Reduction and Carburization of Metal Oxides by Methane-Containing Gas

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This paper presents examination results of reduction and carburization of the oxides of iron, manganese, chromium, and titanium by CH_4–H_2–Ar gas mixture. The reactions were investigated in a laboratory fixed-bed reactor in temperature-programmed and isothermal-reduction experiments. The extents and kinetics of the reduction of metal oxides as a function of gas composition and temperature were determined by on-line, off-gas analysis using a mass spectrometer. Methane-containing gas with high carbon activity (above unity relative to graphite) provided strongly reducing conditions, in which metal oxides were reduced and carburized to metal carbides. Iron oxide was first reduced to metallic iron by hydrogen, and then metallic iron was carburized to cementite by methane. Manganese oxides were reduced to carbide Mn_7C_3; the product of reduction of chromium oxide was carbide Cr_3C. Rutile was reduced to titanium oxycarbide in the following sequence: $TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO_xC_y$. Reduction by methane-containing gas occurs through adsorption and dissociation of methane with formation of adsorbed active carbon. Deposition of solid carbon retards the reduction. © 2005 American Institute of Chemical Engineers *AIChE J,* 52: 300–310, 2006

Keywords: reduction, carburization, methane, metal oxide, carbide

Introduction

Affinity for oxygen increases from iron to manganese and chromium and further to titanium. Whereas iron oxide is readily reduced to metallic iron by gases, hydrogen and carbon monoxide, reduction of manganese oxide MnO_2 and chromium oxide Cr_2O_3 by hydrogen or carbon monoxide does not go beyond lower oxides, and rutile TiO_2 can be reduced only to Ti_2O_3. Reduction of manganese, chromium, and titanium oxides to a carbide state rather than a metallic state can be achieved using solid carbon at high temperatures (>1700°C for titania). Using methane-containing gas (CH_4–H_2–Ar), reduction can proceed at much lower temperatures. Under standard conditions, methane is unstable at temperatures $> 550°C$. At appropriate CH_4/H_2 ratio and temperature, carbon activity in the methane-containing gas can be well above unity (relative to graphite), which provides favorable thermodynamic conditions for reduction to occur at relatively low temperatures.

Manganese and chromium oxides are reduced by CH_4–H_2–Ar gas by the following reactions[1,2]

$$MnO + 10/7CH_4 = 1/7Mn_7C_3 + CO + 20/7H_2 \qquad (1)$$

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

Rutile is reduced in the following sequence[3]: $TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO_xC_y$.

In reduction of iron oxides by CH_4–H_2–Ar gas, iron oxides are reduced to metallic iron by hydrogen, which is converted by methane to cementite.[4] It should be noted that cementite is unstable under standard conditions and cannot be formed in carbothermal solid-state reduction.

Reduction and carburization reactions with methane-containing gas are accompanied by methane decomposition with deposition of solid carbon. Read et al.[5] concluded that the role

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of methane in reduction reactions is to supply carbon, which acts as a reductant. This view is different from the position of the authors of this paper. Carbon deposition brings carbon activity down to unity; in addition, deposited carbon blocks access of the reducing gas to the interior of oxide particles with a detrimental effect on the reduction processes.

Methane-containing gas can be used in industrial applications for the prereduction of manganese and chromium ores, for production of cementite, and synthesis of titanium carbide or oxycarbide. The major aim of the study reported herein was to establish the reduction sequences and mechanisms of reduction of metallic oxides by CH_4–H_2–Ar gas under strongly irreversible conditions. This was achieved by experimental study of: (1) reduction and carburization of iron ore; (2) stability of cementite; (3) temperature-programmed and isothermal reduction of manganese, chromium, and titanium oxides; (4) effect of temperature and gas composition on the reduction of oxides; and (5) phases formed during the reduction processes.

Experimental

Experiments were conducted in a fixed-bed reactor heated in a vertical tube furnace. The experimental setup and procedure were described elsewhere.[3] The reducing gas was obtained by mixing high-purity argon, ultrahigh-purity hydrogen, and methane. In some experiments, chemically pure carbon monoxide was added to the reducing gas. Before being introduced into the reactor, all gases were cleaned from moisture and carbon dioxide using a Hydro Purge II purifier. The gas flow rates and the composition of gas mixture were controlled by Brooks mass flow controllers. The off gas was analyzed using a PRIMA 600 scanning magnetic sector mass spectrometer. The amount of water vapor in the off gas was analyzed using a dew point monitor.

Reduction was studied in isothermal and temperature-programmed experiments. In temperature-programmed reduction experiments, the temperature ramping rate was 2°C/min and the gas environments included Ar, H_2–Ar, and CH_4–H_2–Ar gas mixtures. Oxygen removed from the samples in the reduction experiments was calculated on the basis of CO, CO_2, and H_2O contents in off gas. The extent of reduction was determined as the ratio of oxygen removed by reduction to the total oxygen in an oxide sample. The final extent of reduction was also calculated on the basis of residual oxygen contents in reduced samples, which were measured using an oxygen analyzer (LECO, St. Joseph, MI).

Phase analysis was performed by X-ray diffraction (XRD) and both optical and scanning electron microscopy (SEM). XRD analysis was carried out using a Siemens D5000 X-ray diffractometer with monochromator and a copper–K_α X-ray source. A high-resolution (1.5 nm) Hitachi S4500 field emission SEM was used to study reduced and unreduced phases of the oxides.

Reduction of Iron Ore

The iron carbide process, patented by Stephens[6] in 1977 and commercialized by Nucor[7] in 1994, involves conversion of iron ore fines or concentrates to iron carbide in a fluidized bed reactor at 570°C using a hydrogen–methane gas mixture. This process needs a long residence time of 16–20 h.[7] Increasing temperature increases the rate of cementite formation.[8] However, increasing temperature also increases the rate of free carbon deposition, which accelerates iron carbide decomposition. The Nucor Iron Carbide Plant closed its operation after 2 years of struggling with technical difficulties encountered in maintaining productivity and product quality. Nevertheless, the interest in the iron carbide process has not diminished because it has a number of advantages over blast furnace ironmaking. Further development of iron carbide production requires knowledge of kinetics and mechanisms of iron ore reduction and iron cementation, which have not been well established.

Table 1. Chemical Composition of Iron Ore, wt %

Total Fe	Fe_2O_3	SiO_2	Al_2O_3	TiO_2	P	Mn	S
62.7	89.56	4.81	2.61	0.08	0.087	0.04	0.026

The composition of iron ore used in this work is given in Table 1. The ore was sized in the range 0.35–0.5 mm. The contents of Fe_3O_4, Fe_xO, Fe, and cementite in reduced samples of iron ore were determined quantitatively by XRD. The cementite fraction is defined as the molar fraction of iron in cementite.

Iron ore reduction by hydrogen

Iron ore, at a sample mass of 0.5 g, was reduced by hydrogen in the temperature range of 600–925°C. The effect of gas flow rate on the rate of iron ore reduction was investigated by varying the gas flow rate from 0.5 to 1.3 L/min. The mass of a sample was adjusted correspondingly to maintain a constant gas residence time in the bed. Experiments were performed at 925°C, which was the maximum temperature in the range examined in this work. The reduction gas contained 25 vol % H_2 and 75 vol % Ar. It was established that the resistance arising from the external mass transfer could be neglected when the gas flow rate was >1 L/min.

The rate of reduction increased with increasing reduction temperature. It also increased with increasing hydrogen content in H_2–Ar gas to 55 vol %. A further increase in H_2 content had a slight effect on the rate of iron ore reduction.

Addition of methane to H_2–Ar gas (25 vol % H_2) in the amount of 5 to 25 vol % affected iron ore reduction insignificantly at 750, 850, and 925°C.

Changes in the phase composition in the course of iron ore reduction at 600 and 750°C are shown in Figure 1. At both temperatures hematite was converted to magnetite in <1 min. Then, the reduction of magnetite to wustite proceeded in parallel with reduction of wustite to metallic iron.

Iron ore reduction and iron cementation by CH_4–H_2–Ar

Iron ore reduction/cementation by CH_4–H_2–Ar gas was investigated as a function of temperature and gas composition. In all experiments, gas flow rate was maintained at 1 L/min. A sample mass was 2 g. In the first set of experiments, iron ore was reduced and carburized by Ar–CH_4–H_2 gas mixture, containing 35 vol % CH_4 and 55 vol % H_2 in the temperature range 600–925°C, to investigate the effect of temperature on iron ore reduction/cementation. The cementite fraction as a function of reduction temperature and time is shown in Figure 2. The rate

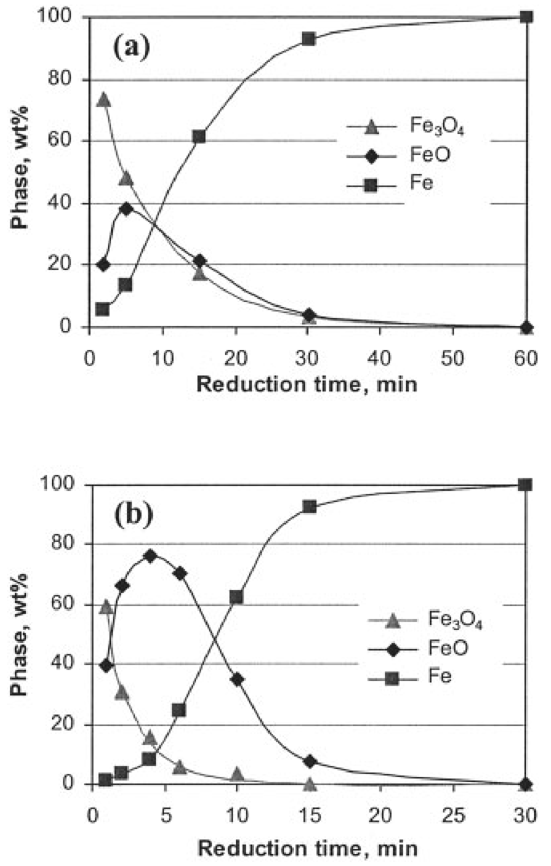

Figure 1. Change in the phase composition of iron ore in the reduction process by H_2–Ar gas (25 vol % H_2) at (a) 600°C and (b) 750°C.[4]

of cementite formation at 600°C was very slow. Increasing temperature increased the rate of cementite formation, although cementite is unstable and decomposes to iron and carbon with further increasing reaction time. It was found that in the temperature range of 600–925°C, cementite was most stable at 750°C. At 750°C iron ore was almost completely converted to cementite in about 15 min. Figure 3 presents XRD spectra of iron ore subjected to reduction and cementation at 700°C, illustrating the process of cementite formation and following decomposition. At this temperature, iron ore was converted to iron carbide in about 30 min. However, increasing reaction time to 60 min and further to 90 min caused decomposition of cementite.

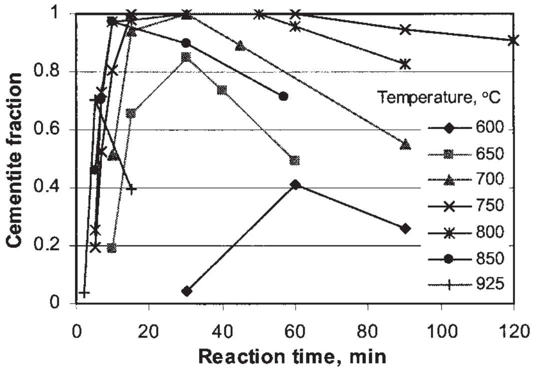

Figure 2. Cementite fraction as a function of reaction temperature and time.[4]

CH_4–H_2–Ar gas composition: 35 vol % CH_4, 55 vol % H_2, and 10 vol % Ar.

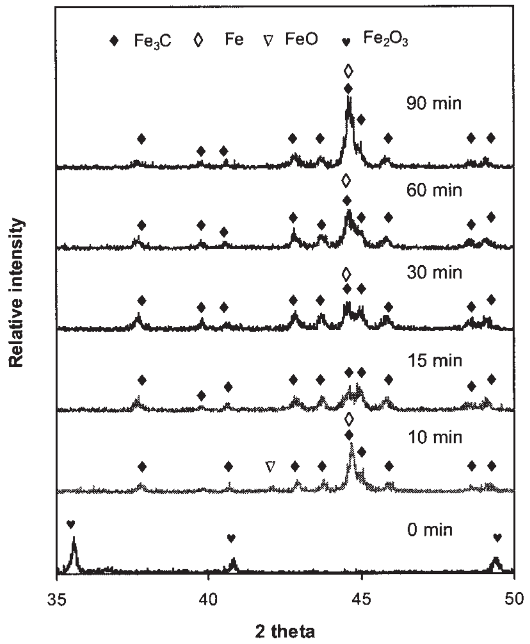

Figure 3. XRD spectra of iron ore subjected to reduction/cementation at 700°C in CH_4–H_2–Ar gas.[4]

Composition: 35 vol % CH_4 and 55 vol % H_2.

In the second set of experiments, temperature was fixed at 750°C. The gas composition was changed to investigate effects of CH_4 and H_2 contents in the gas on iron ore reduction/cementation. In one experimental series, the content of H_2 was kept constant at 55 vol % and the content of CH_4 was changed from 15 to 45 vol %. In the other series, the content of CH_4 was fixed at 35 vol %, whereas the content of H_2 was varied from 15 to 55 vol %. Increasing both methane and hydrogen contents increased the cementite fraction; however, this increase was not significant when methane content was >35 vol %, and hydrogen content was >40 vol %. Further increasing methane content increased free carbon deposition. The optimum gas composition for cementite formation at 750°C was 35 vol % CH_4 and 40–55 vol % H_2.

Reduction of Manganese Oxide

Manganese oxide is reduced by methane to manganese carbide by Reaction 1 with the following Gibbs free energy expression[9]

$$\Delta G^\circ = 377{,}682 - 314.44T\ (\mathrm{J}) \tag{3}$$

At standard conditions, Reaction 1 proceeds spontaneously at temperatures > 928°C, whereas carbothermal reduction of MnO (Reaction 4) starts at 1340°C

$$\mathrm{MnO} + 10/7\mathrm{C} = 1/7\mathrm{Mn_7C_3} + \mathrm{CO} \tag{4}$$

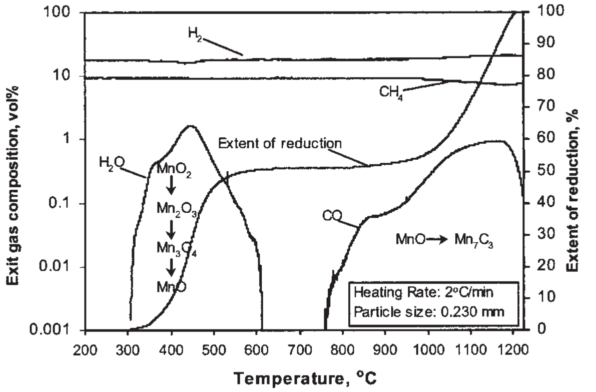

Figure 4. Temperature-programmed reduction of MnO_2 by methane–hydrogen mixture.[1]

Composition: 10 vol % CH_4, 20 vol % H_2, 70 vol % Ar.

$$\Delta G^\circ = 257{,}753.71 - 159.82T \text{ (J)} \tag{5}$$

The equilibrium constant for Reaction 1 is equal to 8.5 at 1000°C, 114 at 1100°C, and 1075 at 1200°C. This indicates that reduction and carburization of MnO to manganese carbide may have a high extent at 1000–1200°C using appropriate gas composition.

In reduction experiments, 2 g of MnO (99+%, maximum size 0.17 mm) or MnO_2 (99+%, maximum size 0.23 mm) was used. MnO was used for isothermal experiments, whereas MnO_2 was used for temperature-programmed reduction. The gas flow rate was 1.0 L/min.

Samples containing manganese carbide quickly swelled and decrepitated in air, which made them difficult to analyze. Kuo and Persson,[10] Kor,[11] and Tanabe et al.[12] also observed the rapid decomposition of manganese carbides in air and found it very difficult to prepare a sample for metallographic examination. They reported that manganese carbide can be stabilized by adding at least 5% Fe. Because of this, in some experiments magnetite (50 μm powder) was added to manganese oxide in the amount of 10 wt % to have about 7 wt % Fe in the carbide phase.

Temperature-programmed reduction of MnO_2

Temperature-programmed reduction of MnO_2 was studied in argon, H_2–Ar (20 vol % H_2 and 80 vol % Ar) and CH_4–H_2–Ar (10 vol % CH_4, 20 vol % H_2, and Ar the balance) gas atmospheres. XRD phase analysis of samples heated to different temperatures showed that in argon, pyrolusite started to decompose to Mn_2O_3 (bixbyite) at approximately 480°C. At 675°C, Mn_2O_3 decomposed to Mn_3O_4 (hausmannite). At 915°C, the oxide was pure Mn_3O_4. Formation of MnO was negligible, even increasing temperature up to 1200°C.

Reduction of MnO_2 by H_2–Ar gas (20 vol % H_2 and 80 vol % Ar) started at 305–320°C. Pure MnO_2 was completely reduced to MnO at 610–620°C. In the temperature-programmed reduction by CH_4–H_2–Ar gas (Figure 4), MnO_2 was reduced to Mn_3O_4 and further to MnO by hydrogen at temperatures very close to the reduction by H_2–Ar gas. The reduction of MnO to manganese carbide started at 760°C and was completed at about 1200°C. In the process of MnO reduction to manganese carbide, only CO was detected in the gas phase.

Isothermal reduction of MnO

Effects of Temperature and Iron Addition on MnO Reduction. Results of the isothermal MnO reduction by CH_4–H_2–Ar gas (15 vol % CH_4, 20 vol % H_2, and 65 vol % Ar) in the temperatures range 1000–1200°C showed that the rate of manganese oxide reduction increased with temperature (Figure 5). Oxygen analysis detected no oxides in a sample after reduction.

When 10 wt % of Fe_3O_4 was added to the MnO samples, complete reduction of the iron oxide contributed 12% to the extent of reduction of the MnO–Fe_3O_4 samples. The first stage of reduction constituted the fast reduction of Fe_3O_4 by hydrogen to metallic iron in addition to reduction of MnO. However, this explains only part of the increase in extent of reduction compared to that of pure MnO at the same temperatures. The addition of Fe_3O_4 increased the rate of reduction of MnO at all temperatures in the range of 1000 to 1200°C. Its effect on the rate of MnO reduction was particularly strong at 1000 and 1050°C. However, at these temperatures, complete reduction of the MnO–Fe_3O_4 samples was not achieved because of blockage of a porous plug by solid carbon deposits. Reduced iron promoted decomposition of methane and deposition of solid carbon. The off gas contained a small amount of H_2O, which was attributed to the iron oxide reduction, whereas pure MnO reduction produced only CO.

The reduction reaction (Reaction 1) is strongly endothermic, and the decrease in the bed temperature during the MnO reduction was observed. The temperature drop was particularly strong (50–60°C) in the beginning of the reduction process.

Effect of Methane Content on MnO Reduction. The effect of methane content in the gas mixture on the rate of MnO reduction was examined at 1200°C at constant hydrogen content of 20 vol %. The methane content was varied from 2.5 to 20 vol %. The extent of reduction vs. time is shown in Figure

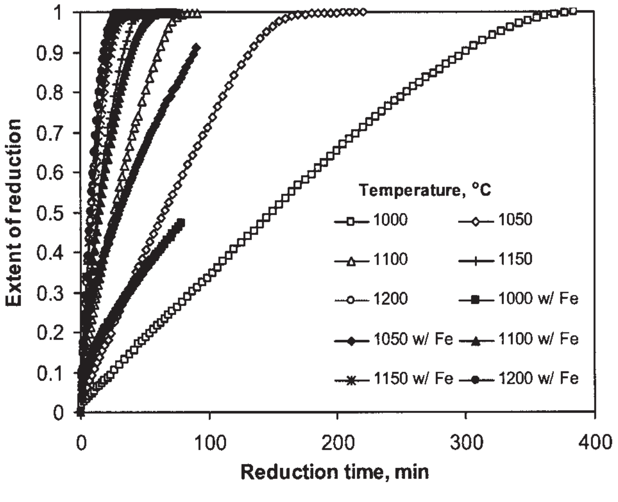

Figure 5. Reduction of pure MnO and MnO with addition of 10 wt % Fe_3O_4 by CH_4–H_2–Ar gas (15 vol % CH_4, 20 vol % H_2, and 65 vol % Ar) at different temperatures.[1]

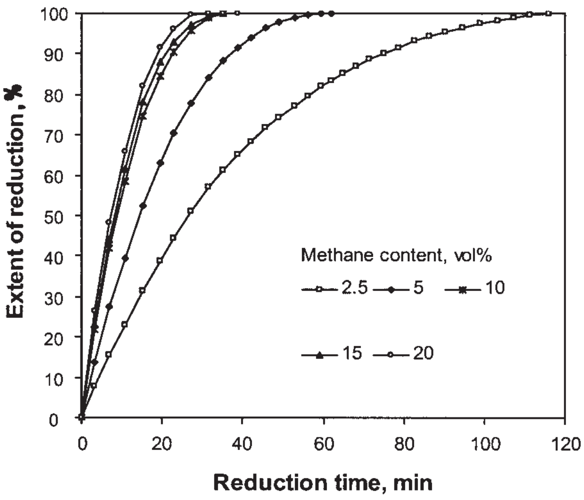

Figure 6. Reduction of MnO by methane-containing gas with different methane content at 1200°C.[1]

Hydrogen content was constant at 20 vol % H_2.

6. The rate of reduction increased with increasing methane content to 10 vol %. A further increase in the methane content to 15 and 20 vol % had only a slight effect on MnO reduction and resulted in strong carbon deposition. Deposited carbon blocked an access of the reducing gas to the particle interior, affected the gas flow through the reactor, and hindered the reduction process.

Effect of Hydrogen Content on MnO Reduction. The effect of hydrogen content in the gas mixture on MnO reduction was investigated at a constant methane content of 15 vol % at 1150°C. The hydrogen content in the gas mixture was varied from 10 to 85%. The rate of MnO reduction increased slightly with increasing hydrogen content in the gas mixtures.

Effect of Carbon Monoxide on MnO Reduction. The effect of carbon monoxide in the gas mixture on MnO reduction was examined at 1150°C at constant methane and hydrogen content of 10 and 20 vol %, respectively. The carbon monoxide content of the gas mixtures was varied from 0 to 5%. The addition of CO to the gas mixtures had a strong retarding effect on the extent of MnO reduction, particularly when CO content in the inlet gas was >1.5 vol %. The extent of reduction achieved after 3 h was <40% when a reducing gas contained 3 vol % of CO.

Reduction of Chromium Oxide

The standard Gibbs free energy of the reaction 2 chromium oxide reduction by methane-containing gas, from Knacke et al.[9] is

$$\Delta G^\circ = 1{,}097{,}519.4 - 989.79T \text{ (J)} \tag{6}$$

Equation 6 gives a temperature of 836°C above which Reaction 2 occurs spontaneously under standard conditions. The carbothermal reduction of pure chromium oxide (Reaction 7) under standard conditions proceeds spontaneously at a temperature > 1113°C (calculated using data from Knacke et al.[9]).

$$3/2Cr_2O_3 + 13/2C = Cr_3C_2 + 9/2CO \tag{7}$$

$$\Delta G^\circ = 1{,}078{,}190 - 777.94T \text{ (J)} \tag{8}$$

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

Reduction of chromium oxide was studied in isothermal and temperature-programmed experiments. Chromium (III) oxide (Cr_2O_3, 98+%, <50 μm) was supplied by Aldrich Chemical. The fine powder was sintered before use. A chromium oxide–water paste was heated in air in a muffle furnace at a ramping rate of 200°C/h to 1400°C, and then held at that temperature for 5 h. Then it was cooled, crushed, and sieved to +1.7–2.3, +1.2–1.7, +0.85–1.2, and +0.6–0.85 mm size ranges. The particle size of the sintered chromium oxide in the range of 0.6 to 2.3 mm had no visible effect on the rate and extent of reduction. The reason behind this was the high open porosity of particles. The particle size in the following experiments was +0.85–1.2 mm.

In temperature-programmed experiments, samples were reduced under Ar, H_2–Ar, and CH_4–H_2–Ar gas mixtures. The temperature was increased from 200 to 1200°C with a ramping rate of 2°C/min. The gas flow rate in all experiments was 1 L/min; at this flow rate, the external mass-transfer resistance could be neglected.

For purposes of comparison, a temperature-programmed 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 content in the off gas (CO_2 and H_2O contents were below detectable levels). 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.

Temperature-programmed reduction of Cr_2O_3

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 7. The reduction of chromium oxide to chromium carbide, Cr_3C_2, started at about 770°C, which is lower than the thermodynamic equilibrium temperature at standard conditions, that is, 836°C according to Eq. 6. Cr_2O_3 was completely reduced to Cr_3C_2 at 910°C. This was confirmed by oxygen analysis and XRD analysis.

Isothermal reduction of Cr_2O_3

Effect of Temperature. The effect of temperature on Cr_2O_3 reduction was studied in the temperature range of 900–1200°C, using gas containing 10 vol % CH_4, 50 vol % H_2, and 40 vol % Ar. The results are shown in Figure 8. Pure Cr_2O_3 was completely reduced under these conditions. Oxygen analysis confirmed that the extent of reduction was close to 100%. The reduction rate increased with increasing temperature, which

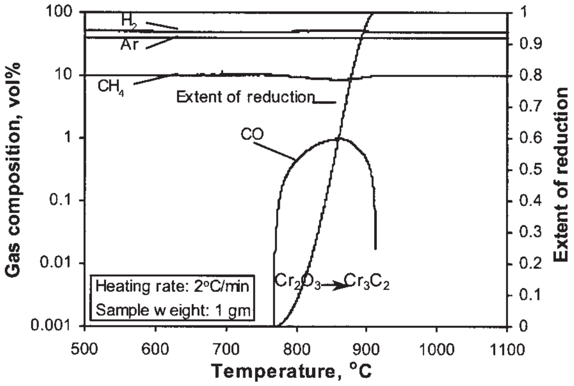

Figure 7. Temperature-programmed reduction of Cr_2O_3 by 10 vol % CH_4–50 vol % H_2–40 vol % Ar mixture.[2]

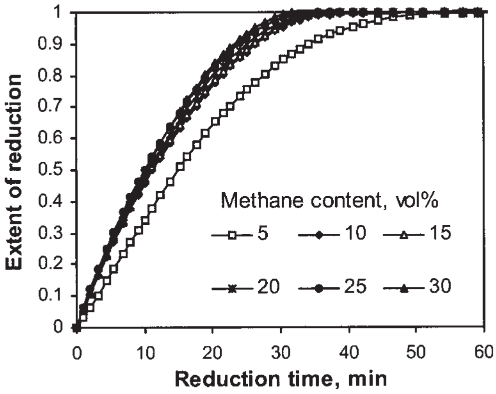

Figure 9. Reduction of Cr_2O_3 by gas with varying methane content at 1000°C.[2]

H_2 content was constant at 50 vol %.

was the most significant between 900 and 1000°C. When the temperature was >1000°C, this increase diminished with increasing temperature. Reduction of chromium oxide was completed in about 100 min at 900°C, 40 min at 1000°C, 37 min at 1050°C, 33 min at 1100°C, 27 min at 1150°C, and 22 min at 1200°C. At high temperatures, increasing temperature has double effects: (1) increase in the reduction rate constant and (2) increase in solid carbon deposition by methane cracking, which hinders reduction reactions. As a result, increasing reduction rate with increasing temperature in the range 1000–1200°C is compromised and becomes marginal.

Effect of Methane and Hydrogen Content. The effect of methane content on chromium oxide reduction was investigated by adding methane to the H_2–Ar gas mixture in the amount of 5, 10, 15, 20, 25, and 30 vol % at 1000°C. The hydrogen content was maintained at 50 vol % and the sample mass was 2 g in all experiments. The effect of methane content on the extent of chromium oxide reduction is presented in Figure 9. At all experimental temperatures, no reduction of pure oxide Cr_2O_3 was observed when the reducing gas had no methane. Increasing methane content in the gas increased the rate of reduction. At methane content over 10 vol %, the increase in the reduction rate became less significant. A further increase in the methane concentration caused methane cracking, which retarded the reduction arising from 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 the hydrogen content from 0 to 70 vol % at constant methane content of 10 vol %. The rate of Cr_2O_3 reduction increased slightly with increasing hydrogen in the reducing gas.

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 % in gas with 15 vol % methane and 50 vol % hydrogen (argon the balance). 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. The off-gas composition was initially analyzed in the reactor without Cr_2O_3 to determine the CO background level. 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 10). Two hours of exposure of Cr_2O_3 to the reducing gas with 7.5 vol % CO at 1000°C resulted in about 0.95 extent of reduction, whereas

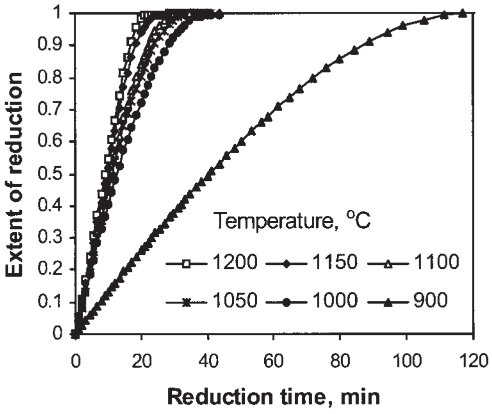

Figure 8. Reduction of Cr_2O_3 by gas containing 10 vol % CH_4–50 vol % H_2–40 vol % Ar at different temperatures.[2]

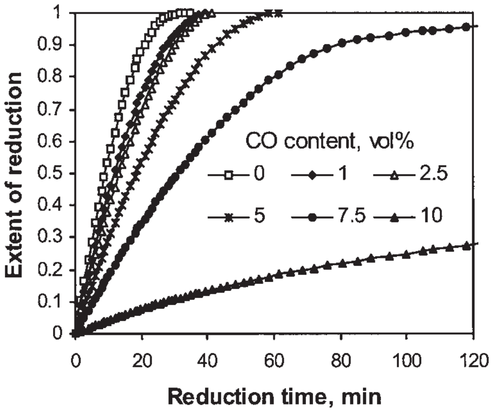

Figure 10. Effect of CO content on the reduction of Cr_2O_3 by CH_4-H_2-Ar gas mixture (15 vol % CH_4–50 vol % H_2) at 1000°C.[2]

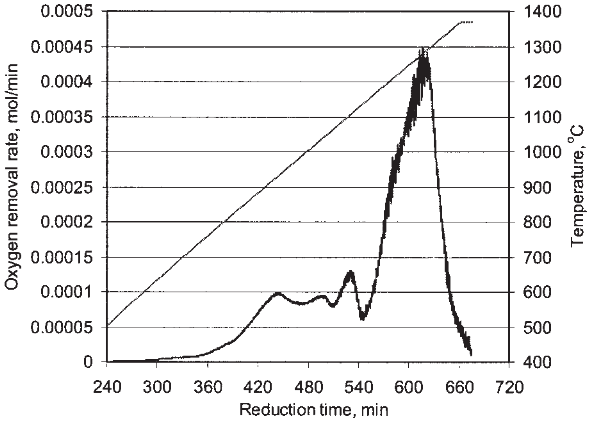

Figure 11. Temperature-programmed reduction of rutile by CH_4–H_2–Ar gas mixture containing 5 vol % CH_4 and 75 vol % H_2.[3]

reduction with CO-free gas was completed in about 30 min. The extent of reduction by the gas containing 10 vol % CO was <0.30 after 2 h of reduction.

Reduction of Titanium Oxide

Reduction of rutile was studied in temperature-programmed and isothermal experiments. Chemical rutile was obtained from Sigma–Aldrich as fine powder of <5 μm. To obtain rutile particles suitable for reduction experiments, the powder was sintered at 1400°C for 2 h and then crushed and sieved to different particle size ranges. Experimental results showed that there were no visible changes in reduction rate and extent when particle size changed from 0.15 to 0.60 mm. The rutile samples used in this study had a particle size in the range of +0.212–0.355 mm. The BET (Brunauer–Emmett–Teller)-specific surface area of the samples was 0.2 m^2/g. A total gas flow rate was maintained at 1 L/min.

Temperature-programmed reduction of TiO_2

The reduction curve (Figure 11) obtained in the reduction of rutile by CH_4–H_2–Ar gas mixture containing 5 vol % CH_4 and 75 vol % H_2, consists of several overlapped peaks. The last and the biggest peak corresponds to the formation of titanium oxycarbide, whereas the prior small peaks are attributed to the stepwise reduction of titania to Ti_2O_3. Titanium oxycarbide is formed from Ti_2O_3, with the maximum rate at about 1290°C. The peak temperature of Ti_2O_3 formation is about 1110°C.

Analysis of phases formed in the progress of reduction showed that reduction of titania by methane–hydrogen gas proceeded in the following consecutive steps:

$$TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO_{1-x}C_x$$

Isothermal reduction of TiO_2

Effect of Temperature. Effect of temperature on rutile reduction by CH_4–H_2–Ar gas mixture (5 vol % CH_4, 75 vol % H_2, and 20 vol % Ar) was examined in the temperature range of 1100–1500°C. Results are presented in Figure 12. At 1100°C, rutile was reduced to Ti_2O_3, with only a minor amount of TiC detected after 6 h of reduction. The rate of TiC formation increased rapidly with increasing temperature to 1450°C. At 1500°C, the reduction rate was about the same as that at 1450°C, although the final extent of reduction was slightly higher.

According to XRD analysis, the main constituent of samples reduced at ≥1250°C was TiC phase, with a small amount of Ti_2O_3 phase detected. However, the extents of reduction calculated from mass spectrometer data and LECO analysis were far from 100%. This means that Ti_2O_3 was reduced to TiC–TiO solid solution (TiO_xC_{1-x}), which has the same cubic crystalline structure as that of TiC.[13] Further reduction of TiO from the solid solution to TiC is thermodynamically feasible, but the reaction was very slow because of the kinetic constraint.

The optimum temperature for titania reduction to titanium oxycarbide was in the range of 1250–1400°C. A further increase in temperature caused deposition of a substantial amount of carbon as a result of methane cracking.

Effect of Methane Content. Effect of methane content on the rutile reduction was examined in the range of 3–10 vol % CH_4, keeping hydrogen content in the reducing gas at 75 vol % and temperature at 1300°C. The results are shown in Figure 13. With increasing methane content to 8 vol %, the reduction rate increased, whereas the final extent of reduction slightly decreased. When the methane content was >9 vol %, the initial high rate of reduction was maintained for only a few minutes and then decreased rapidly to a very low value. In the test with 9 vol % methane, after about 1 h of slow reduction, there appeared the second stage of rapid reduction, which lasted for about 30 min. The final extent of reduction in this test was rather low. In the test with 10 vol % methane, the "second" reduction stage did not appear. The final extent of reduction was about 20%, and the XRD pattern showed that the main constituent in a reduced sample was Ti_3O_5. Methane cracking and solid carbon deposition rate also increased with increasing

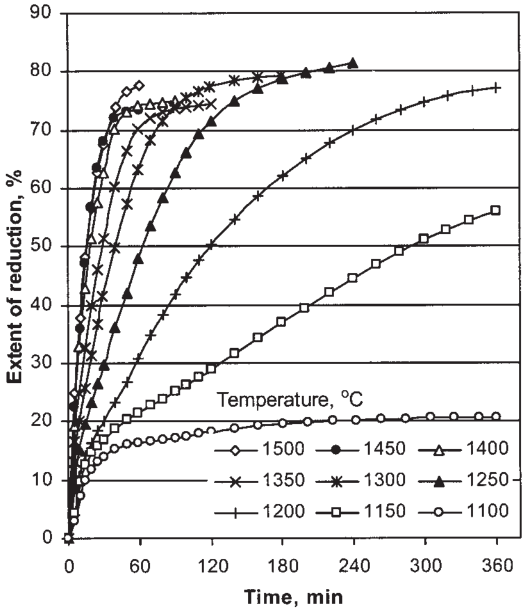

Figure 12. Reduction of titania by CH_4–H_2–Ar gas mixture (5 vol % CH_4–75 vol % H_2) at different temperatures.[3]

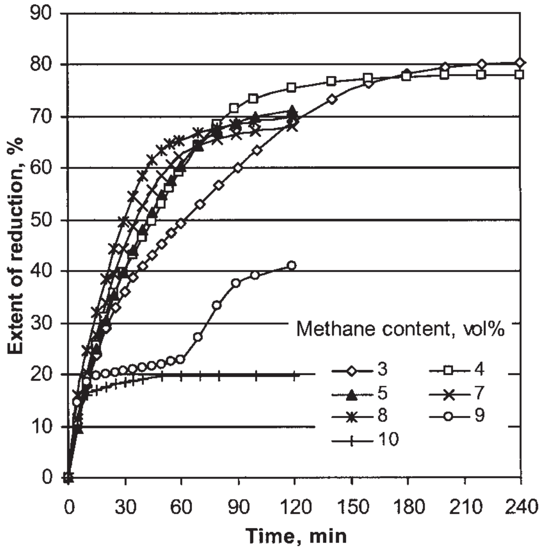

Figure 13. Reduction of titania by CH_4–H_2–Ar gas mixture with different methane contents at 1300°C.[3]

H_2 content was kept constant at 75 vol %.

methane concentration. Solid carbon deposited on the sample surface, thus hindering the further progress of reduction by blocking the surface. Methane had double effects on the reduction process. On one hand, increasing methane content in the gas phase enhanced the rate of reduction; on the other hand, excess methane content in the gas phase caused accumulation of solid carbon on the surface of samples and retarded the reduction. When methane content was 10 vol %, deposited carbon even prevented reduction of Ti_3O_5 to Ti_2O_3.

Effect of Hydrogen Content in the Gas Mixture. Effect of hydrogen content in the gas mixture on the rutile reduction was examined in the range 5–95 vol % at 1300°C and constant methane content of 5 vol %. Hydrogen had a strong effect on the rate and extent of titania reduction only when its content was $<$15 vol %. In the range of 35–95 vol %, hydrogen did not have a visible effect on the titania reduction. Hydrogen plays a role in reduction of TiO_2 to Ti_2O_3. Another crucial role of hydrogen was to suppress methane cracking and solid carbon deposition. The fraction of decomposed methane increased steadily with the decrease in hydrogen in the range 30–95 vol %. When the hydrogen content in the gas phase was $<$30 vol %, the rate of methane cracking increased more sharply.

Effect of Carbon Monoxide and Water Vapor in Gas Mixture. Influences of carbon monoxide and water in the reducing gas on titania reduction were examined at 1300°C with fixed methane and hydrogen contents of 5 and 75 vol %, respectively. The extent of titania reduction decreased steadily with increasing CO content to 10 vol %, then declined sharply with further increase in CO. The retarding effect of water vapor on the rutile reduction was more profound. The extent of titania reduction decreased to $<$50% when only 1.5 vol % of water vapor was added to the reducing gas. Carbon monoxide had a similar effect at 15 vol %.

When the content of H_2O in the reducing gas was $>$1.5 vol % or the content of CO was $>$15 vol %, the Ti_2O_3 phase was not observed, although some amount of titanium oxycarbide phase was always formed at the final reduction stage. This implies that CO and particularly H_2O strongly retarded the reduction of Ti_3O_5 to Ti_2O_3. Addition of water vapor to the system can reverse the direction of reduction of Ti_3O_5 to Ti_2O_3 by hydrogen because the equilibrium partial pressure of water vapor for the reaction is very low.

Discussion

The key factor in the reduction of metal oxides by methane-containing gas is high carbon activity in the gas, plotted in Figure 14 as a function of CH_4 fraction in the CH_4–H_2 gas mixture and temperature.

The high carbon activity—well above unity (relative to graphite)—provides thermodynamic conditions for reduction of manganese, chromium, and titanium oxides at relatively low temperatures and formation of cementite in the reduction of iron ore.

However, under these conditions, methane is unstable and decomposes with deposition of solid carbon. If this reaction prevails over the reduction/carburization reactions, the carbon activity in the system will be equal to unity, and thermodynamic conditions for reduction reactions will be the same as those in the conventional carbothermal process. It can be illustrated by the following:

The reduction process starts with adsorption of methane on the active sites of the oxide surface and its decomposition, described by the following reactions[14]:

$$CH_4\ (gas) = CH_4\ (ad) \tag{9}$$

$$CH_4\ (ad) = CH_3\ (ad) + H\ (ad) \tag{10}$$

$$CH_3\ (ad) = CH_2\ (ad) + H\ (ad) \tag{11}$$

$$CH_2\ (ad) = CH\ (ad) + H\ (ad) \tag{12}$$

$$CH\ (ad) = C\ (ad) + H\ (ad) \tag{13}$$

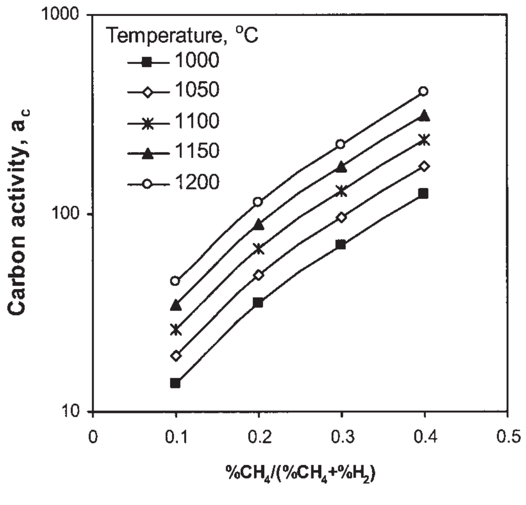

Figure 14. Calculated carbon activity (relative to graphite) in methane–hydrogen gas mixture at different temperatures.

$$2H\ (ad) = H_2\ (g) \qquad (14)$$

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

$$CH_4 \rightarrow \cdots \rightarrow C_{ad} + 2H_2 \qquad (15)$$

in which C_{ad} represents active carbon species adsorbed on solid surface, and is substantially different from deposited solid carbon. On the basis of this reaction, thermodynamic activity of adsorbed carbon may be defined (relative to graphite) by

$$a_C = K(P_{CH_4}/P_{H_2}^2) \qquad (16)$$

where K is the equilibrium constant of Reaction 17 of methane cracking:

$$CH_4 = C_{gr} + 2H_2 \qquad (17)$$

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 16 may be rewritten as

$$a_C = (P_{CH_4}/P_{H_2}^2)/(P_{CH_4}/P_{H_2}^2)_{gr} \qquad (18)$$

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 adsorbed carbon provides higher reducibility and kinetic rate compared with those of carbothermal reduction.

Adsorbed carbon is consumed by reduction/carburization reactions. The key factor is a high rate of this reaction compared with the rate of carbon deposition in Reaction 17. If solid carbon is formed on the sample surface, it blocks the access of reducing gas to metal oxides, and the carbon activity at the oxide surface is decreased to unity, regardless of the high $(P_{CH_4}/P_{H_2}^2)$ ratio in the inlet gas.

The rate of Reaction 15, R, is proportional to the fraction of the surface area available for adsorption, $(1 - \theta)$, and in a general case is a function of partial pressures of methane P_{CH_4} and hydrogen P_{H_2}:

$$R = kAf(P_{CH_4}, P_{H_2})(1 - \theta) \qquad (19)$$

Reduction/carburization reactions serve as a sink for adsorbed carbon. After completion of these reactions, adsorbed carbon is not consumed and forms solid carbon. Deposition of solid carbon in the reduction of the oxides of manganese, chromium, and titanium is much less compared with that of iron oxide, when reduced iron catalyzes the methane cracking. Thus, in the temperature-programmed reduction of chromium oxide (Figure 7), the methane consumption was observed only when Cr_2O_3 is reduced to Cr_3C_2 in the temperature range of 770 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 as a result of methane cracking was $<4\%$ at methane concentrations in the range 5–30 vol %. This means that carbon deposition resulting from methane cracking is not a significant factor in the chromium oxide reduction.

Contrary to the conclusion of Read et al.,[5] that deposited carbon acts as a reductant, our findings have demonstrated that carbon deposition has a detrimental effect on the reduction reactions. It decreases the carbon activity in the system and blocks the access of the reducing gas to the oxide interior. In the case of reduction of iron ore and carburization of iron, it triggers cementite decomposition (dusting phenomenon).

Occurrence of two simultaneous processes—oxide reduction and methane cracking—explains the effect of temperature and gas composition on the extent and rate of reduction reactions. High temperature and CH_4/H_2 partial pressure ratio stimulate methane cracking with deposition of solid carbon. As a result, increase in temperature and CH_4/H_2 partial pressure ratio above some levels has only a slight effect on the extent of reduction (see Figures 2, 5, 6, 8, and 9) or negative effect in the case of reduction of titania (Figures 12 and 13).

Addition of carbon monoxide to the reducing gas in reduction of MnO, Cr_2O_3, and TiO_2 had a strong retarding effect on the reduction reactions. This can be explained either by the reoxidation of carbides or CO adsorption onto active sites of the oxide surface, thus hindering the adsorption of methane.

Manganese and chromium carbides can be reoxidized by the following reactions

$$Mn_7C_3 + 7CO = 7MnO + 10C \qquad (20)$$

$$Cr_3C_2 + 9/2CO = 3/2Cr_2O_3 + 13/2C \qquad (21)$$

The calculated equilibrium partial pressures of CO for Reactions 20 and 21 are much lower than in reduction by methane-containing gas by Reactions 1 and 2. The reduction reactions under experimental conditions used in this work are practically irreversible. The equilibrium CO partial pressure in reactions with CH_4–H_2–Ar gas is very high. However, a partial pressure of CO of 0.01–0.1 atm can be above equilibrium for *carbothermal* reduction and can reoxidize manganese and chromium carbides to oxides according to Reactions 20 and 21, especially at lower temperatures, which explains the strong retarding effect of CO addition to the reducing gas on the reduction rate of MnO and Cr_2O_3.

In the case of reduction of rutile, situation is different. Thermodynamic analysis shows that rutile reduction and carburization with methane can proceed to TiC even in the CO atmosphere. However, this reduction process is retarded in the step of Ti_3O_5 reduction to Ti_2O_3. It can be suggested that Ti_2O_3 is oxidized to Ti_3O_5 by the following reaction

$$3Ti_2O_3 + CO \rightarrow 2Ti_3O_5 + C \qquad (22)$$

Our experimental results showed that Ti_2O_3 was oxidized to Ti_3O_5 at CO partial pressure of 0.2 atm at 1300°C. CO retarded the titania reduction by the following mechanism

$$\begin{tikzcd} Ti_3O_5 \arrow[r, "+H_2/CH_4"] & Ti_2O_3 \arrow[r, "+CH_4"] \arrow[l, bend left, "+CO"] & (TiO\text{–}TiC)_{ss} \end{tikzcd}$$

Water vapor oxidizes Ti_2O_3 to Ti_3O_5 at partial pressure of 0.01–0.02 atm at 1300°C.

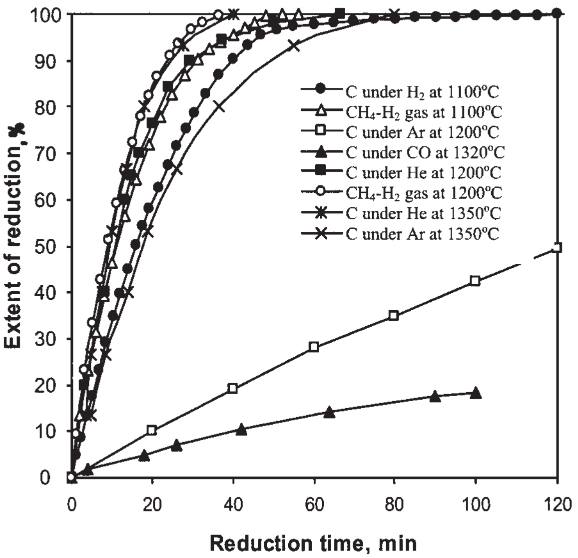

Figure 15. Reduction curves for MnO reduced by graphite in CO, Ar, and He,[15] Ar,[16] He,[17] H_2 atmosphere and by CH_4–H_2–Ar gas at different temperatures.

Figures 15 and 16 compare reduction of manganese and chromium oxides by CH_4–H_2–Ar gas with carbothermal reduction. In temperature-programmed experiments, reduction of MnO by methane containing gas starts at 760°C, whereas carbothermal reduction under hydrogen starts only at 920°C. The reduction of MnO with solid carbon under argon is very slow and is not complete even at 1200°C after 2 h. The rate of carbothermal reduction depends strongly on the gas atmosphere. At 1200°C, the carbothermal reduction of pure MnO under He, investigated by Terayama and Ikeda,[17] is about sevenfold faster than under Ar atmosphere measured by Rankin and Van Deventer.[16] However, the reduction of MnO by methane-containing gas is faster than the carbothermal reduction of MnO under Ar, He, or H_2. Reduction of Cr_2O_3 by the methane-containing gas is also faster than carbothermal reduction. In temperature-programmed experiments, chromium oxide reduction by methane–hydrogen mixture started at 770°C and completed at 910°C, whereas the carbothermal reduction of chromium oxide under hydrogen started at 860°C and completed at about 1040°C.

Conclusions

- In the reduction by methane-containing gas, oxides of iron, manganese, and chromium are converted to carbides, whereas titania is reduced to titanium oxycarbide.
- Methane molecules adsorb on the oxide surfaces and dissociate in steps, releasing hydrogen atoms and forming adsorbed active carbon species that have high reducing capacity compared to that of solid carbon in carbothermal reduction processes.
- The high carbon activity of the reducing gas is the key to achieve high rates and extents of reduction of metal oxides by methane-containing gas. However, it also causes deposition of solid carbon, which has a strong retarding effect on the reduction processes.
- In the temperature range of 600–925°C, cementite is the most stable at about 750°C, which is the optimal temperature for cementite formation. At this temperature, reduction/cementation of iron ore to cementite completes in about 15 min using gas containing 55 vol % H_2, 35 vol % CH_4, and 10 vol % Ar. The optimum hydrogen and methane concentrations in gas for cementite formation at 750°C are found to be 40–55 vol % H_2 and 35 vol % CH_4.
- Manganese oxides are reduced to manganese carbide Mn_7C_3 by the methane-containing gas through the sequence: $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow Mn_7C_3$. The reduction rates increase with increasing temperature in the temperature range of 1000–1200°C. At 1200°C, reduction of MnO is close to completion in <30 min. The reduction rate increases with increasing methane content in the gas mixtures up to 10–15 vol % CH_4. Increasing hydrogen content >20 vol % favors the reduction process. The addition of Fe_3O_4 to manganese oxide increases the rate of reduction.
- The optimal conditions for Cr_2O_3 reduction to the chromium carbide by methane-containing gas include temperature in the range of 1100–1200°C, methane concentration 15–20 vol %, and hydrogen concentration >20 vol %.
- Titania is reduced by methane–hydrogen gas to the titanium oxycarbide in the following steps: $TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 \rightarrow TiO_{1-x}C_x$. The optimal conditions for titanium carbide synthesis include temperature in the range of 1250–1400°C, methane content of 8 vol %, and hydrogen content $>$ 35 vol %.
- Addition of CO to the reducing gas strongly retards the reduction processes.
- Reduction of manganese, chromium, and titanium oxides by methane-containing gas is faster than corresponding carbothermal reductions, which makes it promising in the processing of manganese, chromium, and titanium ores.

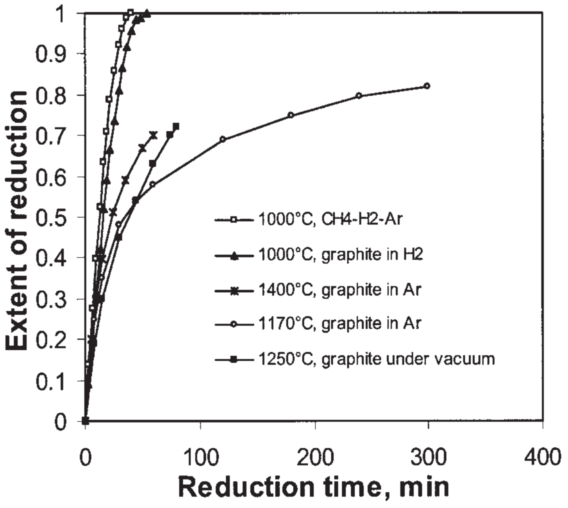

Figure 16. Reduction curves for pure Cr_2O_3 reduction by graphite in Ar at 1400°C[10] and 1170°C,[11] by graphite under vacuum at 1250°C,[12] by graphite in H_2 at 1000°C and by 10 vol % CH_4–50 vol % H_2–40 vol % Ar gas mixture at 1000°C.[2]

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