Solid-State Reduction of Chromium Oxide by Methane-Containing Gas

NATHANIEL ANACLETO and OLEG OSTROVSKI

Reduction of chromium oxide, Cr_2O_3, was investigated in a fixed bed laboratory reactor in the temperature range 900 °C to 1200 °C using CH_4-H_2-Ar gas mixture. The extent and rate of reduction as functions of gas composition and temperature were determined by on-line off-gas analysis using a mass spectrometer. Samples at different stages of reduction were examined by scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. The chromium oxide was reduced to chromium carbide Cr_3C_2 with a degree of reduction close to 100 pct. The rate of reduction increased with temperature and methane content in the reducing gas. Carbon monoxide, added to the reducing gas, strongly retarded the rate of Cr_2O_3 reduction. The hydrogen content had a slight effect on the reduction rate. High extent and rate of reduction by methane-containing gas in comparison with carbothermal reduction were attributed to high carbon activity in the reducing gas—15 to 50 (relative to graphite).

I. INTRODUCTION

Hɪɢʜ carbon ferrochromium production is dominated by the electric-arc furnace (EAF) process. The EAF ferrochromium making requires high-quality lump chromium ore, coke, and approximately 4000 kWh of electrical energy per tonne of ferrochromium, which all drive the investigation into alternative ferrochromium production technologies.[1]
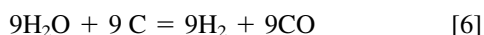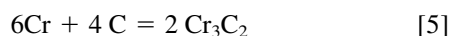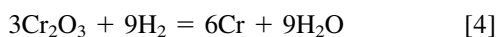
In prereduction of chromium ore by hydrogen or carbon monoxide, only iron oxides are reduced. However, using methane-hydrogen gas, iron and chromium oxides can be converted to carbides.[2,3] Methane reduces chromium oxide by the following reaction:

$$Cr_2O_{3(s)} + 13/3CH_{4(g)} = 2/3Cr_3C_{2(s)} + 3CO_{(g)} + 26/3H_{2(g)} \qquad [1]$$
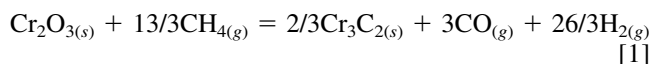
The standard Gibbs free energy of this reaction derived using data from Knacke et al.[4] is

$$\Delta G^\circ = 1{,}097{,}519.4 - 989.79T \text{ (J)} \qquad [2]$$

Reduction of chromium oxides by methane-hydrogen gas was studied by Read et al.[2] and Qayyum and Reave.[3] Read et al.[2] concluded that the role of methane was to supply carbon, which diffuses into the oxide. In accordance with their work,[2] the overall reduction Reaction [1] is a sum of Reactions [3] through [6].

$$13CH_4 = 13\,C + 26H_2 \qquad [3]$$

$$3Cr_2O_3 + 9H_2 = 6Cr + 9H_2O \qquad [4]$$

$$6Cr + 4\,C = 2\,Cr_3C_2 \qquad [5]$$

$$9H_2O + 9\,C = 9H_2 + 9CO \qquad [6]$$

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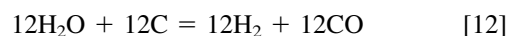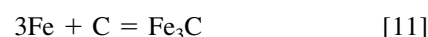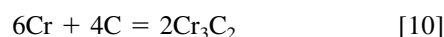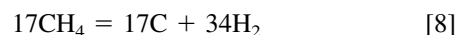
This conclusion was mainly based on the experimental fact that the reaction rate was independent of the methane partial pressure in the range of 0.02 to 0.25 atm, and backed by the observation that nonisothermal reduction of chromium oxide by solid carbon in the hydrogen atmosphere was similar to that by methane-hydrogen gas mixture.

Qayyum and Reave[3] modified the reduction mechanism, suggesting that under conditions when methane is stable (low CH_4/H_2 ratio) chromite is reduced by Reaction [7], which is similar to Reaction [1]:

$$3FeO \cdot Cr_2O_3 + 17CH_4 = Fe_3C + 2Cr_3C_2 + 12CO + 34H_2 \qquad [7]$$
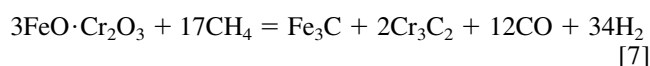
At high temperatures and CH_4/H_2 ratios, when methane is unstable, the following reactions were suggested.[3]

$$17CH_4 = 17C + 34H_2 \qquad [8]$$

$$3FeO \cdot Cr_2O_3 + 12H_2 = 6Cr + 3Fe + 12H_2O \qquad [9]$$

$$6Cr + 4C = 2Cr_3C_2 \qquad [10]$$

$$3Fe + C = Fe_3C \qquad [11]$$

$$12H_2O + 12C = 12H_2 + 12CO \qquad [12]$$

Reaction mechanisms proposed by Read et al.[2] and Qayyum and Reave[3] are quite different from those suggested in iron oxide reduction to cementite[5] or titania reduction to titanium oxycarbide.[6] Namely, high carbon activity in the methane-hydrogen gas mixture is needed for iron and titanium carburization. Methane cracking and free carbon deposition have a detrimental effect on this process. It is well known that cementite is not formed by the reaction of metallic iron with carbon, as suggested by Reaction [11].

The carbothermal reduction of pure chromium oxide (Reaction [13]) under standard conditions proceeds spontaneously at temperatures above 1113 °C (calculated using data from Knacke et al.[4]).

$$3/2Cr_2O_{3(s)} + 13/2C_{(s)} = Cr_3C_{2(s)} + 9/2CO_{(g)} \qquad [13]$$
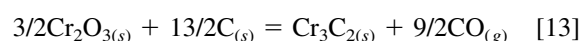
$$\Delta G^\circ = 1{,}078{,}190 - 777.94T \text{ (J)} \qquad [14]$$

Reduction of Cr_2O_3 with hydrogen or carbon monoxide to metallic chromium requires much higher temperatures. At standard conditions, Reaction [1] proceeds spontaneously at temperatures above 841 °C, which is much lower compared to the carbothermal reduction of chromium oxides. This makes reduction of chromium oxides by methane-containing gas quite promising. The aim of this article was to study non-isothermal and isothermal reduction of chromium oxides by CH_4-H_2-Ar gas at different temperatures and gas compositions and to establish the reduction sequence and mechanism.

The scope of this article was limited by consideration of reduction of pure chromium oxides by methane-containing gas. Reduction of chromite ore, which includes iron oxides, magnesia (in the form of spinel), and other impurities, which have a significant effect on the reduction behavior, requires further examination.

II. EXPERIMENTAL

Experiments were conducted in a fixed bed reactor heated in a vertical tube furnace. The experimental setup and procedure were described elsewhere.[6] The reducing gas was obtained by mixing high-purity argon, ultra-high-purity hydrogen, and methane. In some experiments, chemically pure carbon monoxide was added to reducing gas. Before being introduced to the reactor, all gases were cleaned from moisture and carbon dioxide using a Hydro Purge II® gas purifier (Alltech associates, Inc., Deerfield, IL). The hydrogen gas line had an additional activated charcoal purifier to remove hydrocarbons. Brooks mass flow meters (model 5850E) regulated gas flow rates and composition of the gas mixture. The exit gas was analyzed using a PRIMA 600 scanning magnetic sector mass spectrometer (Fisons Instruments, Middlewich, UK). The amount of water vapor in the exit gas was also analyzed using a dew point monitor.

Chromium (III) oxide (Cr_2O_3, 98+ pct, <50 μm) was supplied by Aldrich Chemical Company. The fine powder was sintered before use. A chromium oxide-water paste was heated in a muffle furnace at a rate of 200 °C per hour to 1400 °C in air, and held for 5 hours. Then it was cooled, crushed, and sieved to +1.7 to 2.3 mm, +1.2 to 1.7 mm, +0.85 to 1.2 mm, and +0.6 to 0.85 mm size ranges. The particle size of the sintered chromium oxide in the range of 0.6 to 2.3 mm had no a visible effect on the rate and extent of reduction. The reason behind this was high open porosity. Because of this, the particle size in all experiments was 1.2 mm.

Reduction of chromium oxide was studied in isothermal and nonisothermal experiments. The heating rate in nonisothermal experiments was 2 °C/min under Ar, H_2-Ar, and CH_4-H_2-Ar gas mixtures from 200 °C to 1200 °C. A nonisothermal reduction of Cr_2O_3 by solid carbon under argon-hydrogen atmosphere was also examined. A 1-g sample of chromium oxide was mixed with 0.4 g of graphite. It was then pelletized and placed in the reactor.

Oxygen removed from the sample in the reduction experiment was calculated on the basis of CO and H_2O content in the exit gas (CO_2 was below a detectable level). The extent of reduction was determined as a ratio of oxygen loss to oxygen in chromium oxide Cr_2O_3. The final extent of reduction was also calculated on the basis of residual oxygen content in the reduced sample, which was measured using a LECO* oxygen analyzer.

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*LECO is a trademark of LECO Corporation, St. Joseph, MI.

Phase analysis was performed by X-ray diffraction (XRD), optical and scanning electron microscopy. The XRD analysis was carried out using an SIEMENS D5000 (Siemens Aktiengesellschaft, Germany) X-ray diffractometer with a monochromator and a copper K_α X-ray source. The scanning range was from 20 to 80 deg at a speed of 0.6 deg/min, with a step of 0.01 deg. A high-resolution (1.5-nm) Hitachi S4500 (Hitachi Instruments, Inc., San Jose, CA) field emission scanning electron microscopy (SEM) was used to study reduced and unreduced phases of the chromium oxide.

III. RESULTS

Reduction of chromium oxide was studied at different gas flow rates, temperatures, and particle sizes. The effects of gas compositions by varying CH_4 and H_2 in the gas mixture and addition of CO to the reducing gas were also investigated.

A. Nonisothermal Reduction of Cr_2O_3

Nonisothermal reduction was conducted to identify stages of Cr_2O_3 reduction by the CH_4-H_2-Ar gas mixture. Behavior of the sintered chromium oxide was also examined upon heating in pure argon and argon-hydrogen mixture. The heating of Cr_2O_3 under argon had no effect on the chromium oxidation state. Chromium oxide was not reduced by hydrogen under the given experimental conditions. However, Cr_2O_3 was reduced by CH_4-H_2-Ar, as shown in Figure 1. The reduction of chromium oxide to chromium carbide, Cr_3C_2, started at approximately 770 °C. Cr_2O_3 was completely reduced to Cr_3C_2 at 910 °C. This was confirmed by LECO oxygen analysis and XRD analysis.

B. Effect of Gas Flow Rate in Isothermal Reduction

The effect of gas flow rate on the rate of chromium oxide reduction was investigated in the range from 0.5 to 1.5 L/min. The sample weight was changed proportionally to keep the
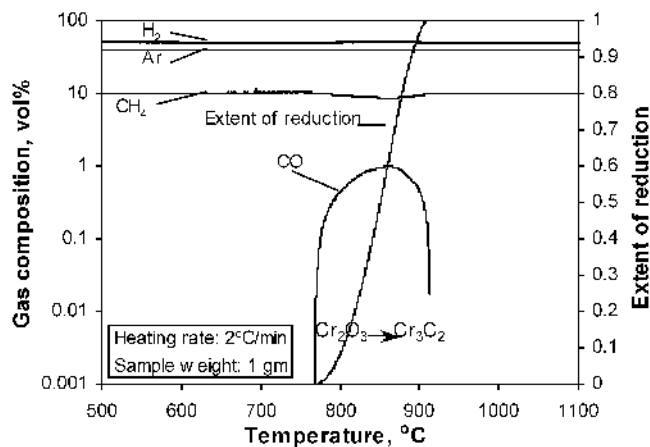

Fig. 1—Nonisothermal reduction of Cr_2O_3 by 10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar mixture.

gas residence time in the bed constant. Experiments were performed at 1100 °C. The reduction gas contained 10 vol pct CH_4, 50 vol pct H_2, and 40 vol pct Ar. The degree of reduction of chromium oxide as a function of gas flow rate is presented in Figure 2. The rate of reduction slightly increased with increasing gas flow rate from 0.5 to 1.0 L/min. Further increase in gas flow rate had no visible effect on chromium oxide reduction. Therefore, the resistance due to the external mass transfer can be neglected when the gas flow rate is above 1.0 L/min. On this basis, the gas flow rate in all experiments was 1 L/min.

C. Effect of Temperature on Cr_2O_3 Reduction

The effect of temperature on Cr_2O_3 reduction was studied in the temperature range 900 °C to 1200 °C using gas containing 10 vol pct CH_4, 50 vol pct H_2, and 40 vol pct Ar, and is shown in Figure 3. Pure Cr_2O_3 was completely reduced
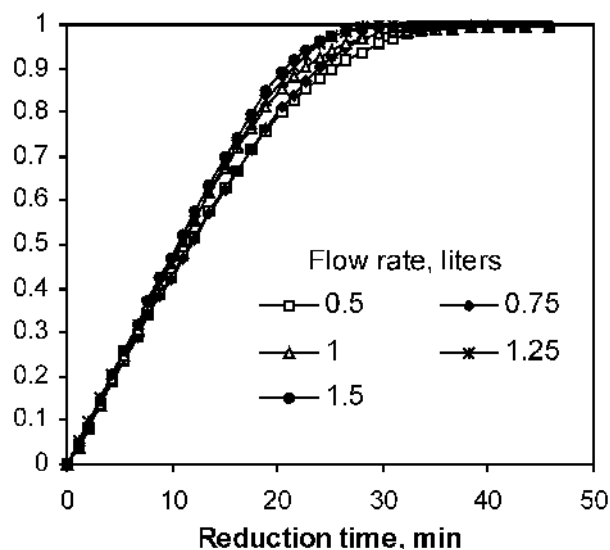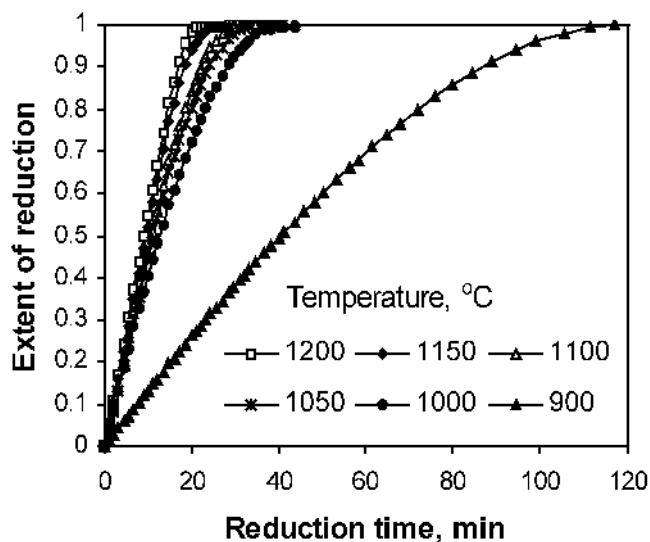
under these conditions with the rate increasing with temperature. Increase in temperature increases the reaction rate constant and diffusion coefficients in gas phases. LECO oxygen analysis confirmed that the extent of reduction was close to 1.0. Reduction of chromium oxide was completed in about 100 minutes at 900 °C, 40 minutes at 1000 °C, 37 minutes at 1050 °C, 33 minutes at 1100 °C, 27 minutes at 1150 °C, and 22 minutes at 1200 °C. The increase of rate of reduction with temperature was found to be most significant between 900 °C and 1000 °C. When the temperature was higher than 1000 °C, this increase slowed down with the increase of temperature. At high temperatures, the increase in temperature has a double effect: (1) increase in the reduction rate constant and (2) decrease in the reaction gas-solid interface due to sintering. As a result, the increase in the reduction rate with increasing temperature in the range 1000 °C to 1200 °C is marginal.

D. Effect of Methane and Hydrogen Content on Cr_2O_3 Reduction

The effect of methane on chromium oxide reduction was investigated by adding methane to the H_2-Ar gas mixture in the amounts of 5, 10, 15, 20, 25, and 30 vol pct at 1000 °C. The hydrogen content was maintained at 50 vol pct and the sample mass was 2 g in all experiments. The effect of methane content on the degree of chromium oxide reduction is presented in Figure 4. At experimental temperatures, no reduction of pure oxide Cr_2O_3 was observed when the reducing gas had no methane. The increasing methane content in the gas increased the rate of reduction. At methane content over 10 vol pct, the increase in the reduction rate slowed. Further increase in the methane concentration caused methane cracking, which retarded the reduction due to carbon deposition. This was manifested in the slight decrease in the extent of reduction at higher methane content.

The effect of hydrogen content in the gas mixture on the rate of chromium oxide reduction was examined at 1000 °C by varying hydrogen content from 0 to 70 vol pct at constant methane content of 10 vol pct. The rate of Cr_2O_3 reduction increased slightly with increasing hydrogen in the reducing gas.

Fig. 2—Reduction of Cr_2O_3 with different gas flow rates (10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar) at 1100 °C.

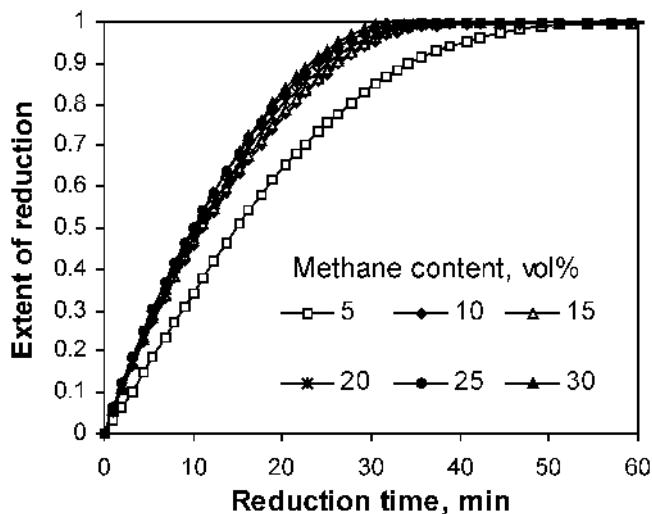

Fig. 3—Reduction of Cr_2O_3 by gas containing 10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar at different temperatures.

Fig. 4—Reduction of Cr_2O_3 by gas with varying methane content at 1000 °C (H_2 content was constant at 50 vol pct).

E. *Effect of Carbon Monoxide*

The effect of carbon monoxide on the rate of pure chromium oxide reduction was examined at 1000 °C by varying the CO content from 0 to 10 vol pct in gas with 15 vol pct methane and 50 vol pct hydrogen (argon the balance). The off-gas composition was initially analyzed in the reactor without Cr_2O_3 to determine the CO background level. It should be noted that CO in the off-gas measured by the mass spectrometer in reduction experiments was the sum of CO formed by the reduction reaction and the initial CO in the inlet gas mixture.

Carbon monoxide in the inlet gas had a strong retarding effect on the rate of Cr_2O_3 reduction and limited the extent of reduction (Figure 5). Two hours of exposure of Cr_2O_3 to the reducing gas with 7.5 vol pct CO at 1000 °C resulted in about 0.95 extent of reduction, while reduction with CO-free gas was completed in about 30 minutes. The degree of reduc-
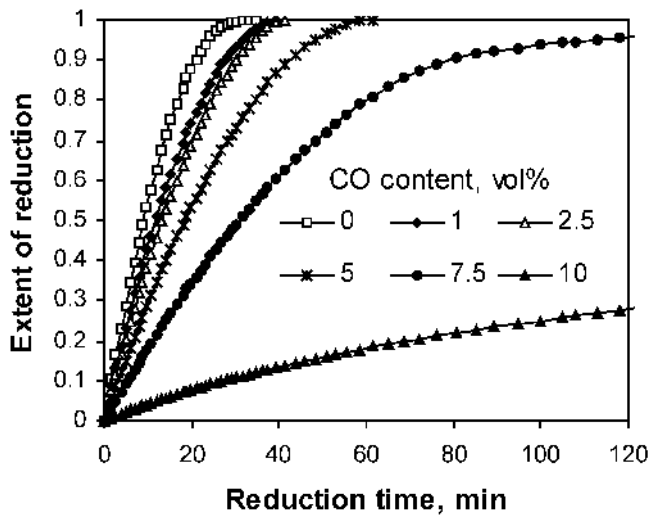
tion by the gas containing 10 vol pct CO was less than 0.30 after 2 hours of reduction.

F. *XRD Patterns at Various Stages of Reduction*

X-ray diffraction patterns of samples at various stages of reduction of Cr_2O_3 by methane gas mixture at 1050 °C and 1200 °C are displayed in Figures 6 and 7. Formation of chromium carbide, identified as Cr_3C_2, was completed after 40 and 20 minutes at 1050 °C and 1200 °C, respectively.

G. *Morphology of Chromium Oxide and Carbide*

The SEM images of chromium oxide and reduced samples are shown in Figures 8 and 9. Chromium oxide after sintering was composed of 3- to 5-μm grains. The grains' surfaces were rough with cracks and fractures on the edges. The grains of the chromium carbide obtained in the reduction process (Figure 9) were of larger size and were more porous.

Fig. 5—Effect of CO content on the reduction of Cr_2O_3 by methane-hydrogen-argon mixture (15 vol pct CH_4-50 vol pct H_2) at 1000 °C.

Fig. 7—X-ray diffraction patterns of Cr_2O_3 samples at various stages of reduction by 10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar gas at 1200 °C.
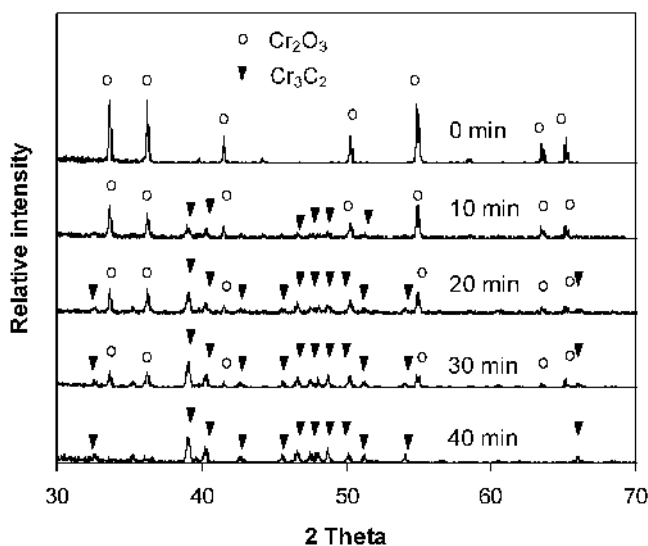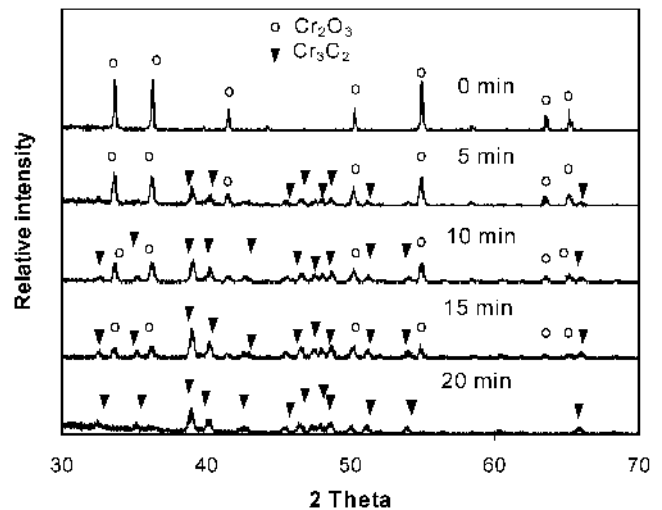

Fig. 6—X-ray diffraction patterns of Cr_2O_3 samples at various stages of reduction by 10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar gas at 1050 °C.

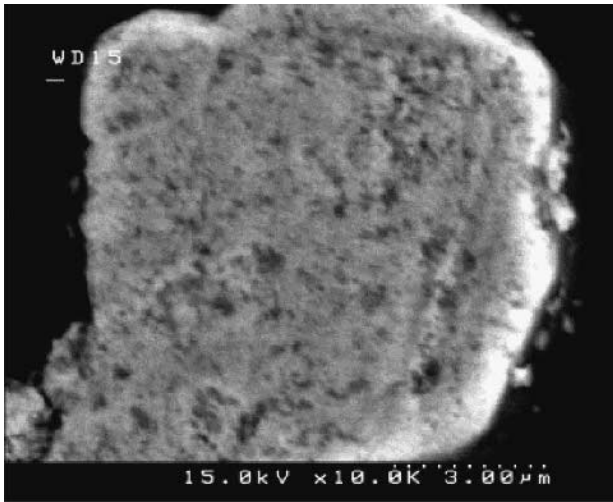Fig. 8—SEM image of chromium oxide Cr_2O_3 before reduction.

Fig. 9—SEM image of chromium carbide Cr_3C_2 obtained in the reduction experiment at 1200 °C.

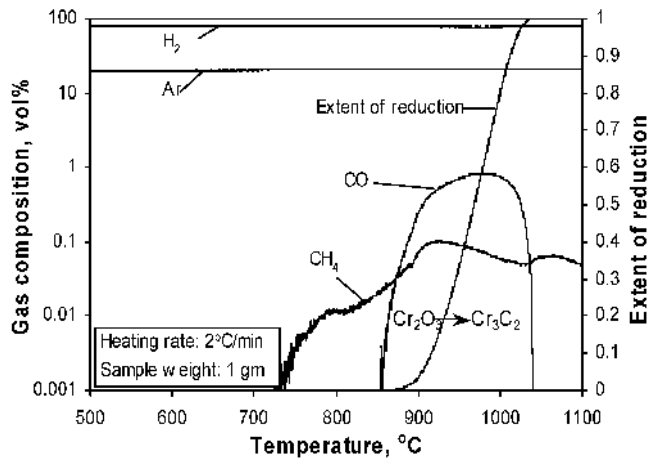Fig. 11—Nonisothermal reduction curves obtained by Read et al.[2] and in the present work, using methane-containing gas.

Fig. 10—Nonisothermal carbothermal reduction of Cr_2O_3 (Cr_2O_3/C mole ratio = 0.2/1) in the 80 vol pct H_2-20 vol pct Ar gas atmosphere.

Fig. 12—Nonisothermal reduction curves obtained in the carbothermal reduction of Cr_2O_3 under hydrogen by Read et al.[2] and in the present work.

H. *Carbothemal Reduction of Cr_2O_3 under Hydrogen*

Nonisothermal reduction of the pelletized chromium oxide with solid carbon (Cr_2O_3/C mole ratio = 0.2/1) was examined under 20 vol pct Ar-80 vol pct H_2 gas mixture. Figure 10 shows the reduction of chromium oxide to chromium carbide started at 860 °C and completed at 1040 °C. Methane gas formed by the reaction between solid carbon and hydrogen was detected at temperatures of 740 °C and above.

IV. DISCUSSION

The nonisothermal reduction curves of Cr_2O_3 by methane-containing gas, obtained by Read et al.[2] and in the present work, are compared in Figure 11. Read et al.[2] observed the maximum reduction rate at approximately 1050 °C with complete reduction of Cr_2O_3 to Cr_3C_2 at 1200 °C. In this work, the maximum reduction rate was observed at 850 °C, and the reduction was completed at 912 °C. This difference in temperature may be related to the ramping rate, which
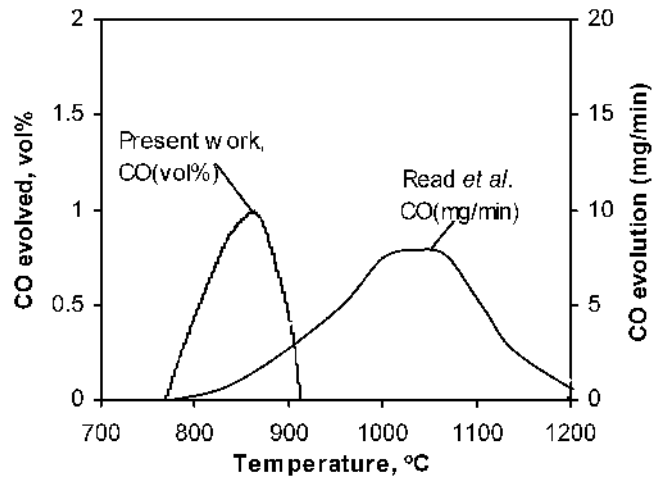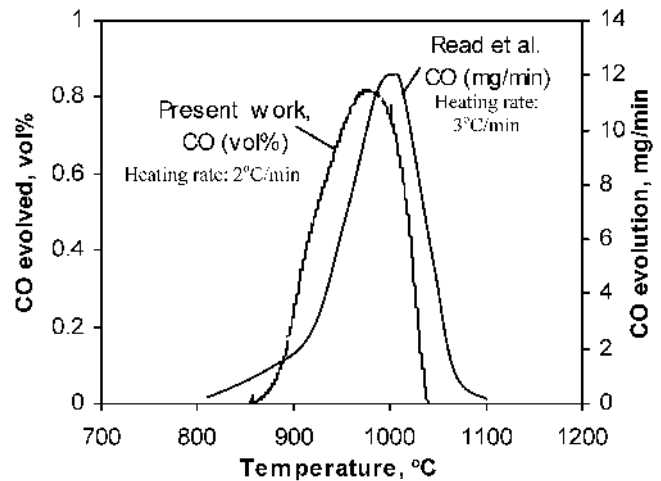
was 2 °C/min in this work compared to 4 °C/min in the work of Read et al.[2] Different gas composition and a sample mass used in the test could also affect the results. In experiments conducted by Read et al.,[2] the reducing gas contained 14 vol pct CH_4 and 86 vol pct H_2, while the gas used in this investigation contained 10 vol pct CH_4, 50 vol pct H_2, and 40 vol pct Ar. Read et al.[2] used a more massive pellet than that used in this work.

Our results obtained in nonisothermal carbothermal reduction of chromium oxide under H_2 were similar to those of Read et al.[2] (Figure 12), although the heating rate was also different. However, in this work, the reduction of chromium oxide by methane-containing gas was much faster than in carbothermal reduction. At temperatures examined in this work, the reduction of Cr_2O_3 with solid carbon (graphite) under argon was very slow and was not complete at 1200 °C. Carbothermal reduction under hydrogen was faster than that under argon.

Figure 13 presents reduction curves for Cr_2O_3 reduction by graphite in argon at 1400 °C[10] and 1170 °C[11], by graphite

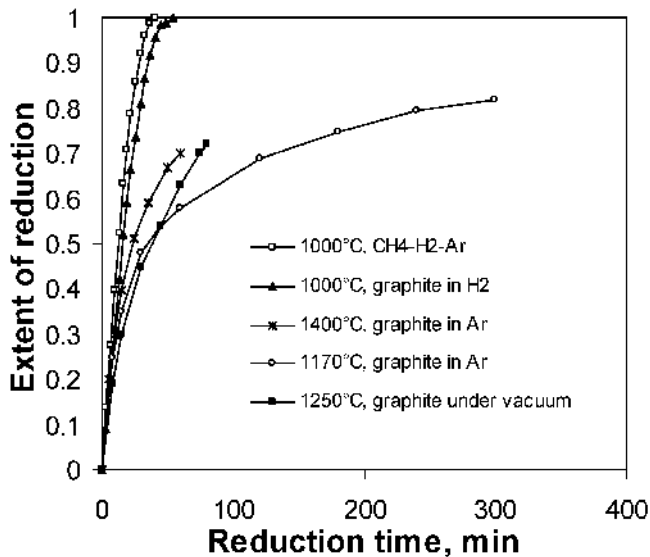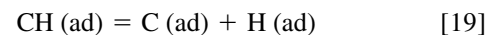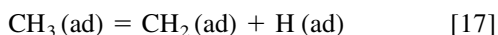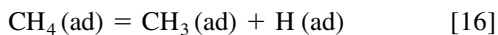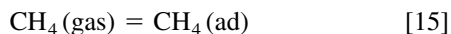Fig. 13—Reduction curves for pure Cr_2O_3 reduction by graphite in argon at 1400 °C[10] and 1170 °C,[11] by graphite under vacuum at 1250 °C,[12] by graphite in hydrogen at 1000 °C, and by 10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar gas mixture at 1000 °C.

in hydrogen at 1000 °C, and by 10 vol pct CH_4-50 vol pct H_2-40 vol pct Ar at 1000 °C. The rate of reduction by methane-containing gas at 1000 °C was faster than by graphite in argon at 1400 °C. All reduction curves, obtained in this work and by other authors, are for the same oxide—pure Cr_2O_3. This figure shows that the reduction rate of Cr_2O_3 by methane-containing gas is faster than the carbothermal reduction of Cr_2O_3 under Ar, H_2, or vacuum.

The difference in the reduction rate of Cr_2O_3 by methane-containing gas and by solid carbon reflects a difference in the reduction mechanism. This is contrary to Read *et al.*,[2] who concluded that methane acts as a solid carbon supplier, and, therefore, the mechanisms of reduction of chromium oxide by solid carbon in the hydrogen atmosphere and by methane-hydrogen gas are the same.

Results presented previously show that the rate of chromium oxide reduction increase with increasing temperature and methane content. Increases in temperature and the partial pressure P_{CH_4}/P_{H_2} ratio decrease methane stability. However, carbon deposition was found to be minimal in the temperature range 900 °C to 1200 °C. Formation of chromium carbide was completed after 20 minutes at 1200 °C, but solid carbon was not detected at different stages of reduction by XRD analysis. This means that the rate of reduction and carburization of chromium oxide by methane is faster than solid carbon deposition.

It is paramount that carbon thermodynamic activity in the CH_4-H_2-Ar gas is well above unity—in our experiments, in the range of 15 to 50 relative to graphite. The reduction process starts with adsorption of methane on the active sites of the oxide surface and its decomposition, described by the following reactions:[13]

$$CH_4\,(gas) = CH_4\,(ad) \qquad [15]$$

$$CH_4\,(ad) = CH_3\,(ad) + H\,(ad) \qquad [16]$$

$$CH_3\,(ad) = CH_2\,(ad) + H\,(ad) \qquad [17]$$

$$CH_2\,(ad) = CH\,(ad) + H\,(ad) \qquad [18]$$

$$CH\,(ad) = C\,(ad) + H\,(ad) \qquad [19]$$

$$2H\,(ad) = H_2\,(g) \qquad [20]$$

The overall reaction of methane adsorption and cracking may be presented as

$$CH_4 \rightarrow \ldots \rightarrow C_{ad} + 2H_2 \qquad [21]$$
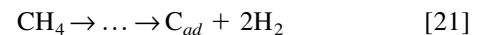
On the basis of this reaction, thermodynamic activity of adsorbed carbon may be defined (relative to graphite) by

$$a_C = K(P_{CH_4}/P_{H_2}^2) \qquad [22]$$

where K is the equilibrium constant of Reaction [23] of methane cracking,

$$CH_4 = C_{gr} + 2H_2 \qquad [23]$$
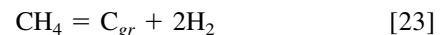
The $(P_{CH_4}/P_{H_2}^2)$ ratio in the gas phase in equilibrium with graphite is fixed at constant temperature and will be referred to as $(P_{CH_4}/P_{H_2}^2)_{gr}$. Equation [22] may be rewritten in the form

$$a_C = (P_{CH_4}/P_{H_2}^2)/(P_{CH_4}/P_{H_2}^2)_{gr} \qquad [24]$$

When $(P_{CH_4}/P_{H_2}^2) > (P_{CH_4}/P_{H_2}^2)_{gr}$, activity of adsorbed carbon will be >1. This active carbon provides a higher extent of the reduction reaction in comparison with the carbothermal reduction. Adsorbed carbon is consumed by reduction/carburization reduction. The key factor is a high rate of this reaction in comparison with the rate of carbon deposition in Reaction [23]. If solid carbon is formed on the sample surface, the $(P_{CH_4}/P_{H_2}^2)$ ratio at the gas/solid interface will be maintained equal to $(P_{CH_4}/P_{H_2}^2)_{gr}$ regardless of the high $(P_{CH_4}/P_{H_2}^2)$ ratio in the inlet gas.

The rate of Reaction [21], R, is proportional to the fraction of the surface area available for adsorption, $(1 - \theta)$, and in the general case is a function of partial pressures of methane P_{CH_4} and hydrogen P_{H_2}:

$$R = kAf(P_{CH_4}, P_{H_2})(1 - \theta) \qquad [25]$$

Reduction/carburization reaction serves as a sink for adsorbed carbon. After completion of this reaction, adsorbed carbon is not consumed and forms solid carbon. Deposition of solid carbon in the reduction of chromium oxide is much less in comparison with iron oxide, when reduced iron catalyzes the methane cracking. In the nonisothermal reduction (Figure 1), the methane consumption was observed only during the reduction of Cr_2O_3 to Cr_3C_2 from 770 °C to 912 °C. The amount of decomposed methane after reduction of Cr_2O_3 was relatively small. The fraction of decomposed methane at 1000 °C due to methane cracking was less than 4 pct at a methane concentration in the range of 5 to 30 vol pct. This means that carbon deposition due to methane cracking is not a significant factor in the chromium oxide reduction.

Another key factor in the reduction of Cr_2O_3 by the methane-containing gas is the kinetics of solid-gas reaction, which is faster than the kinetics of solid-solid carbothermal reduction, although the latter also takes place through the gas phase (oxide is reduced by CO, which is regenerated by the Boudouard reaction).

The addition of CO to the reducing gas retarded the reduction process. This was caused either by reoxidation of chromium carbide or preferential CO adsorption onto active sites of the chromium oxide hindering the adsorption of reducing gases. Chromium carbide can be reoxidized by the reaction

$$Cr_3C_{2(s)} + 9/2CO_{(g)} = 3/2Cr_2O_{3(s)} + 13/2C_{(s)} \quad [26]$$

The calculated equilibrium partial pressure of CO for Cr_2O_3 reduction by methane and solid carbon at different temperatures is shown in Figure 14. The equilibrium CO partial pressure in carbothermal reduction is much lower than in reduction by methane. Under the experimental conditions employed in this work, CO partial pressure during reduction by methane can exceed equilibrium partial pressure of CO for the carbothermal reduction. The reduction reaction by gas containing 10 vol pct CH_4 and 50 vol pct H_2 is practically irreversible at high temperature. The equilibrium CO partial pressure is very high. However, a partial pressure of CO of 0.1 to 0.15 atm in experiments at 1000 °C is close to equilibrium for carbothermal reduction. Addition of 10 vol pct CO to the reducing gas could reoxidize chromium carbide to Cr_2O_3 in accordance with Reaction [26], which explains the strong retarding effect of CO addition to the reducing gas on the reduction rate of Cr_2O_3.

In accordance with the Cr-C phase diagram, three stable carbides Cr_3C_2, Cr_7C_3, and $Cr_{23}C_6$ can be formed. Pei and Wijk[7] reported that in the reduction of chromium oxides by solid carbon, the chromium oxide was first reduced to chrom-
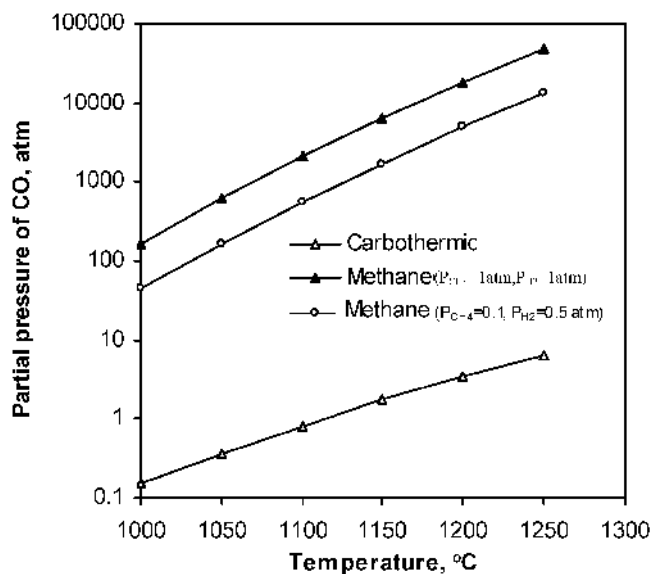
ous oxide (CrO). At higher temperatures and low carbon monoxide concentrations, all three stable carbides were formed.[3,8,9] In this work, neither CrO nor lower carbides of Cr_7C_3 and $Cr_{23}C_6$ were detected. The XRD analysis of Cr_2O_3 reduced by methane-containing gas revealed the presence of Cr_3C_2 only. Formation of Cr_3C_2, which has the highest C/Cr ratio, can be attributed to high carbon activity in the reducing CH_4-H_2-Ar gas mixture.

V. CONCLUSIONS

Chromium oxide Cr_2O_3 was reduced by methane-containing gas to chromium carbide Cr_3C_2 by Reaction [1]. The reduction rate increased with temperature in the range of 900 °C to 1200 °C, methane concentration up to 10 vol pct, and hydrogen concentration up to 50 vol pct. Addition of CO to the reducing gas retarded the reduction process. The particle size of the sintered chromium oxide had no significant effect on the rate and extent of reduction. The optimal conditions for Cr_2O_3 reduction to the chromium carbide by methane-containing gas include temperature in the range 1100 °C to 1200 °C, methane concentration 15 to 20 vol pct, and hydrogen concentration above 20 vol pct.

In nonisothermal experiments, chromium oxide reduction by methane-hydrogen mixture started at 770 °C and completed at 910 °C, where as the carbothermal reduction of chromium oxide under hydrogen started at 860 °C and completed at around 1040 °C. The rate of reduction by CH_4-H_2-Ar gas was much faster than that by graphite, which is attributed to high carbon activity in the reducing gas.

This article presents new data and mechanisms of reduction of chromium oxide by methane-containing gas. It stimulates further study of reduction of chromium ore, which may be an attractive modification of ferro-chromium making technology.

Fig. 14—Calculated equilibrium partial pressure of CO in the Cr_2O_3 reduction by methane-containing gas and graphite as a function of temperature.

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