7],however, in they also found that reduction of Cr_2O_3 to Cr_3C_2 required 1200°C to reach completion, compared to only 1100°C in the present investigation. This difference in temperatures may be related to the ramping rate, which was 2°C/min in this work compared to 4°C/min in the work of Read *et al.*[7].

The gas composition used in the non-isothermal reduction tests presented in this paper were also different from the work of Read *et al.*[7]. They used gas consisted of 14 vol% CH_4 and 86 vol % H_2 compared to gas containing 5 vol% CH_4, 25 vol% H_2 and 70 vol% Ar in this investigation. During non-isothermal reduction of a composite pellet containing chromium oxide + solid carbon (5 wt%) in pure H_2 with a ramping rate of 3°C/min, carbide formation was completed at 1100°C, the same as in our test with CH_4-H_2-Ar gas.

Carbide formed in the reduction process was identified as Cr_3C_2. This may be attributed to the high carbon activity in the reducing CH_4-H_2-Ar gas, as shown in Fig. 14. Lower carbides, Cr_7C_3 or $Cr_{23}C_6$, may be formed at lower carbon activities.

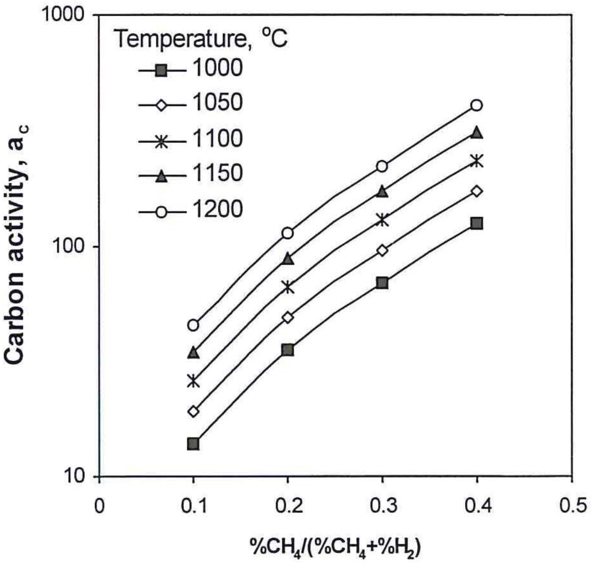

Figure 14 Calculated carbon activity of methane-hydrogen gas mixture at different temperatures.

Pei and Wijk[9,10] reported that in the reduction of chromium oxides dissolved in slag by solid carbon, the chromium oxide was found to be first reduced to chromous oxide CrO. Under the present conditions, neither CrO nor lower carbides of Cr_7C_3 and $Cr_{23}C_6$ were detected.

Effect of gas composition on reduction and carburisation of Cr_2O_3

Read *et al.* 1974[7] suggested that chromium oxide is reduced by carbon formed from methane cracking. However, on the basis of experimental results obtained in this paper, it may be concluded that chromium oxide is reduced by methane directly via reaction (3). Moreover, methane cracking with deposition of solid carbon has a negative effect on Cr_2O_3 reduction, and finally stops the reduction. The Cr_2O_3 reduction rate increases with methane concentration in the reducing gas from 5 to 20 vol%. Above this value, methane concentration has a slight effect on the reduction rate. Temperature affects the Cr_2O_3 reduction in a similar manner. It strongly increases the Cr_2O_3 reduction rate in the interval 1000-1200°C, and has a very slight effect above 1250°C.

An increase in the temperature and methane concentration in the reducing gas increases the rate of reaction (3), and also increases the rate of methane cracking. Carbon deposited as a result of the methane cracking process blocks access of the reducing gas to the oxide, and decreases carbon activity in the system to unity, having a retarding effect on the Cr_2O_3 reduction. Direct Cr_2O_3 reduction by methane containing gas under conditions employed in this work is faster than methane cracking. This is necessary to achieve a high degree of reduction.

Moreover, at temperatures examined in this paper, the reduction of Cr_2O_3 with solid carbon (graphite) is very slow and is not complete even at 1250°C. The solid-gas reaction (3) is much faster than solid-solid carbothermic Cr_2O_3 reduction (reaction (1)). Figure 15 presents reduction curves for pure Cr_2O_3 reduced by graphite in argon at 1400°C[11] and 1170°C[8] and by CH_4-H_2-Ar at 1200°C. The rate of reduction by CH_4-H_2-Ar at 1200°C is twice as fast by graphite in argon at 1400°C.

The calculated equilibrium gas composition for Cr2O3 reduction to Cr3C2 by methane-containing gas at different temperatures is shown in Figure 16.

Reaction (3) is irreversible at high temperatures. However, if the partial pressure of CO generated by reaction (3) exceeds the equilibrium partial pressure of CO for reaction (7), then chromium carbide can be re-oxidised by the reaction:

$$Cr_3C_2 + 9/2CO = 3/2\ Cr_2O_3 + 13/2C \quad (7)$$

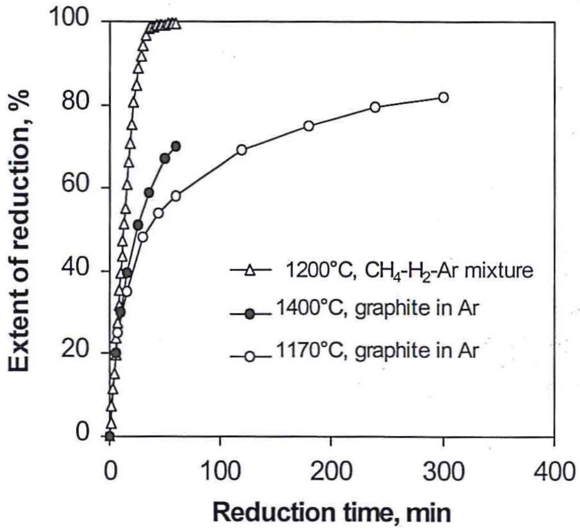

Figure 15 Reduction curves for pure Cr_2O_3 reduced by graphite in argon at 1400°C[11] and 1170°C[8] and by CH_4-H_2-Ar gas mixture at 1200°C

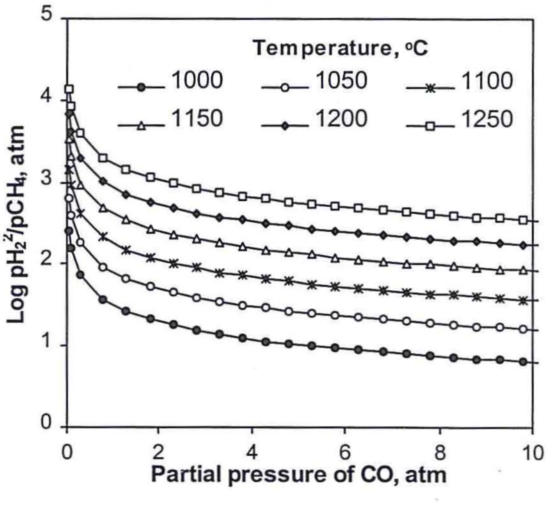

Figure 16 Equilibrium gas composition for the reaction of Cr_2O_3 reduction by CH_4-H_2 gas at different temperatures.

Figure 17 shows the equilibrium partial pressure of CO for reaction (7) in the temperature range of 950

- 1300°C. It is quite low at temperatures below 1000°C, which explains the strong retarding effect of carbon monoxide in the reducing gas at relatively low temperatures.

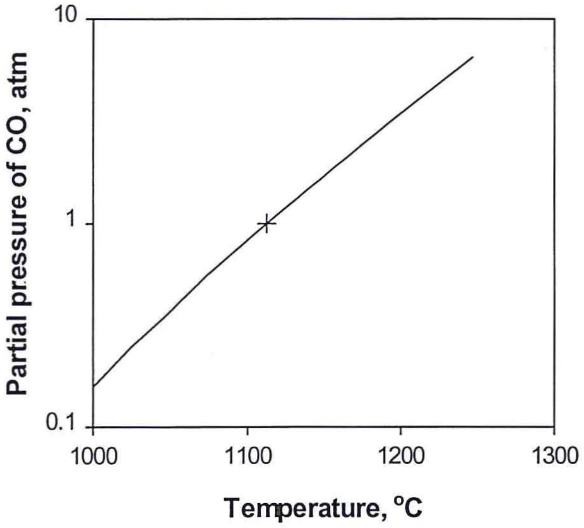

Figure 17 Equilibrium partial pressure of CO as a function of temperature; marked value corresponds to 1 atm.

V. CONCLUSION

Chromium oxide is reduced to chromium carbide by the methane-containing gas in the temperature range of 1000-1250°C. The reduction rate increases with temperature. The reduction rate also increases with methane content in the reducing gas to 15-20 vol% CH_4 and hydrogen content to 50 vol%. The presence of CO in the reducing gas retards the reduction process.

The optimal conditions for Cr_2O_3 reduction to chromium carbide by methane-containing gas include: a temperature of 1100-1200°C, a methane concentration of 15-20 vol%, and hydrogen above 20 vol%.

The rate of reduction by CH_4-H_2-Ar is much faster than that by graphite.

ACKNOWLEDGMENT

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