Carbothermal reduction of a primary ilmenite concentrate in different gas atmospheres

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The carbothermal reduction of a primary ilmenite concentrate was studied in hydrogen, argon, and helium. Ilmenite and graphite were uniformly mixed and pressed into pellets. Reduction was studied in isothermal and temperature-programmed reduction experiments in a tube reactor with continuously flowing gas. CO, CO_2, and CH_4 contents in the off-gas were measured online using infrared sensors. The phase composition of reduced samples was characterized by X-ray diffraction (XRD). Oxygen and carbon contents in reduced samples were determined by LECO analyzers (LECO Corporation, St. Joseph, MI). The main phases in the ilmenite concentrate were ilmenite and pseudorutile. The reaction started with the reduction of pseudorutile to ilmenite and titania, followed by the reduction of ilmenite to metallic iron and titania. Titania was reduced to Ti_3O_5 and even more to Ti_2O_3, which was converted to titanium oxycarbide. Reduction was faster in hydrogen than in helium and argon, which was attributed to involvement of hydrogen in the reduction reactions. The formation of titanium oxycarbide in hydrogen started at 1000 °C and was completed in 300 minutes at 1200 °C, and 30 minutes at 1500 °C. The formation of titanium oxycarbide in argon and helium started at 1200 °C and was not completed after 300 minutes at 1300 °C.

I. INTRODUCTION

METALLIC titanium and titania white pigment are produced from titanium tetrachloride, which is obtained by the chlorination of high-quality titania ores or synthetic rutile and slag with high titania contents. Ilmenite ore is the main titanium resource, which consists of titanium and iron oxides and impurities, such as MnO, SiO_2, MgO, Al_2O_3, CaO, V_2O_5, Cr_2O_3, and others.[1] It is necessary to remove iron from ilmenite ores to obtain titanium-rich material for chlorination. Many methods have been proposed to refine ilmenite, including smelting, direct acid leaching, selective chlorination, and reduction.[2–5] Selective reduction of iron oxides and following leaching, such as the Becher process, is one of the most effective technologies to produce synthetic rutile.

Merk and Pickles[6] studied the reduction of ilmenite by carbon monoxide at 500 °C to 1100 °C. The increase in temperature had a significant effect on the reduction rate. The reduction rate and final degree of reduction were affected by the formation of a metallic shell of iron that inhibited the transfer of CO to the reaction zone. By ball milling of the carbon–ilmenite mixture, Chen et al.[7] decreased the temperature of the carbothermal reduction of mineral ilmenite to rutile and metallic iron. A longer milling time resulted in a lower reduction

temperature and a higher reduction rate. Park and Ostrovski[8,9] studied the reduction of titaniferrous ore using a H_2-Ar gas mixture in the temperature range from 700 °C to 1100 °C and a CO-Ar-CO_2 gas mixture at 1100 °C to 1200 °C. A rise in the temperature as well as in the hydrogen or carbon monoxide content in the atmospheres increased the reduction rate.

The chlorination of titania requires a high temperature of 800 °C to 1100 °C. Impurities are also chlorinated in this temperature range. However, titanium carbide or oxycarbide can be chlorinated at low temperatures,[10] at which the chlorination of impurities can be avoided. Therefore, requirements of materials to be chlorinated can be released, so that titanium resources are used more effectively. The carbothermal reduction of ilmenite to titanium oxycarbide was studied.[11–17] Terry and Chinyamakobvu[12] investigated the production of titanium oxycarbide-iron composites by carbothermal reduction of ilmenite with coal in flowing argon. They reported an excellent dispersion of Ti(O,C) in an Fe matrix at temperatures above 1450 °C. Coley et al.[11] reduced Western Australia ilmenite using collie coal at 1314 °C to 1517 °C. It was suggested that titanium oxycarbide was formed from Ti_3O_5 at temperatures below 1413 °C and from Ti_2O_3 above the temperature. Welham and Williams[14] reported the decrease of TiC formation temperature from ilmenite to 1100 °C by mechanical activation and suggested that iron promoted formation of TiC by enhancing carbon transport through the iron phase. They also suggested that TiC, rather than the oxycarbide phase, was formed by the carbothermal reduction of ilmenite. Wang and Yuan[18] reported no formation of titanium oxycarbide in the carbothermal reduction of natural ilmenite up to

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1400 °C. There are still inconsistencies in understanding of the kinetics and mechanisms of the reduction of ilmenite. Zhang and Ostrovski[15–17] investigated the reduction of natural, sintered, and preoxidized ilmenite concentrates in hydrogen–methane mixtures. The reduction of iron was completed at 950 °C for 180 minutes. The formation of titanium oxycarbide was close to completion at 1150 °C for 60 minutes. Recent works demonstrated that the kinetics of the carbothermal reduction of metal oxides is strongly affected by the gas atmospheres.[19–21] This study examines the reduction of an ilmenite concentrate in hydrogen, helium, and argon gases, as well as the changes of phase composition in the course of the reduction process.

II. EXPERIMENTAL

The ilmenite concentrate used in this investigation was the primary ilmenite supplied by Iluka Resources Limited (Perth, Western Australia). The chemical composition of the ilmenite concentrate is presented in Table I. It contained 53.9 wt pct of TiO_2; the particle size was in the range of 50 to 300 μm with an average size of 152 μm. As-received ilmenite particles and synthetic graphite (99.5 pct purity, <20 μm in particle size, supplied by Sigma Aldrich, Castle Hill, Australia) were wet mixed and pressed into cylindrical pellets.[19] The ilmenite-graphite mixture contained 10 mol pct extra graphite to the stoichiometric amount of carbon necessary to reduce the oxides of titanium, iron, and manganese present in the ilmenite. Other oxides were considered to be unreducible under given experimental conditions. The pellets with a mass of about 2 g were 8 mm in diameter and about 12 mm high.

The reduction of primary ilmenite by graphite in H_2, Ar, and He gases was studied in a laboratory fixed-bed reactor in a vertical tube electric furnace. The experimental setup and gas systems were presented elsewhere.[22] The gases used in the investigation were of 99.999 pct purity. The outlet gas was analyzed online by an infrared $CO/CO_2/CH_4$ analyzer (Advanced Optima AO2020, ABB, Ladenburgh, Germany). The total gas flow rate was maintained at 1.00 NL/min.

The reduced pellets were analyzed by X-ray diffraction (XRD) with Philips X'Pert-Pro MPD diffractometer (PANalytical, Lelyweg, the Netherlands) with CuKα radiation. The oxygen and carbon contents in reduced samples were determined using LECO analyses (TC-436DR oxygen and nitrogen analyzer and CS-444 carbon and sulfur analyzer).

The extent of reduction was defined as a fraction of oxygen in titanium, iron, and manganese oxides removed in the course of reduction, and it was calculated based on the gas composition as well as the oxygen and carbon contents of reduced samples. The error of measured oxygen content by LECO analysis depends on the residual oxygen content in the reduced sample. For a sample with an extent of reduction 90 pct, the error was about 0.1 pct, which gave an error in the extent of reduction 0.3 pct. Including other errors such as in weighing and gas flow rate, the overall error of the final extent of reduction was estimated to be less than 1 pct.

III. RESULTS

A. Temperature-Programmed Reduction

Temperature-programmed reduction (TPR) experiments were carried out in a temperature range from 350 °C to 1600 °C, with heating rate of 3 °C/min.

Figure 1 compares the rates of reduction characterized by the rates of evolution of CO in reduction experiments in different gas atmospheres. When the reduction was in hydrogen, water was also evolved as presented in Figure 1. In the reduction experiments in argon or helium, the concentration of water vapor in the off-gas was negligible.

In general, the reduction curves in hydrogen consist of two water peaks in a low temperature range, followed by a main peak of CO formation. In comparison, the reduction curves in helium and argon consist of two overlapped CO peaks, which appear in a higher temperature range than that in hydrogen. To reveal the essence of reduction in different gas atmospheres, reduction experiments were stopped at different stages, and the samples were subjected to XRD analysis.
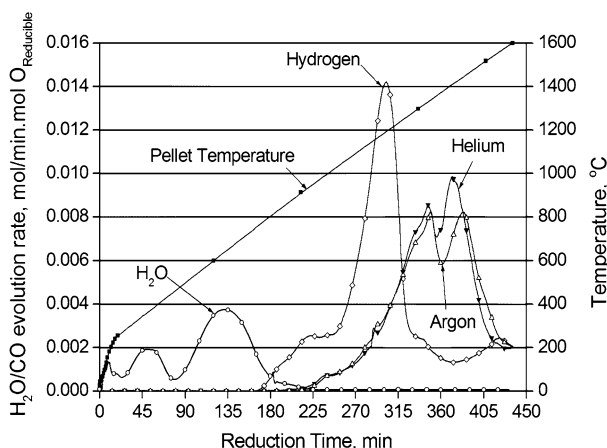

Fig. 1—Temperature programmed reduction of primary ilmenite in different gas atmospheres. The furnace temperature was ramped from 350 °C to 1600 °C at 3 °C /min.

Table I. Chemical Composition of Primary Ilmenite Concentrate

| Component	TiO_2	Total Fe	FeO	Fe_2O_3	MnO	SiO_2	ZrO_2	P_2O_5
Wt pct	53.9	30.5	18.0	23.6	1.63	0.27	0.09	0.01
Component	Al_2O_3	S	Nb_2O_5	Cr_2O_3	CaO	MgO	V_2O_5	Ti/Fe
Wt pct	0.40	0.004	0.10	0.047	<0.01	0.18	0.17	1.27:1

Figure 2 presents the XRD patterns of the samples in progress of reduction in hydrogen. The phases detected by XRD in the samples reduced in hydrogen and argon to different temperatures are summarized in Table II.

As shown in Figure 2, the primary ilmenite concentrate contained mainly ilmenite and pseudorutile phases. The phases in naturally occurred ilmenite did not crystallize well and exhibited relatively weak XRD peaks; other phases than ilmenite and pseudorutile may exist but were not detected. When reduction was carried out in hydrogen, the reaction started with reduction by hydrogen. The small water peak at the very beginning of reduction when temperature was below 200 °C probably was from the release of physically adsorbed moisture in samples and the reaction system. The following peak until 510 °C represents the first stage of hydrogen reduction, with a maximum value of 0.0019 mol H_2O/min·mol $O_{Reducible}$. The second stage of reduction by hydrogen produced an H_2O peak with reduction rate of 0.0037 mol/min·mol $O_{Reducible}$ at 630 °C. This stage lasted until 960 °C, which slightly overlapped with evolution of CO starting at 780 °C. In the sample reduced to 290 °C, peaks of titania appeared in addition to the original peaks of ilmenite and pseudorutile phases. At 510 °C, peaks for titania, and especially for ilmenite, obviously became stronger, and those for pseudorutile disappeared. The first stage of reduction by hydrogen with H_2O evolution corresponds to reduction of pseudorutile:

$$Fe_2Ti_3O_9 + H_2 \rightarrow 2FeTiO_3 + TiO_2 + H_2O \qquad [1]$$

At 510 °C, a weak peak for metallic iron also appeared at 2theta = 44.9 deg, indicating beginning of metallization. At 800 °C, the ilmenite peaks were undetectable, whereas the peaks for metallic iron and titania became stronger. This corresponds to the reduction of ilmenite by hydrogen:

$$FeTiO_3 + H_2 \rightarrow Fe + TiO_2 + H_2O \qquad [2]$$
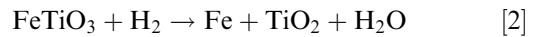
CO evolution in hydrogen started at about 780 °C, with an overlapped smaller peak preceding the main peak. Between 800 °C and 1025 °C, titania peaks in Figure 2 became weaker and then disappeared, which corresponds to the appearance of new phases of Ti_3O_5 and Ti_2O_3.

The reduction of titania to Ti_3O_5 and then to Ti_2O_3 can be by hydrogen or carbon. An experiment was carried out with a pellet of primary ilmenite without mixing of graphite. Figure 3 compares the curves of H_2O evolution in experiments with and without graphite. The two main peaks of H_2O evolution coincided.
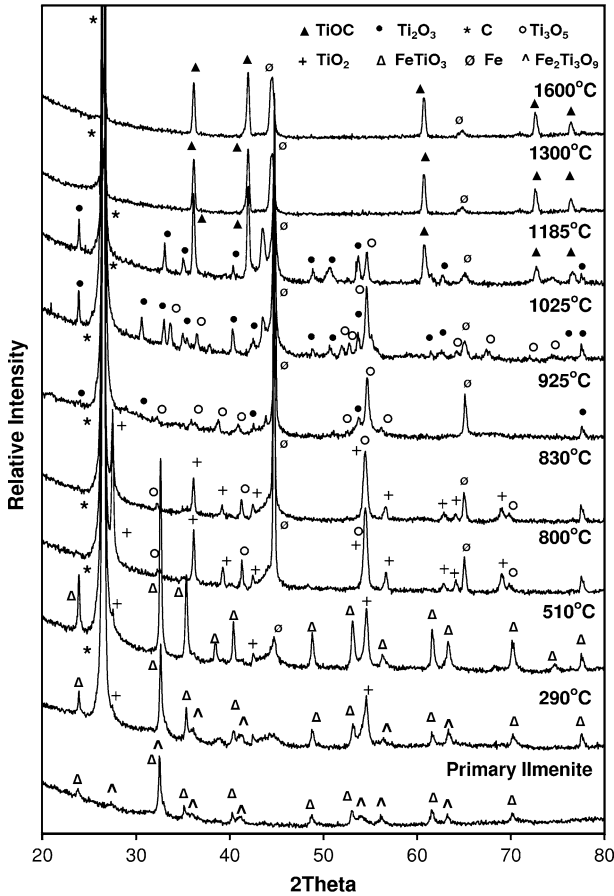

Fig. 2—XRD patterns of primary ilmenite in the progress of temperature programmed reduction in hydrogen. The furnace temperature was ramped at 3 °C /min.

Table II. Phase Composition of Primary Ilmenite Reduced in Hydrogen and Argon to Different Temperatures in Temperature Programmed Reduction Experiments

Temperature, °C	290	510	800	830	925	1025	1185	1600
H_2	C	C	C	C	C	C	C	TiO_xC_y
	$FeTiO_3$	$FeTiO_3$	Fe	Fe	Fe	Fe	Fe	Fe
	$Fe_2Ti_3O_9$	TiO_2	TiO_2	TiO_2	Ti_3O_5	Ti_2O_3	TiO_xC_y	C
	TiO_2	Fe	Ti_3O_5	Ti_3O_5	Ti_2O_3	Ti_3O_5	Ti_2O_3	

Temperature, °C	1000	1220	1320	1370	1420	1600
Ar	C	C	C	C	C	TiO_xC_y
	$FeTiO_3$	Fe	Fe	Fe	Fe	Fe
	TiO_2	Ti_3O_5	Ti_3O_5	Ti_2O_3	TiO_xC_y	C
		Ti_2O_3	Ti_2O_3	Ti_3O_5	Ti_2O_3	Ti_2O_3
		TiO_2		TiO_xC_y	Ti_3O_5	

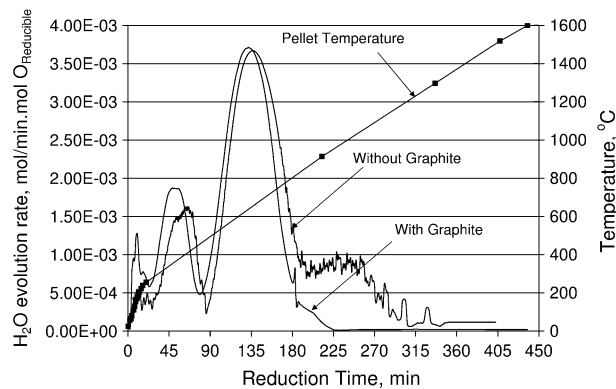Note: Phases are presented in the descending order in accordance with the relative intensity of XRD strongest peaks of individual phases.

Fig. 3—H₂O evolution rate during temperature programmed reduction of primary ilmenite in hydrogen. The furnace temperature was ramped from 350 °C to 1600 °C at 3 °C /min.

The H₂O evolution curve for the sample without graphite included an additional peak at elevated temperatures 900 °C to 1200 °C. This peak was not observed in experiments with a ilmenite-graphite mixture because of water reaction with graphite. The final product of ilmenite reduction by hydrogen without graphite contained metallic iron and Ti₂O₃.

The reduction reactions by hydrogen in the presence of graphite can be presented as follows:

$$3TiO_2 + H_2 = Ti_3O_5 + H_2O \qquad [3]$$

$$2Ti_3O_5 + H_2 = 3Ti_2O_3 + H_2O \qquad [4]$$

$$H_2O + C = H_2 + CO \qquad [5]$$
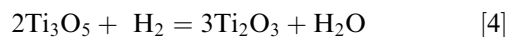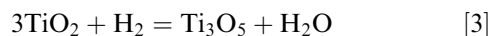
The subsequent reduction of Ti₂O₃ proceeded with carbon as a reductant with CO evolution. At 1185 °C, the maximum CO evolution rate of 0.0141 mol/min·mol O$_{Reducible}$ was achieved. A large amount of titanium oxycarbide phase was observed in the sample at this temperature, with unreduced titanium suboxides, Ti₃O₅, and Ti₂O₃. The rate of CO evolution sharply decreased after 1185 °C because of depletion of titanium suboxides, and the reduction was completed at about 1300 °C. Ti₂O₃ was reduced to TiO and TiC, which formed the solid solution TiO$_x$C$_y$. The reduction reactions can be presented as:

$$Ti_2O_3 + C = 2[TiO]_{ss} + CO \qquad [6]$$

$$Ti_2O_3 + 5C = 2[TiC]_{ss} + 3CO \qquad [7]$$
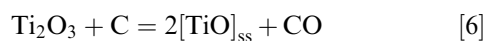
where subscript "ss" means a chemical in the solid solution. The subsequent extension of the slow evolution of CO may be attributed to the reduction of TiO from oxycarbide solid solution to form carbide:

$$[TiO]_{ss} + 2C = [TiC]_{ss} + CO \qquad [8]$$

The reduction curves obtained in argon and helium were very similar. Reduction started at about 880 °C. The first peak appeared at 1320 °C, with a CO evolution

rate of 0.0085 mol/min·mol O$_{Reducible}$ in helium and 0.0081 mol/min·mol O$_{Reducible}$ in argon. The second peak was at 1400 °C in helium and 1450 °C in argon. The maximum CO evolution rates corresponding to the second peak were 0.0097 mol/min·mol O$_{Reducible}$ in helium and 0.0081 mol/min·mol O$_{Reducible}$ in argon.

The XRD spectra of samples reduced in helium and in argon to the same stage were similar. The phases identified by the XRD analysis of samples in the progress of reduction in argon are also presented in Table II. When the temperature was ramped to 1000 °C, strong peaks of TiO₂ and ilmenite were observed, whereas the Fe₂Ti₃O₉ phase became undetectable. At 1220 °C, ilmenite was converted to metallic iron and titania was converted to Ti₂O₃ and Ti₃O₅. At 1320 °C, corresponding to the first peak of CO evolution, the reduced sample consisted of Fe, Ti₂O₃, Ti₃O₅, and carbon. At 1370 °C, TiO$_x$C$_y$ became detectable, and its amount increased with boosting the reduction temperature to 1420 °C and then to 1600 °C, at which the experiment was stopped. The final sample contained metallic iron, titanium oxycarbide, residual carbon, and Ti₂O₃. Therefore, the carburization of titanium was not completed until 1600 °C. Basically, the carbothermal reduction of ilmenite concentrate in argon and helium followed the same sequence of reduction as in hydrogen. However, the reduction temperature needed for each step to occur was significantly higher in argon and helium than in hydrogen.

B. *Isothermal Reduction*

The effect of temperature on the extent of reduction of primary ilmenite concentrate was investigated in isothermal experiments, under hydrogen, argon and helium gas atmospheres. The extent of reduction of the primary ilmenite in different gases in the temperature range of 1000 °C to 1500 °C is presented in Figure 4. The phase composition of samples reduced in hydrogen and argon at different temperatures for 300 minutes, identified by XRD, are summarized in Table III. The samples reduced in helium had the same phase composition as those reduced in argon.

The initial stage of the ilmenite reduction in hydrogen (Figure 4(a)) was fast because of iron oxide reduction. At 1000 °C, the extent of reduction achieved 37 pct within 30 minutes. However, the subsequent conversion of titanium oxide to oxycarbide was relatively slow. After 300 minutes of reduction at 1000 °C, primary ilmenite was reduced to Ti₂O₃, TiO$_x$C$_y$ and metallic iron, with a total extent of reduction of 68 pct. Increasing the reduction temperature to 1100 °C significantly enhanced the formation of titanium oxycarbide. The extent of reduction increased to 89 pct, and a very small amount of residual Ti₂O₃ was detected in the sample reduced at 1100 °C. Increasing the temperature even more to 1200 °C resulted in a significant increase of the rate and extent of reduction, in which the extent of reduction reached 95 pct after 300 minutes of reaction. TiO$_x$C$_y$ was identified as the only titanium compound. The reduction was enhanced by increasing the temperature to 1300 °C to 1500 °C. At 1300 °C, the formation
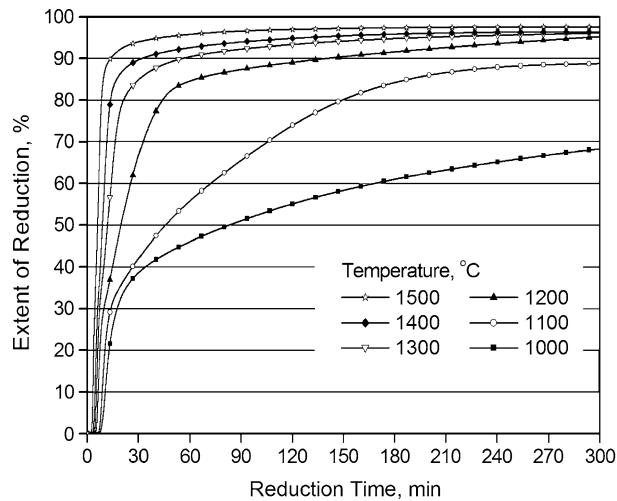
(a) Hydrogen
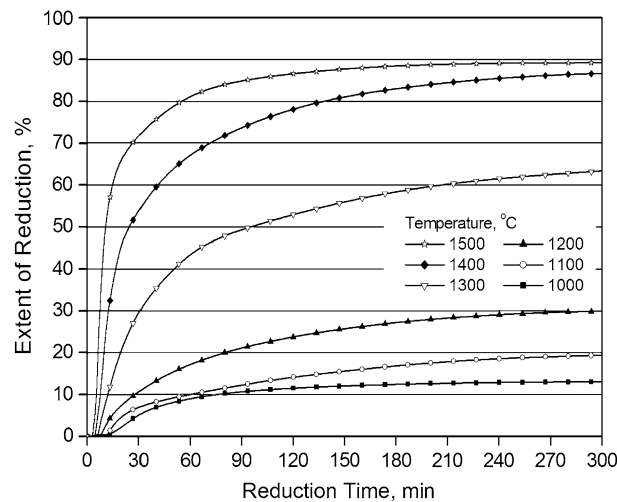
(b) Argon
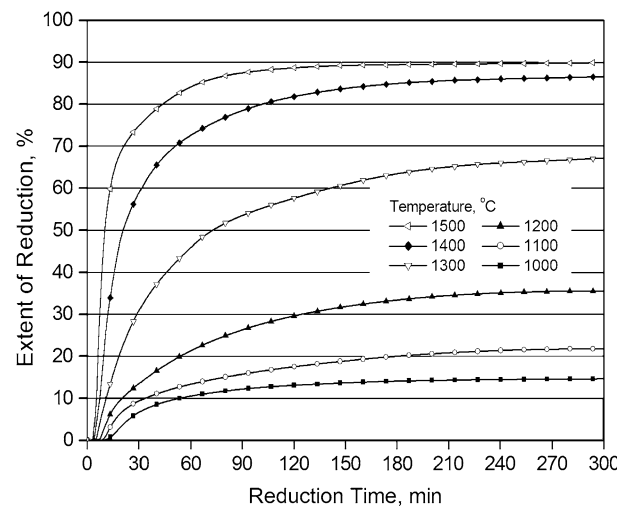
(c) Helium

Fig. 4—Effect of temperature on the extent of reduction of primary ilmenite in different gas atmospheres.

Table III. Phase Composition of Primary Ilmenite Reduced in Hydrogen or Argon at Different Temperatures for 300 Min

Temperature (°C)	1000	1100	1200	1300	1400	1500
H_2	C	C	C	Fe	TiO_xC_y	TiO_xC_y
	Fe	Fe	Fe	TiO_xC_y	Fe	Fe
	Ti_2O_3	TiO_xC_y	TiO_xC_y	C	C	C
	TiO_xC_y	Ti_2O_3				
Ar	C	C	C	C	Fe	TiO_xC_y
	$FeTiO_3$	Fe	Fe	Fe	TiO_xC_y	Fe
	Fe	Ti_3O_5	Ti_2O_3	TiO_xC_y	C	C
	TiO_2	TiO_2	Ti_3O_5	Ti_2O_3	Ti_2O_3	Ti_2O_3
		$FeTiO_3$	TiO_xC_y	Ti_3O_5	Ti_3O_5	

Note: The phases are presented in descending order in accordance with the relative intensity of XRD strongest peaks of individual phases.

of titanium oxycarbide completed in about 120 minutes, with an extent of reduction of 93.2 pct. The reduction period was shortened to 30 minutes at 1400 °C and the reduction extent reached 91 pct. At 1500 °C, titania was converted to titanium oxycarbide in less than 30 minutes, which corresponds to the extent of reduction of 92 pct. However, the final extent of reduction after 300 minutes of reduction did not change significantly in the temperature range 1200 °C to 1500 °C. This is consistent with the results of the reduction of rutile,[19] as the removal of oxygen from the titanium oxycarbide phase by reaction [8] is slow.

When the carbothermal reduction was carried out in argon (Figure 4(b)), the reduction rate was significantly slower than in hydrogen. The carbothermal reduction of primary ilmenite was slow at 1000 °C to 1200 °C. After 300 minutes reduction at 1000 °C, an extent of reduction calculated from CO evolution was only 13 pct. XRD analysis detected TiO_2, metallic iron and unconverted $FeTiO_3$ (Table III). Titania was partially reduced to Ti_3O_5 at 1100 °C with an extent of reduction 19 pct. Conversion of ilmenite to metallic iron and titania was still incomplete. The titanium oxycarbide phase was first detected at 1200 °C after 300 minutes reduction, with Ti_2O_3 and Ti_3O_5 being the main titanium containing phases. Ilmenite was undetected by XRD, although the calculated extent of reduction, 30 pct, was lower than the level that corresponds to the complete reduction of iron oxides. A subsequent increase of reduction temperature to 1300 °C increased the extent of reduction to 63 pct; the reduction product contained TiO_xC_y, Ti_2O_3, Ti_3O_5, metallic iron, and residual graphite. The reduction was strongly enhanced by increasing the temperature to 1400 °C to 1500 °C. At 1400 °C, the extent of reduction continued to rise with increasing reduction time, reaching 87 pct in 300 minutes. The extent of reduction at 1500 °C achieved 87 pct in about 120 minutes, and it increased only slightly with the extension of reduction time. The Ti_2O_3 phase was still detectable in the samples reduced at 1400 °C and 1500 °C for 300 minutes.

Figure [4](c) and (b) show that the reduction progressed slightly faster in helium than in argon. The extent of reduction achieved 87 pct after 300 minutes at 1400 °C and 90 pct at 1500 °C.
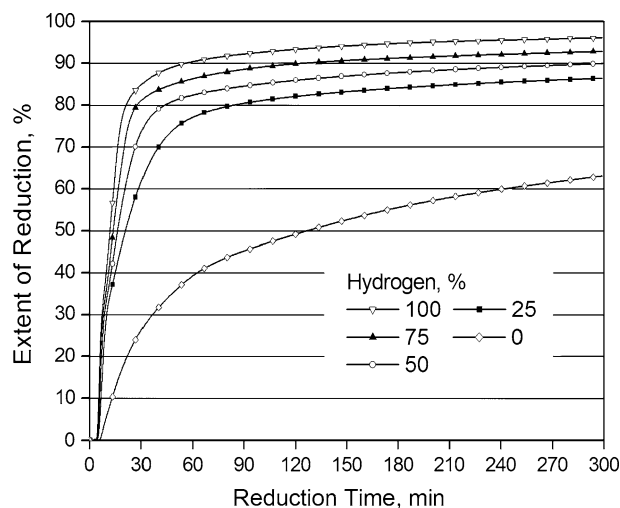
(a) Hydrogen-Argon mixtures
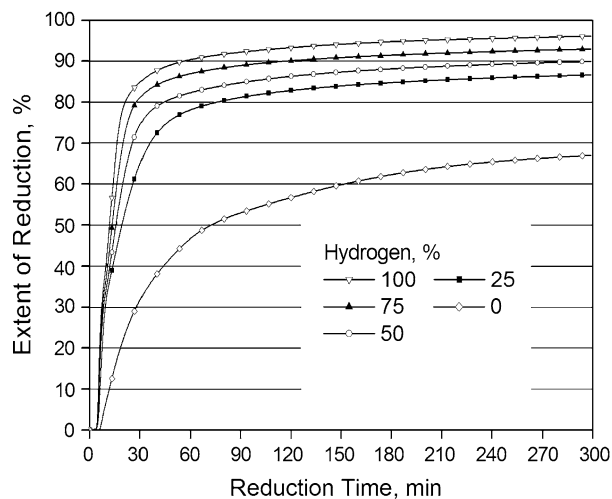
(b) Hydrogen-Helium mixtures

Fig. 5—Effect of hydrogen content in the H_2-Ar and H_2-He gas mixtures on reduction of primary ilmenite at 1300 °C.

The effect of hydrogen content in H_2-Ar and H_2-He gas mixtures on the carbothermal reduction of primary ilmenite was examined at 1300 °C. Reduction curves with different hydrogen content are presented in Figure [5]. The extent of reduction in pure argon after 300 minutes of reaction was 63 pct (Figure [5](a)). The addition of 25 vol pct hydrogen significantly increased the rate and extent of reduction. The final extent of reduction increased to 87 pct. The subsequent increase in hydrogen content to 50 to 100 vol pct consistently accelerated the reduction process.

A similar effect of hydrogen was observed in the carbothermal reduction of primary ilmenite in the hydrogen-helium mixtures (Figure [5](b)). Generally, the extent of reduction curves obtained in experiments in H_2-Ar and H_2-He gas mixtures with the same hydrogen content were close.

C. Phase Development in the Progress of Reduction

In the reduction experiments at 1100 °C in hydrogen and at 1300 °C in argon and helium, the samples reduced for different time were analyzed by XRD. The phase composition of samples reduced in hydrogen and argon are presented in Table [IV]. The XRD spectra of samples reduced in helium were similar to those obtained in argon.

After 5 minutes of reduction in hydrogen, the reduced sample contained TiO_2, $FeTiO_3$, and some amount of metallic iron. After 15 minutes, both TiO_2 and $FeTiO_3$ phases disappeared, and correspondingly, a significant amount of Ti_3O_5, Ti_2O_3 and metallic iron was detected. It should be noted that it took about 15 to 20 minutes for the sample temperature to reach the experimental value, so the reaction within the first 15 to 20 minutes occurred at temperatures below 1100 °C. TiO_xC_y phase was observed at 30 minutes, when Ti_3O_5 was further converting to Ti_2O_3. After 240 minutes of reaction, when Ti_3O_5 was totally reduced, titanium oxycarbide became the major phase containing titanium coexisting with small amount of Ti_2O_3. After 300 minutes of reduction, the sample consisted of metallic Fe, TiO_xC_y, Ti_2O_3, and residual carbon.

The carbothermal reduction of primary ilmenite concentrate in argon and helium followed the same sequence but progressed slower than in hydrogen,

Table IV. Phase Composition of Primary Ilmenite in Progress of Reduction in Hydrogen at 1100 °C and Argon at 1300 °C

Time, min	5	15	30	60	120	180	240	300
H_2	C	C	C	C	C	C	Fe	Fe
	Fe	Fe	Fe	Fe	Fe	Fe	TiO_xC_y	TiO_xC_y
	$FeTiO_3$	Ti_3O_5	Ti_2O_3	Ti_2O_3	TiO_xC_y	TiO_xC_y	C	C
	TiO_2	Ti_2O_3	TiO_xC_y	TiO_xC_y	Ti_2O_3	Ti_2O_3	Ti_2O_3	Ti_2O_3
			Ti_3O_5					
Ar	C	C	C	C	C	C	C	C
	$FeTiO_3$	Fe	Fe	Fe	Fe	Fe	Fe	Fe
	TiO_2	Ti_3O_5	Ti_3O_5	Ti_3O_5	Ti_2O_3	Ti_2O_3	Ti_2O_3	TiO_xC_y
		$FeTiO_3$	Ti_2O_3	Ti_2O_3	TiO_xC_y	TiO_xC_y	TiO_xC_y	Ti_2O_3
					Ti_3O_5	Ti_3O_5	Ti_3O_5	Ti_3O_5

Note: The phases are presented in descending order in accordance with the relative intensity of XRD strongest peaks of individual phases.

although the temperature was raised to 1300 °C. As shown in Table IV, after 5 minutes of reduction in argon at 1300 °C, the main phases were ilmenite and TiO_2. No peaks for $Fe_2Ti_3O_9$ were identified, and no metallic iron was observed. Ti_3O_5 and metallic Fe were formed after 15 minutes, whereas the ilmenite phase was not completely depleted. Extending reduction to 30 minutes completed the reduction of ilmenite. The conversion of Ti_3O_5 to Ti_2O_3 started from 30 minutes and lasted the whole following period of reduction without completion at 300 minutes. TiO_xC_y was first observed at 120 minutes with increasing amount along with progress of reduction. After 300 minutes of reduction, the reduced sample contained metallic iron, TiO_xC_y, residual Ti_3O_5, Ti_2O_3, and graphite.

Table V presents the extent of reduction and composition of samples reduced at different temperatures for various time in hydrogen. The titanium oxycarbide composition was calculated only for samples when no titanium suboxides were detected by XRD. The titanium oxycarbide produced by reduction at 1200 °C for 300 minutes contained 15.8 mol pct TiO. When the reduction temperature increased to 1300 °C, the TiO content in the titanium oxycarbide was 31.6 mol pct after 30 minutes. The TiO content decreased to 26.4 and 21.9 mol pct with increasing reduction time to 60 and 120 minutes, respectively. Finally, the TiO content decreased to 10.1 mol pct with increasing reduction time to 300 minutes. At 1400 °C, the titanium oxycarbide contained up to 27.4 mol pct TiO after 30 minutes of reduction and 10 mol pct after 300 minutes. At 1500 °C, titanium oxycarbide with 24.1 mol pct TiO was obtained after 30 minutes reduction. The TiO content was reduced to 14.7 mol pct after 60 minutes and 8.6 mol pct after 300 minutes. The oxygen content in the titanium oxycarbide decreased by either extending the reduction time or increasing the reduction temperature. Increasing the reduction temperature was more effective than extending reduction time.

IV. DISCUSSION

The ilmenite concentrate consisted of mainly ilmenite and pseudorutile phases. An analysis of phases in progress of carbothermal reduction showed that the reaction started with reduction of pseudorutile to ilmenite and titania, followed by the subsequent reduction of ilmenite to metallic iron and titania. Titania was reduced to Ti_3O_5 and then to Ti_2O_3, which was converted to titanium oxycarbide. The above sequence of reduction was followed both in hydrogen and in inert gases, argon, and helium.

Gas atmosphere and temperature had pronounced effects on the rate and extent of the carbothermal reduction of the primary ilmenite concentrate. The extent of reduction of ilmenite in different gases at various temperatures for 300 minutes is presented in Figure 6. In hydrogen, increasing temperature from 1000 °C to 1200 °C increased the extent of reduction from 68 pct to 95 pct. Further increase in temperature to 1500 °C had a marginal effect on the extent of reduction. In argon and helium, the extent of reduction was below 40 pct at 1000 °C to 1200 °C. The complete conversion of titanium oxides to oxycarbide needed 1400 °C to 1500 °C.

Pseudorutile in ilmenite ore contains hydrated water; however, a negligible amount of water was released in the course of reduction of primary ilmenite concentrate in argon or helium. This means that water was removed when the ore was processed to the dry concentrate. Therefore, in reduction experiments in hydrogen, water was formed as a result of reduction reactions. This was also confirmed by XRD analysis of ilmenite concentrate in the progress of reduction.

Hydrogen played a major role in the reduction of pseudorutile and ilmenite to metallic iron and titania, as well as the subsequent reduction of titania to Ti_2O_3 (Figures 1 and 3). The maximum rate of reduction of iron oxides corresponded to a temperature of 630 °C (Figure 1).

Table V. Extent of Reduction and Titanium Oxycarbide Composition of Primary Ilmenite Reduced in Hydrogen

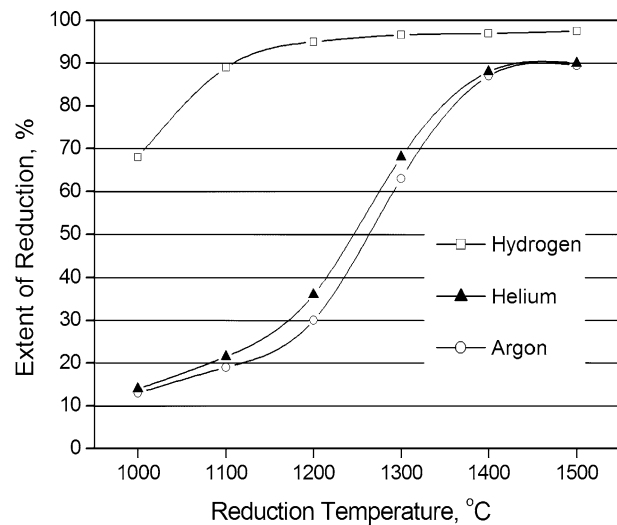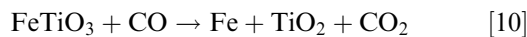| Reduction temperature, °C	Reduction time, min	Extent of reduction, pct	Composition
1200	300	95.0	$TiO_{0.158}C_{0.842}$
1300	30	89.6	$TiO_{0.316}C_{0.684}$
1300	60	91.3	$TiO_{0.264}C_{0.736}$
1300	120	93.2	$TiO_{0.219}C_{0.781}$
1300	180	94.6	$TiO_{0.197}C_{0.803}$
1300	240	95.0	$TiO_{0.151}C_{0.849}$
1300	300	96.6	$TiO_{0.101}C_{0.899}$
1400	30	91.0	$TiO_{0.274}C_{0.726}$
1400	60	93.8	$TiO_{0.189}C_{0.811}$
1400	300	97.0	$TiO_{0.100}C_{0.900}$
1500	30	94.0	$TiO_{0.192}C_{0.808}$
1500	60	95.2	$TiO_{0.147}C_{0.853}$
1500	300	97.5	$TiO_{0.086}C_{0.914}$

Fig. 6—Comparison of the extent of reduction of primary ilmenite in different gas atmospheres at various temperatures. Reduction period was 300 min.

A thermodynamic analysis of reduction of iron oxides by carbon shows that the reduction is feasible at similar low temperatures. The equilibrium temperature for reaction [5] under standard conditions calculated using data[23] is 667 °C. This means that at temperatures above 667 °C reduction of iron oxides to metallic iron by carbon is thermodynamically preferable in comparison with reduction by hydrogen. However, the reduction of pseudorutile was not observed in reduction experiments in argon and helium until 880 °C (Figure 1), and peaks for metallic iron were undetectable even at 1000 °C (Table II). The direct reduction by carbon is initiated at the contact points between metal oxides and carbon particles. The subsequent reaction between the solid phases proceeds through the gas phase:

$$Fe_2Ti_3O_9 + CO \rightarrow 2FeTiO_3 + TiO_2 + CO_2 \quad [9]$$

$$FeTiO_3 + CO \rightarrow Fe + TiO_2 + CO_2 \quad [10]$$

$$CO_2 + C = 2CO \quad [11]$$

As shown by reactions [9] through [11], the oxides are reduced by CO, which is regenerated by a reaction with carbon. However, reaction [11] needs elevated temperatures to proceed, which explains why the reduction of pseudorutile and ilmenite was not observed in the sample reduced in inert atmosphere at temperature below 880 °C.

The subsequent reduction of TiO_2 to Ti_3O_5 and Ti_2O_3 and the conversion of Ti_2O_3 to titanium oxycarbide in argon and helium also proceed through the gas phase. Ti_2O_3 is reduced to TiO and TiC, which form a solid solution by reactions [12] and [13].

$$Ti_2O_3 + CO = 2[TiO]_{ss} + CO_2 \quad [12]$$

$$Ti_2O_3 + 7CO = 2[TiC]_{ss} + 5CO_2 \quad [13]$$
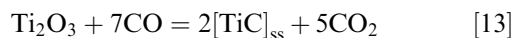
When the reduction is carried out in hydrogen or hydrogen containing gas, hydrogen is involved in reduction reactions [1] through [5]. It also reacts with graphite to form methane:

$$C + 2H_2 = CH_4 \quad [14]$$

The methane can reduce titanium oxide to oxycarbide:

$$Ti_2O_3 + CH_4 = 2[TiO]_{ss} + CO + 2H_2 \quad [15]$$

$$Ti_2O_3 + 5CH_4 = 2[TiC]_{ss} + 3CO + 10H_2 \quad [16]$$

The formation of reaction intermediates CH_4 or CO_2 in the carbothermal reduction does not change the thermodynamics of related reduction reactions, but it affects the reaction kinetics. The thermodynamic analysis of reduction reactions presented in Reference 19 showed that the concentration of CH_4 is by 4 to 5 orders higher than that of CO_2. This explains why the carbothermal reduction was much faster in hydrogen than in argon and helium.
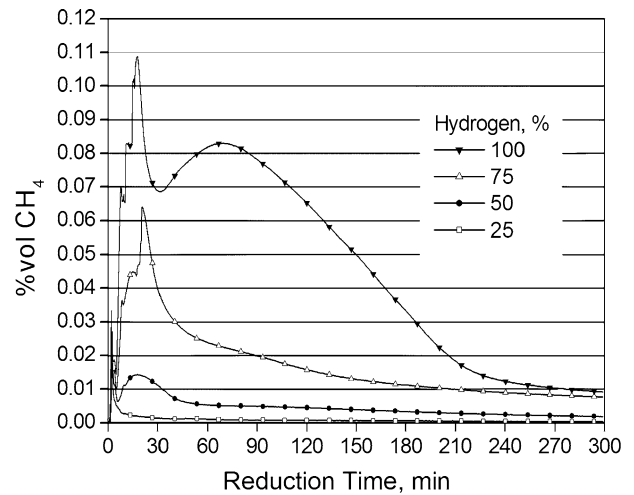

Fig. 7—Concentration of CH_4 in the off-gas in the process of carbothermal reduction of primary ilmenite in hydrogen-argon gas mixtures at 1300 °C.
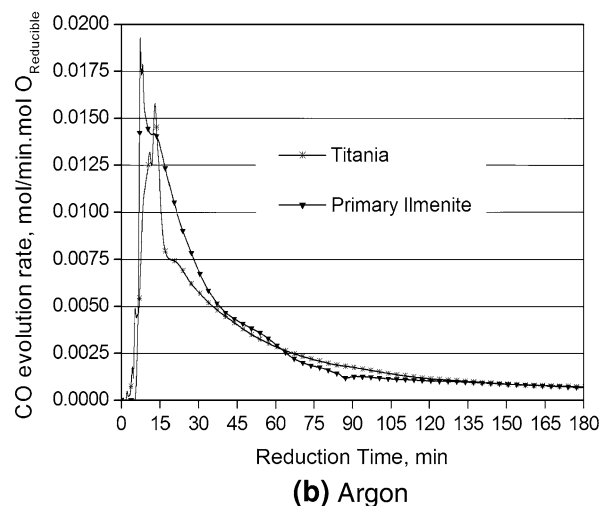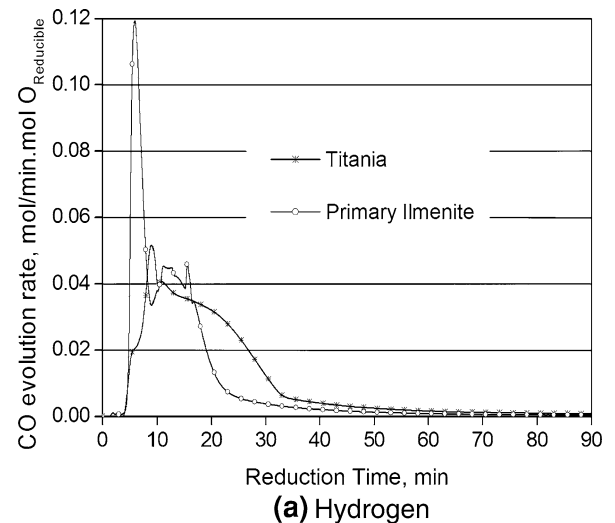

(a) Hydrogen

(b) Argon

Fig. 8—CO evolution rate during reduction of titania and primary ilmenite at 1300 °C in different gas atmospheres.

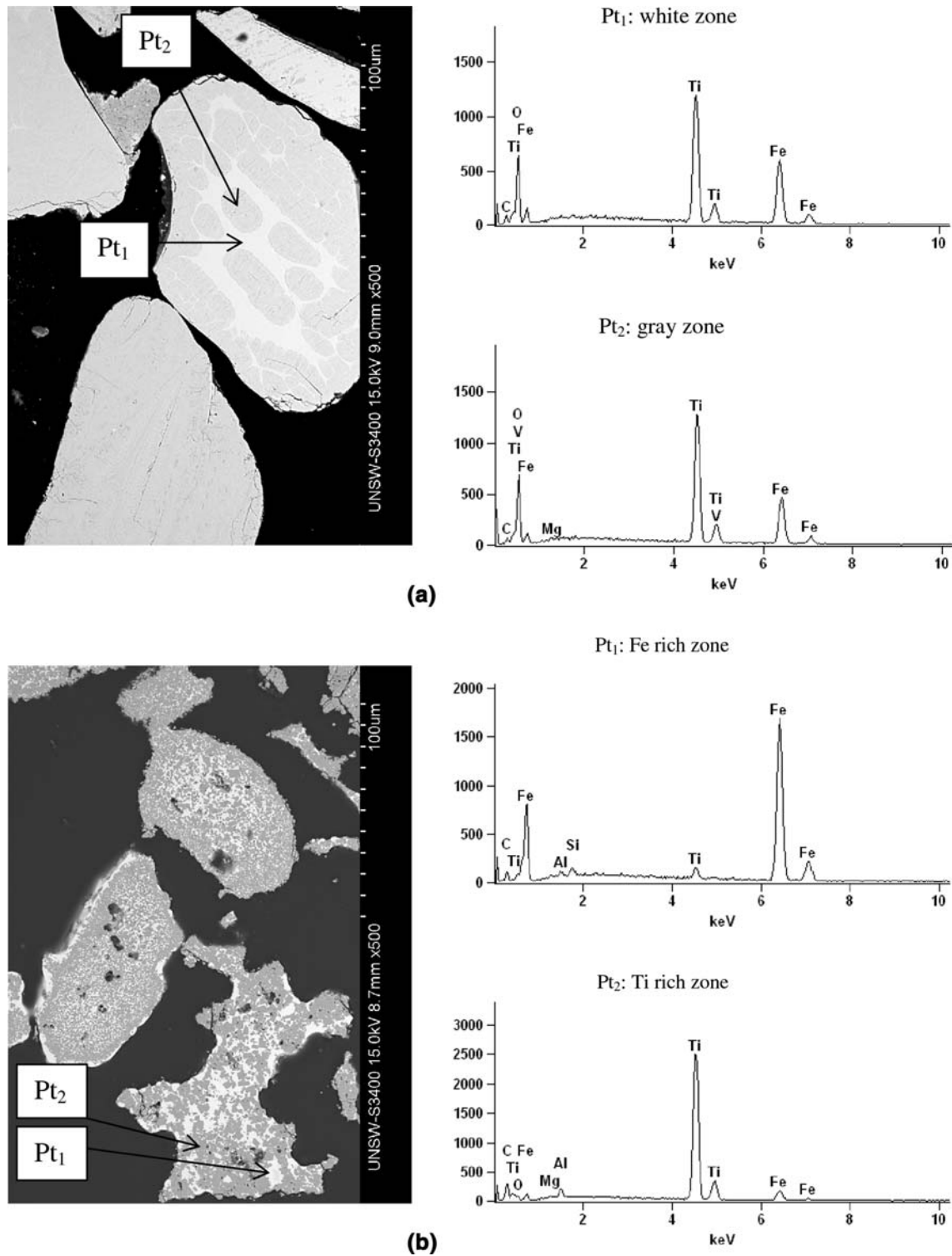Fig. 9—BSE images and EDS analysis of unreduced and reduced primary ilmenite. Samples were reduced at 1300 °C for 300 min in different gases. (*a*) Unreduced ilmenite; (*b*) reduced in hydrogen; (*c*) reduced in argon; and (*d*) reduced in helium.

The formation of methane in the reduction experiments in hydrogen was confirmed experimentally by analyzing the off-gas composition. At 1300 °C, the methane content was measured to be more than 1000 ppm. The observed change of methane content during reduction with hydrogen content in hydrogen-argon mixtures is presented in Figure 7. Increasing partial pressure of hydrogen increases equilibrium
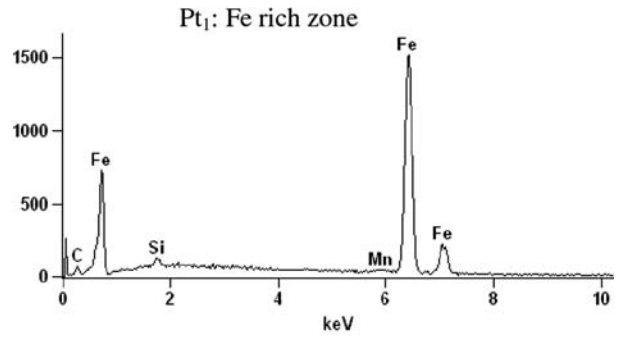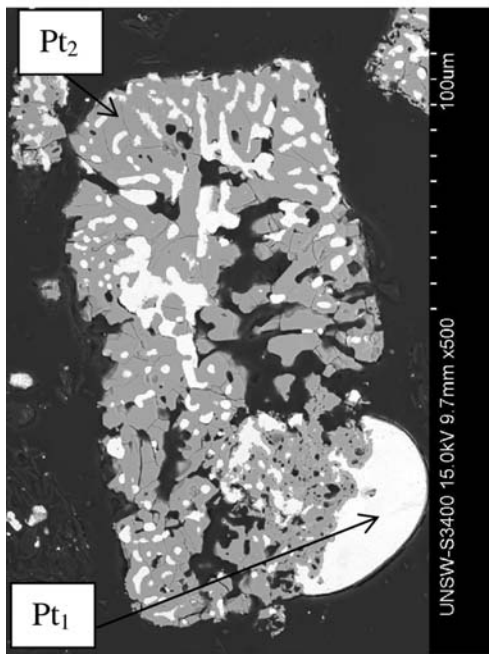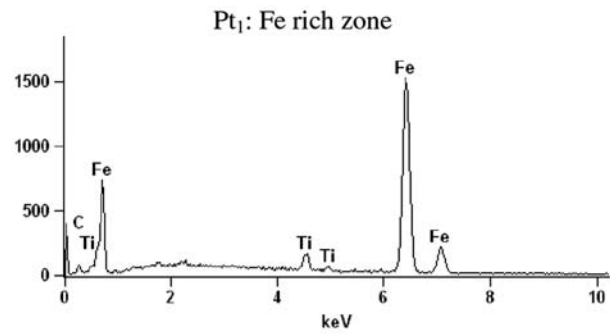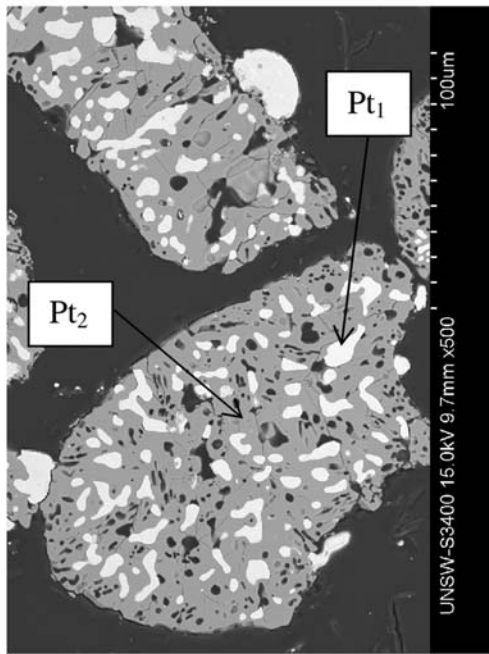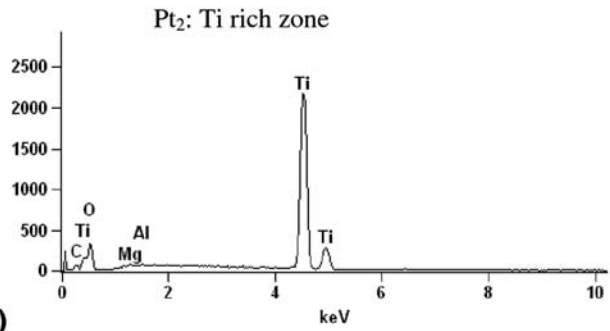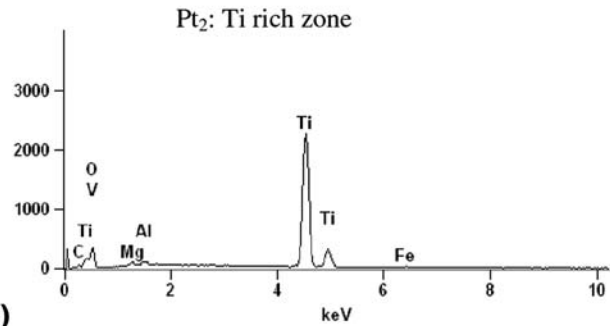
Fig. 9—Continued.

partial pressure of methane, and it enhances the formation of titanium oxycarbide in the course of carbothermal reduction of ilmenite concentrate.

Figure 8 compares the CO evolution rates during reduction of the primary ilmenite concentrate and titania at 1300 °C in hydrogen and argon. The rate of reduction in hydrogen can still be represented by the CO evolution rate because, at a high temperature, the water content in the off-gas was low. In Figure 8(a), the reduction curve for ilmenite concentrate shows two stages, with the first stage being the fast reduction of iron oxides to metallic iron. The formation of titanium oxycarbide at the second stage was also faster in the case of ilmenite concentrate: It was completed in about

25 minutes for ilmenite concentrate and 35 minutes for pure titania. When the reduction was in an inert gas (Figure 8(b)), the difference in reduction rates for ilmenite concentrate and pure titania was much smaller. Especially at the later stage of the reduction process when titanium oxides were converted to titanium oxycarbide, the CO evolution rates for titania and ilmenite were close.

Figure 9 presents the back-scattered electron (BSE) images of the primary ilmenite concentrate before reduction and reduced in different atmospheres. Although the BSE images show two zones of distinct contrast in the ilmenite concentrate prior to reduction, their EDS spectra were very similar, showing no significant difference in titanium and iron contents between the zones (Figure 9(a)). After reduction in hydrogen, fine grains of metallic iron were uniformly distributed within the matrix of titanium rich phase (Figure 9(b)). When the reduction was in argon and helium (Figures 9(c) and 9(d)), iron phase was coarse and formed globules. This can be explained by slow rate of metallization of iron in the inert gas atmosphere, resulted in fewer nuclei and their growth.

V. CONCLUSIONS

The results of a study of carbothermal reduction of a primary ilmenite concentrate by temperature programmed reduction and isothermal reduction experiments at 1000 °C to 1500 °C in different gas atmospheres can be summarized as follows.

1. The main phases in the primary ilmenite were pseudorutile and ilmenite.
2. Pseudorutile was first reduced to ilmenite and titania, followed by the reduction of ilmenite to metallic iron and titania. Titania was reduced to Ti_3O_5 and then Ti_2O_3, which was converted to titanium oxycarbide.
3. The carbothermal reduction of primary ilmenite concentrate was faster in hydrogen and occurred at a lower temperature than in argon and helium. The reduction in argon and helium had about the same rate and extent.
4. Titanium oxycarbide started to form at 1000 °C in hydrogen. The conversion of primary ilmenite concentrate to metallic iron and titanium oxycarbide at 1200 °C was complete in 300 minutes. This period was reduced to 90 minutes at 1300 °C, 60 minutes at 1400 °C, and 30 minutes at 1500 °C.
5. In a carbothermal reduction in argon and helium, titanium oxycarbide started to form at 1200 °C. The conversion of titania to titanium oxycarbide was incomplete after 300 minutes reduction at 1300 °C.
6. The faster reduction in hydrogen containing gas was attributed to the involvement of hydrogen in the reduction reactions. Iron oxides were directly reduced by hydrogen; hydrogen also reduced titania to Ti_2O_3. Methane formed by reacting hydrogen with carbon accelerated reduction of Ti_2O_3 to titanium oxycarbide.
7. In the reduction of primary ilmenite in hydrogen, metallic iron was in the form of fine grains which were distributed uniformly in the titanium oxycarbide matrix, while coarse globules were formed in the reduction of the ilmenite concentrate in argon and helium.

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