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Effect of Gas Atmosphere on Carbothermal Reduction and Nitridation of Titanium Dioxide

SHEIKH A. REZAN, GUANGQING ZHANG, and OLEG OSTROVSKI

This article examined the reduction/nitridation of rutile in the He-N_2, Ar-N_2, and He (Ar)-H_2-N_2 gas mixtures, as well as pure nitrogen, in the temperature-programmed and isothermal experiments in a fixed-bed reactor. The extents of reduction and nitridation were determined from the off gas composition and LECO analysis. The off-gas composition was monitored using the infrared sensor (CO, CO_2, and CH_4) and dew point analyzer (H_2O). The phase composition of the reduced samples was analyzed using X-ray diffraction (XRD). The temperature and gas composition had a strong effect on the rutile reduction. The reduction was the fastest in the H_2-N_2 gas mixture, followed by a reduction in nitrogen; the rate of reduction/nitridation in the He-N_2 gas mixture was marginally higher than in the Ar-N_2 gas. The rate of titania reduction/nitridation in the He (Ar)-H_2-N_2 gas increased with the replacement of He (Ar) with hydrogen. The article also discusses the mechanisms of reduction/nitridation in different gas atmospheres.

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I. INTRODUCTION

TITANIUM minerals in the form of natural rutile or ilmenite are processed into titania white pigment and metallic titanium. Ilmenite ore is a major source of titanium; it contains titanium and iron oxides in different proportion (chemical compound ilmenite is $FeTiO_3$) and other impurities. Commercial processing of ilmenite ore includes upgrading of the ore to synthetic rutile or titania-rich slag followed by chlorination and reoxidation of titanium tetrachloride to titania in the pigment production or reduction of $TiCl_4$ to titanium metal using magnesium (Kroll process) or sodium (Hunter process). The technologies for titanium metal production under development also use titanium tetrachloride either directly or for the production of titania, which is processed to titanium metal.

The chlorination of TiO_2 is implemented in the presence of coke at the temperature of 1073 K to 1373 K (800 °C to 1100 °C) in a fluidized bed. At this temperatures, impurities are also chlorinated what dictates requirements to the raw materials.

Titanium oxycarbide Ti(O,C) or oxycarbonitride Ti(O,C,N) can be chlorinated at 473 K to 673 K (200 °C to 400 °C)[1,2]; chlorination at these temperatures has lower requirements for raw materials quality and lower maintenance cost in comparison with the commercial high-temperature processes.

The effect of Ti(O,C) or Ti(O,C,N) composition on chlorination is marginal[1,2]; however, the chlorination rate of titanium suboxides is significantly slower compared with Ti(O,C) or Ti(O,C,N). A study of the synthesis of titanium oxycarbide in References 3 through 5 and oxycarbonitride in this article targeted the subsequent understanding of the effects of operation parameters and mechanisms in the conversion of titania to Ti(O,C) or Ti(O,C,N).

Zhang and Ostrovski investigated systematically the synthesis of titanium oxycarbide with a reduction of rutile[6,7] and ilmenite concentrates[8–10] by methane-containing gas. The optimum conditions for titanium carbide formation included temperature in the range of 1523 K to 1723 K (1250 °C to 1450 °C), methane content of 8 vol pct, and hydrogen content above 35 vol pct. However, reduced iron from ilmenite catalyzes methane decomposition with a deposition of solid carbon, which has a negative effect on the synthesis of titanium carbide.

Dewan *et al.*[3–5] investigated the synthesis of titanium oxycarbide by carbothermal reduction of titania and ilmenite concentrates in different gas atmospheres. The conversion of titania to titanium carbide was the fastest in hydrogen and can be implemented at lower temperatures compared with a reduction in inert gas.

Compared with titanium oxycarbide, the synthesis of titanium oxycarbonitride is more favorable both thermodynamically and kinetically. The carbothermal synthesis of titanium oxycarbonitride $TiO_xC_yN_z$ in the H_2-N_2 gas atmosphere was discussed previously.[11] It was demonstrated that the conversion of titania to $TiO_xC_yN_z$ at 1423 K (1150 °C) in the H_2-N_2 atmosphere followed the sequence: $TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiO_xC_yN_z$. The conversion of titania into titanium

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oxycarbonitride at 1423 K (1150 °C) was completed in 180 minutes; the conversion time decreased to 30 minutes at 1573 K (1300 °C). Increasing the temperature resulted in the formation of titanium oxycarbonitride with a higher TiC content. Porosity had a minor effect on the reduction/nitridation of titania with the tendency to increase the reduction rate with increasing porosity.

The carbothermal reduction of metal oxides occurs through the gas phase and is affected strongly by the gas atmosphere. This finding was demonstrated by Kononov *et al.*[12] in the reduction of manganese oxides and ores, and by Dewan *et al.*[3] in the carbothermal synthesis of titanium carbide and oxycarbide.

Jha and Yoon[13] examined carbothermal reduction/nitridation of titania in the N_2-CO-H_2 and Ar-NH_3-H_2 gas mixtures of different compositions. However, their data on the effect of gas atmosphere on synthesis of titanium carbonitride are inconclusive. The product of reduction/nitridation reaction in Reference 13 included Ti_3O_5 and TiCN phases. The TiCN phase was not observed in Reference 11; titania in the H_2-N_2 gas atmosphere was reduced to titanium oxycarbonitride.

The aim of this article is to study the effect of gas atmosphere on the carbothermal reduction/nitridation of titania. Reduction/nitridation experiments were conducted in the He-N_2, Ar-N_2, He-H_2-N_2, and Ar-H_2-N_2 gas mixtures and pure nitrogen. The difference between the carbothermal reduction of titania in the He-N_2 and Ar-N_2 gas atmospheres is in the mass transfer in the gas phase; diffusion coefficients of gas species in He are significantly higher than in Ar. For example, the diffusion coefficient of CO in He is approximately four times of that in Ar. Diffusion coefficients of gaseous species in He and H_2 gases are approximately the same. However, hydrogen is a reactive gas. A comparison of the reduction behavior in the He-N_2 and H_2-N_2 gas atmospheres will shed a light on the role of hydrogen in carbothermal synthesis of titanium oxycarbonitride.

II. EXPERIMENTAL

A titanium dioxide–graphite mixture was prepared by wet mixing with the addition of 0.3 wt pct carboxymethylcellulose. The carbon-to-titanium molar ratio was 4.5, with 50 pct excess carbon relative to the amount needed for the reduction of titania to titanium carbide. The powder mixture was pressed at 20 kN for 2 minutes into pellets with a diameter of 8 mm and a thickness of ~11 mm. The mass of a pellet was ~1.0 g. The sample porosity was 34.8 pct. The experimental setup and procedure were presented in the previous papers.[3,11]

The carbothermal reduction/nitridation was carried out in the mixtures of nitrogen with argon, helium, or hydrogen, or in pure nitrogen. A gas mixture was formed by mixing the individual gases. The flow rate of gases was controlled by Brooks mass flow controllers (model 5850E; Brooks Instruments, Hatfield, PA). An infrared CO/CO_2/CH_4 sensor (Advanced Optima Uras 14; ABB, Ladenburgh, Germany) was used to monitor concentrations of CO, CO_2, and CH_4 in the effluent gas. A dew point monitor to measure water vapor content in the off-gas was installed in the gas outlet line between the reaction vessel and the CO/CH_4/CO_2 analyzer.

In the temperature-programmed reduction experiments, the furnace temperature was ramped from 623 K to 1873 K (350 °C to 1600 °C) at a heating rate of 2 K min^{-1}. The gas composition was monitored continuously in the course of the sample heating/reduction. The sample temperature in isothermal experiments reached the assigned value in 13 to 15 minutes.

The phase composition of samples taken in the progress of reduction was analyzed by powder X-ray diffraction (Siemens D5000; Siemens Aktiengesellschaft, Germany, and Philips X'pert Multipurpose X-Ray Diffraction System; PANalytical B.V., Almelo, the Netherlands). The oxygen, nitrogen, and carbon contents of the reduced samples were measured using LECO analyzers. For carbon, the LECO CS-224 Carbon/Sulfur analyzer (LECO Corporation, St Joseph, MI) was used. In this analysis, carbon in a sample was oxidized in oxygen at 1473 K (1200 °C) to CO_2, which was measured by an infrared detector. A 0.1- to 0.2-g sample was placed in an alumina crucible with a catalyst to accelerate the reaction. The oxygen and nitrogen contents were determined by the LECO TC-436DR Oxygen/Nitrogen analyzer. A sample inside a tin capsule was placed into a nickel basket, which was loaded into a graphite crucible. By heating the sample to a high temperature, all oxygen present in a sample reacted with the carbon of graphite crucible forming CO and CO_2, whereas nitrogen was converted to N_2 gas. The CO and CO_2 produced were detected by infrared sensors. The N_2 content was measured by thermal conductivity sensors after the removal of CO and CO_2.

The extent of reduction was calculated from the off-gas composition and the composition of reduced samples by LECO analysis. When titanium suboxides were undetectable by X-ray diffraction (XRD) in the reduced samples, the composition of titanium oxycarbonitride was calculated using oxygen, nitrogen, and carbon concentrations from the LECO analysis.

The extent of reduction (X) of rutile was defined as the fraction of oxygen removed in the process of reduction of titania into Ti(O,C,N). The extent of nitridation X_N was defined as the fraction of titanium that was present as nitride (TiN) in the reduced sample (X_N = 100 pct when TiN is the only phase in the reduced sample). Similarly, the extent of carburization X_C was defined as the fraction of titanium that was present as carbide (TiC) in the reduced sample (X_C = 100 pct when titania is totally converted to TiC). For the phase Ti(O,C,N), the molar fractions of titanium monoxide, carbide, and nitride are defined with the notation $TiO_xC_yN_z$.

The errors in measurement of oxygen, nitrogen, and carbon contents by LECO analyses were 2 to 3 wt pct. The relative errors of calculated extents of reduction and nitridation were dependent on the contents of oxygen, nitrogen, and carbon in the reduced samples. In general, the errors of calculated extents of reduction and nitridation were below 1 pct and 3 pct, correspondingly.

III. RESULTS

A. *Temperature-Programmed Reduction*

The temperature programmed reduction (TPR) experiments were conducted in pure nitrogen, and in the He-N_2 (50 vol pct N_2) and Ar-N_2 (50 vol pct N_2) gas mixtures with the gas flow rate 1.5 L min^{-1}.

The CO evolution curves in the course of rutile reduction in different gas atmospheres are presented in Figure 1. This figure also includes the CO evolution curve obtained in rutile reduction in a 50 vol pct H_2-50 vol pct N_2 gas mixture.[11] Table I shows the LECO data and phase composition of the reduced samples after completion of the TPR experiments. The highest CO evolution rate and highest final extent of reduction and nitridation were obtained for a sample reduced in the H_2-N_2 gas mixture. The peak of CO evolution (maximum reduction rate) corresponded to approximately 1473 K (1200 °C). The rate of reduction in nitrogen was slower than in the H_2-N_2 gas mixture; in this case, the maximum reduction rate was observed at approximately 1573 K (1300 °C). However, the nitrogen content in titanium oxycarbonitride was approximately the same as in the sample reduced in the H_2-N_2 gas mixture. The reduction curves obtained in the He-N_2 and Ar-N_2 gas mixtures were close to each other; the final extent of reduction achieved in the He-N_2 gas mixture was 1.3 pct higher than in the Ar-N_2 gas mixture. A reduction in the He-N_2 and Ar-N_2 gases was slower than in N_2 and H_2-N_2.

The XRD patterns of the samples reduced in different gas atmospheres were similar. All the samples contained titanium oxycarbonitride and residual carbon. The major difference was the height of the carbon peaks, which was the lowest for the sample reduced in the H_2-N_2 gas mixture. This is attributed to partial loss of carbon because of gasification reaction with hydrogen to form methane.[3] As shown in Table I, total carbon content in this sample, measured by LECO, was 15.3 wt pct, whereas it was above 30 wt pct in the samples reduced in the gas without hydrogen.

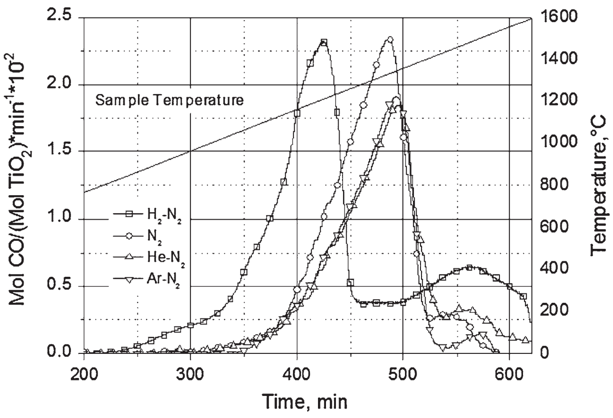

Fig. 1—CO evolution rate in the temperature-programmed reduction of titania in various gas atmospheres. A gas mixture contained 50 vol pct N_2 and 50 vol pct of another gas.

B. *Isothermal Reduction*

1. *Reduction of titania in nitrogen*

Reduction curves obtained in nitrogen at 1473 K to 1773 K (1200 °C to 1500 °C) are presented in Figure 2. The XRD patterns of samples after 180 minutes of reduction at different temperatures are shown in Figure 3. After 180 minutes of reduction at 1473 K (1200 °C), a sample was reduced only to 45.8 pct. The reduced sample contained titanium oxycarbonitride, Ti_3O_5, and a small amount of TiO_2. The extent and rate of reduction increased with increasing temperature. The effect of temperature was particularly strong when temperature increased from 1473 K to 1523 K (1200 °C to 1250 °C). The extent of reduction jumped to 78.5 pct as a result of conversion of Ti_3O_5 into titanium oxycarbonitride. Traces of rutile were observed in the XRD spectra of samples reduced at 1473 K to 1573 K (1200 °C to 1300 °C); titania became undetectable in the samples reduced at higher temperatures. Ti_3O_5 was present in the samples reduced at 1473 K to 1673 K (1200 °C to 1400 °C). Titania was converted to titanium oxycarbonitride totally at 1723 K to 1773 K (1450 °C to 1500 °C). The reduction in N_2 was much slower than in the H_2-N_2 gas mixture,[11] in which titanium suboxides became undetectable after 180 minutes at 1423 K (1150 °C), and 89.6 pct of the reduction was reached. The shape of the reduction curve in N_2 at 1723 K (1450 °C) was similar to that in the H_2-N_2 gas mixture at 1523 K (1250 °C); however, the final extent of reduction in N_2 at 1723 K (1450 °C) was close to the extent of reduction in the H_2-N_2 gas mixture at 1423 K (1150 °C), which was close to 90 pct. After reduction at 1773 K (1500 °C) for 180 minutes, the extents of reduction and nitridation reached 93.7 pct and 78.1 pct, respectively.

2. *Reduction of titania in the He-N_2 and Ar-N_2 gas mixtures*

The reduction curves obtained in the 50 vol pct He-50 vol pct N_2 gas mixture at 1473 K to 1773 K (1200 °C to 1500 °C) are shown in Figure 4. Figure 5 presents the XRD patterns of the reduced samples for 180 minutes. A LECO analysis of the reduced samples

Table I. Chemical and Phase Compositions of Samples Reduced in the TPR Experiments

Gas	Oxygen (wt pct)	Nitrogen (wt pct)	Carbon (wt pct)	X (pct)	X_N (pct)	Phases
50 vol pct H_2-50 vol pct N_2	0.4	14.9	15.3	99.3	71.2	$TiO_{0.01}C_{0.27}N_{0.71}$ + C
100 vol pct N_2	0.7	11.8	31.9	98.3	70.9	$TiO_{0.03}C_{0.26}N_{0.71}$ + C
50 vol pct He-50 vol pct N_2	1.3	11.1	32.2	96.6	66.2	$TiO_{0.07}C_{0.27}N_{0.66}$ + C
50 vol pct Ar-50 vol pct N_2	1.8	10.5	32.8	95.3	61.8	$TiO_{0.09}C_{0.29}N_{0.62}$ + C

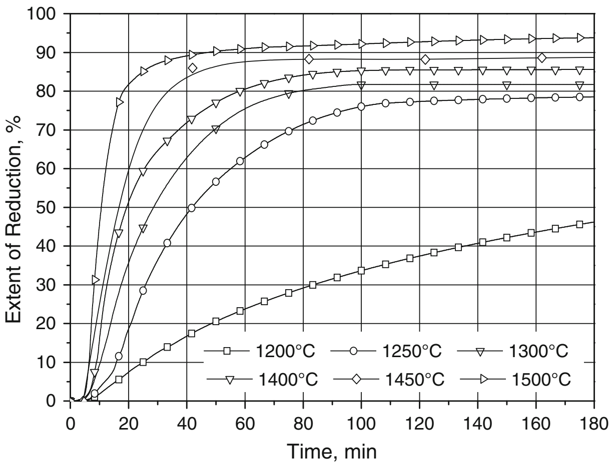

Fig. 2—Extent of reduction of titania in nitrogen at 1473 K to 1773 K (1200 °C to 1500 °C).

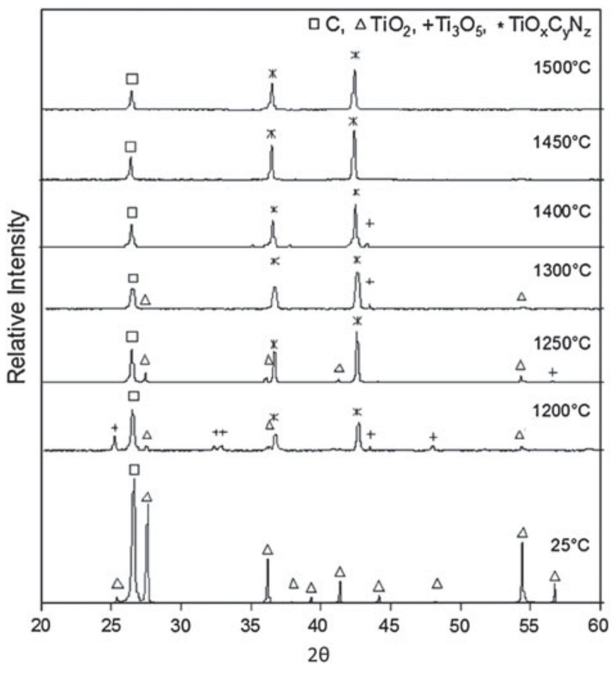

Fig. 3—XRD patterns of samples reduced in N_2 at different temperatures for 180 min.

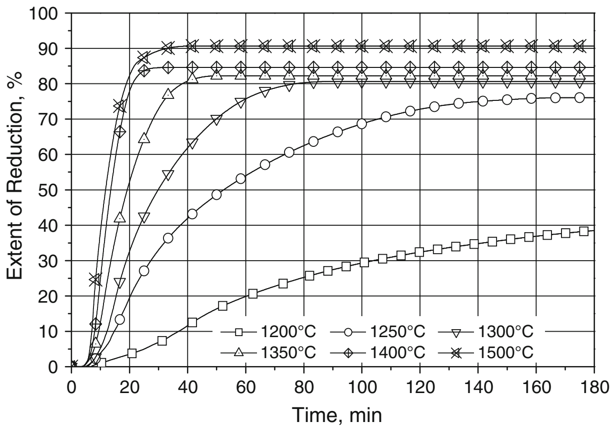

Fig. 4—Extent of reduction of titania in the 50 vol pct He-50 vol pct N_2 gas mixture at 1473 K to 1773 K (1200 °C to 1500 °C).

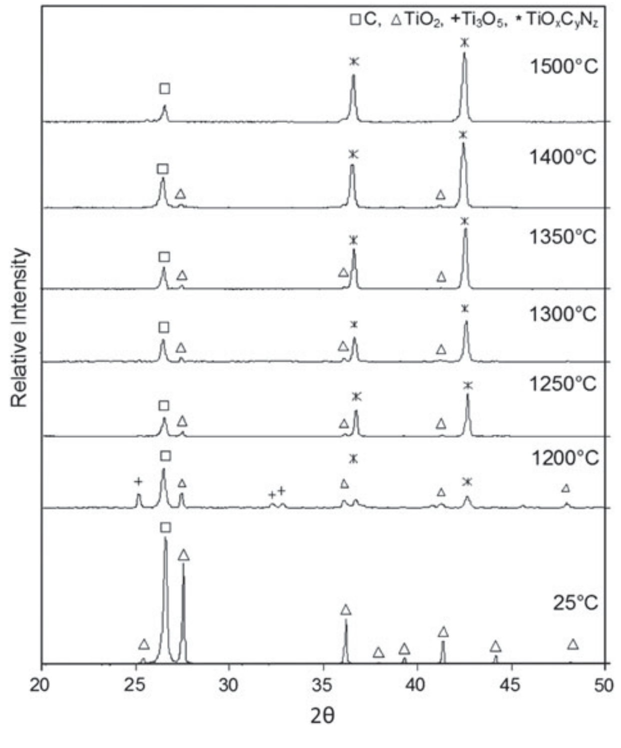

Fig. 5—XRD patterns of the samples reduced in the 50 vol pct He-50 vol pct N_2 gas mixture at different temperatures for 180 min.

and their composition are given in Table II. The rate and extent of reduction were lower than the values obtained in the H_2-N_2 gas mixture[11] and in pure N_2 (Figure 2). The sample reduced at 1473 K (1200 °C) for 180 minutes had an extent of reduction 38.5 pct; the XRD pattern shows that rutile was reduced mostly to Ti_3O_5 with formation of a small amount of titanium oxycarbonitride. Increasing the temperature from 1473 K to 1523 K (1200 °C to 1250 °C) increased the rate of reduction significantly, which boosted the extent of reduction to 76.2 pct. Traces of titania were observed in the XRD spectrum of a sample reduced at 1673 K (1400 °C), although Ti_3O_5 was not detected in the XRD pattern of the sample reduced at 1523 K (1250 °C). Titania was totally converted to titanium oxycarbonitride only at 1773 K (1500 °C), when the extent of reduction increased to 90.7 pct and the extent of nitridation reached 78.4 pct. The reduction curves obtained in the reduction of titania in the Ar-N_2 gas mixture were similar to those obtained in the He-N_2 gas, although the rate of reduction in the Ar-N_2 gas mixture was slightly lower.

The phase development in the course of reduction of titania in the 50 vol pct He-50 vol pct N_2 gas mixture was studied at 1573 K (1300 °C). The XRD patterns of the samples taken in the course of reduction are presented in Figure 6. After 10 minutes of reduction, the detected phases included suboxides Ti_4O_7 and Ti_3O_5 in addition to unreduced titania and residual carbon. Titanium oxycarbonitride was detected after 20 minutes of reduction, when the major oxide became Ti_3O_5, whereas Ti_4O_7 became undetectable. Subsequent reduction involved the conversion of Ti_3O_5 to titanium oxycarbonitride. The Ti_3O_5 phase did not disappear until 120 minutes of reduction. The TiO_2 peaks in the samples reduced from 10 to 180 minutes were small; however, no obvious change in their height in the progress of reduction was observed. A careful inspection showed that the residual titania was present only in a thin surface layer of the sample pellet, which was related to the trace amount of oxygen and moisture in the inlet gas.

The phase development in the progress of titania reduction in the 50 vol pct Ar-50 vol pct N_2 gas mixture was studied also at 1573 K (1300 °C). The phase development in the Ar-N_2 gas mixture was similar to that in the He-N_2 gas mixture.

3. *Effect of H_2 and N_2 contents in the gas phase on the reduction of titania*

Reduction experiments were conducted at 1473 K (1200 °C) in the H_2-N_2-He gas mixture of different composition. In these experiments, either the H_2 content in the gas mixture was varied at constant 50 vol pct N_2 content or the N_2 content was varied at constant 50 vol pct H_2 content.

In reduction experiments, methane was detected in effluent gas; the concentration in experiments with 50 vol pct H_2-50 vol pct N_2 reached 100 ppm at 1473 K (1200 °C) and decreased with increasing temperature.

The reduction curves with varied H_2 concentration are given in Figure 7. The LECO analysis and phase composition determined by the XRD analysis of reduced samples are presented in Table III. The H_2 content had a strong effect on the rate and extent of reduction and nitridation. As shown in Figure 7, the carbothermal reduction in the 50 vol pct He-50 vol pct N_2 gas mixture was slow; the final extent of reduction and nitridation after 180 minutes was less than 40 pct and 20 pct, respectively. The reduction products included Ti_3O_5 and a small amount of titanium oxycarbonitride. Titania conversion was not complete in this case. The addition of 5 vol pct H_2 increased the extent of reduction significantly to 74.4 pct and the extent of nitridation to 55.7 pct. Some amount of Ti_3O_5 was detected in the reduced sample as the only titanium oxide. The extents of reduction and nitridation increased to 86.1 pct and 71.0 pct, respectively, with an addition of 10 vol pct of H_2 to the gas mixture, and titanium suboxides were not detected in the reduced sample. Subsequent increasing H_2 content to 30 and 50 vol pct shortened the reduction period to 100 minutes and 70 minutes, respectively. The final extent of reduction was not affected significantly by the H_2 content in the range of 10 to 50 vol pct; the effect of hydrogen on the extent of nitridation was more remarkable, it increased to 85.7 pct with 50 vol pct addition of H_2 in the gas atmosphere.

Figure 8 presents the reduction curves obtained in experiments with varied N_2 content. A LECO analysis and phase composition determined by the XRD analysis of reduced samples are presented in Table IV.In the gas mixture of 50 vol pct H_2-50 vol pct He without N_2 addition, a reduction of 75 pct was achieved. It increased to 90.2 pct when 5 vol pct N_2 was added to

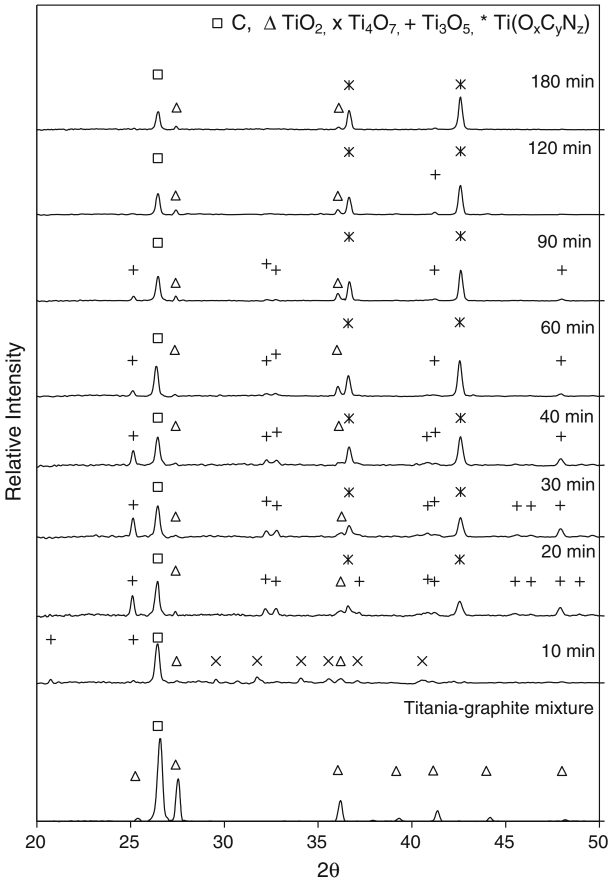

Fig. 6—XRD patterns of samples in progress of reduction in the 50 vol pct He-50 vol pct N_2 gas mixture at 1573 K (1300 °C).

Table II. Chemical and Phase Compositions of Samples Reduced in the 50 Vol Pct He-50 Vol Pct N_2 Gas Mixture for 180 Min

Time (min)	Oxygen (wt pct)	Nitrogen (wt pct)	Carbon (wt pct)	X (pct)	X_N (pct)	Phases
1200	16.9	2.3	38.2	38.5	19.1	$TiO_2 + Ti_3O_5 + TiO_xC_yN_z + C$
1250	7.9	8.9	33.4	76.2	61.6	$TiO_2 + TiO_xC_yN_z + C$
1300	6.6	10.4	32.2	80.2	71.5	$TiO_2 + TiO_xC_yN_z + C$
1350	6.3	11.5	31.9	82.4	74.4	$TiO_2 + TiO_xC_yN_z + C$
1400	5.6	12.4	26.0	84.7	78.3	$TiO_2 + TiO_xC_yN_z + C$
1500	3.6	13.0	24.8	90.7	78.4	$TiO_{0.19}C_{0.03}N_{0.78} + C$

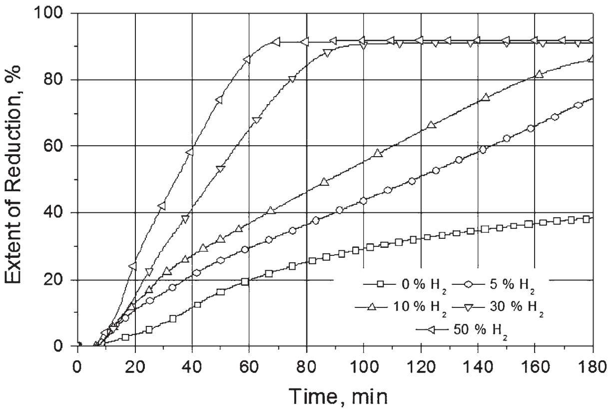

Fig. 7—Extent of the reduction of titania in the H_2-N_2-He gas mixtures (50 vol pct N_2) with varied H_2 concentration at 1473 K (1200 °C).

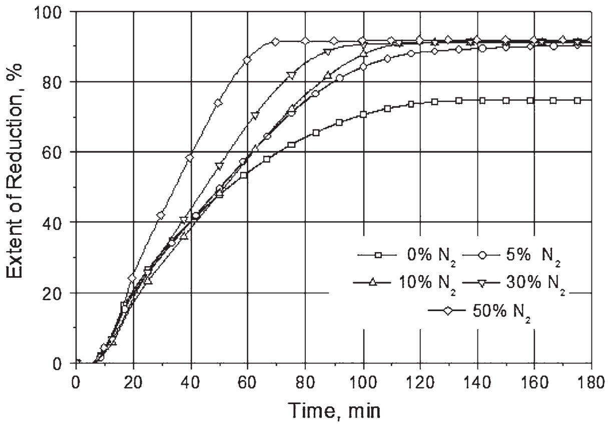

Fig. 8—Extent of the reduction of titania in the H_2-N_2-He gas mixtures (50 vol pct H_2) with varied N_2 concentration at 1473 K (1200 °C).

Table III. Chemical and Phase Compositions of Samples Reduced in the H_2-N_2-He Gas Mixtures (50 vol pct N_2) with Different H_2 Concentration at 1473 K (1200 °C) for 180 Min

H_2 Content (vol pct)	Oxygen (wt pct)	Nitrogen (wt pct)	Carbon (wt pct)	X (pct)	X_N (pct)	Phases
0	16.9	2.3	38.2	38.5	19.1	$TiO_2 + Ti_3O_5 + TiO_xC_yN_z$ + C
5	8.3	7.9	34.4	74.4	55.7	$Ti_3O_5 + TiO_xC_yN_z$ + C
10	4.8	10.8	31.7	86.1	71.0	$TiO_{0.28}C_{0.001}N_{0.71}$ + C
30	3.2	12.9	29.6	91.0	81.5	$TiO_{0.17}C_{0.01}N_{0.82}$ + C
50	2.6	13.6	28.4	92.9	85.7	$TiO_{0.13}C_{0.01}N_{0.86}$ + C

the gas mixture. Increasing N_2 content in the reducing gas did not significantly increase the extent of reduction. With 50 vol pct N_2 addition, the extent of reduction was 92.9 pct. However, the rate of reduction increased remarkably and the reduction time shortened corresponding to the increase in the N_2 content in the gas mixture. Without N_2 addition, titanium oxycarbide was formed in carbothermal reduction of titania, and a small amount of Ti_2O_3 was detected in the reduced sample. The addition of 5 vol pct N_2 resulted in the formation of titanium oxycarbonitride, and 59 pct of the titanium was nitridated. No titanium suboxide was detected by XRD. The extent of nitridation increased further to 67.8, 80.4, and 85.7 pct, correspondingly with 10, 30, and 50 vol pct N_2 in the reduction atmosphere.

IV. DISCUSSION

A reaction sequence in reduction/nitridation of titania in the H_2-N_2 gas mixture was discussed previously.[11] The phases detected by the XRD analysis in the progress of reduction/nitridation in the H_2-N_2 gas mixture at 1423 K (1150 °C) were developed in the following sequence:

$$TiO_2 \rightarrow Ti_5O_9 \rightarrow Ti_4O_7 \rightarrow Ti_3O_5 \rightarrow TiO_xC_yN_z \quad [1]$$

A similar reduction/nitridation sequence was observed in experiments in the He-N_2 gas mixture at 1573 K (1300 °C), although the conversion of titania to titanium oxycarbonitride was not completed.

An analysis of the reduction curves and phase development in the progress of reduction shows that the conversion of titania to Ti_3O_5 was fast; the subsequent conversion of Ti_3O_5 to titanium oxycarbonitride was relatively slow and can be considered as the rate controlling stage of the carbothermal reduction of titania. The reduction of Ti_3O_5 to titanium oxycarbonitride, which is a solid solution of titanium oxide, carbide, and nitride, can be presented by the following equation:

$$\begin{aligned} &Ti_3O_5 + (5-3x+3y)C + (3/2)zN_2 \\ &\quad = 3(x[TiO] + y[TiC] + z[TiN]) + (5-3x)CO \quad [2] \end{aligned}$$

$$\begin{aligned} \Delta G_2 &= x\Delta G^\circ_{TiO} + y\Delta G^\circ_{TiC} + z\Delta G^\circ_{TiN} \\ &\quad + 3RT\ln\frac{(a_{TiO})^x(a_{TiC})^y(a_{TiN})^z P_{CO}^{5/3-x}}{P_{N_2}^{z/2}} \\ &= x(599.0 - 0.3255T) + y(1279.1 - 0.7948T) \\ &\quad + z(836.4 - 0.5601T) \\ &\quad + 3RT\ln\frac{(a_{TiO})^x(a_{TiC})^y(a_{TiN})^z P_{CO}^{5/3-x}}{P_{N_2}^{z/2}} \end{aligned}$$

where a_i represents the activity of TiO, TiC, and TiN in titanium oxycarbonitride; ΔG°_{TiO} and ΔG°_{TiC} are the standard Gibbs free energy change for formation of TiO and TiC by the reaction of Ti_3O_5 with graphite; and ΔG°_{TiN} is the standard Gibbs free energy change for the

Table IV. Chemical and Phase Compositions of Samples Reduced in the H_2-N_2-He Gas Mixtures (50 vol pct H_2) with Different N_2 Concentration at 1473 K (1200 °C) for 180 Min

N_2 Content (vol pct)	Oxygen (wt pct)	Nitrogen (wt pct)	Carbon (wt pct)	X (pct)	X_N (pct)	Phases
0	7.7	0.0	36.4	75.0	0.0	Ti_2O_3 + $TiO_xC_yN_z$ + C
5	3.6	9.6	32.6	90.2	59.2	$TiO_{0.20}C_{0.21}N_{0.59}$ + C
10	3.3	10.7	31.6	91.0	67.8	$TiO_{0.18}C_{0.14}N_{0.68}$ + C
30	3.2	12.8	29.7	91.3	80.4	$TiO_{0.17}C_{0.03}N_{0.80}$ + C
50	2.6	13.6	30.2	92.9	85.7	$TiO_{0.14}C_{0.001}N_{0.86}$ + C

formation of TiN by a reaction of Ti_3O_5 with graphite and N_2. The Gibbs free energy change for reaction [2] and other reactions considered in this article was calculated using data from NIST-JANAF Thermochemical Tables in the temperature range of 1300 K to 1800 K (1027 °C to 1527 °C).[14]

Carbothermal reduction starts with solid–solid reaction at the contact points of the graphite-titania particles. Subsequent reduction proceeds through the gas phase. Carbon is transferred from graphite to oxide in the form of CO when titania is reduced in the N_2, N_2-He, or N_2-Ar gas mixtures, or as CH_4 when H_2 is present in the gas phase.

The conversion of Ti_3O_5 to $TiO_xC_yN_z$ by CO can be presented by the following reaction:

$$\mathrm{Ti_3O_5} + (5 - 3x + 6y)\mathrm{CO} + (1.5z)\mathrm{N_2} = 3(x[\mathrm{TiO}] + y[\mathrm{TiC}] + z[\mathrm{TiN}]) + (5 - 3x + 3y)\mathrm{CO_2} \quad [3]$$

$$\begin{aligned}\Delta G_3 &= x\Delta G^*_{\mathrm{TiO}} + y\Delta G^*_{\mathrm{TiC}} + z\Delta G^*_{\mathrm{TiN}} + 3RT\ln\frac{(a_{\mathrm{TiO}})^x(a_{\mathrm{TiC}})^y(a_{\mathrm{TiN}})^z P_{\mathrm{CO_2}}^{5/3-x+y}}{P_{\mathrm{CO}}^{5/3-x+2y}P_{\mathrm{N_2}}^{z/2}}\\ &= x(269.2 + 0.0157T) + y(-40.2 + 0.5699T) + z(11.8 + 0.2928T)\\ &\quad + 3RT\ln\frac{(a_{\mathrm{TiO}})^x(a_{\mathrm{TiC}})^y(a_{\mathrm{TiN}})^z P_{\mathrm{CO_2}}^{5/3-x+y}}{P_{\mathrm{CO}}^{5/3-x+2y}P_{\mathrm{N_2}}^{z/2}}\end{aligned}$$

where $\Delta G^*_{\mathrm{TiO}}$ and $\Delta G^*_{\mathrm{TiC}}$ are the standard Gibbs free energy change for formation of TiO and TiC by reaction of Ti_3O_5 with CO; $\Delta G^*_{\mathrm{TiN}}$ is the Gibbs free energy change for formation of TiN by reaction of Ti_3O_5 with CO and N_2. CO_2 formed in reaction [3] is converted to CO by the Boudouard reaction [4]:

$$\mathrm{CO_2} + \mathrm{C} = 2\mathrm{CO} \quad [4]$$

$$\Delta G^\circ_4 = -21.1 + 0.190T \quad [\mathrm{kJ}]$$

When H_2 is present in the gas phase, it reacts with carbon to form methane, which reduces Ti_3O_5 to titanium oxycarbonitride:

$$\mathrm{C} + 2\mathrm{H_2} = \mathrm{CH_4} \quad [5]$$

$$\Delta G^\circ_5 = -92.5 + 0.112T \quad [\mathrm{kJ}]$$

$$\mathrm{Ti_3O_5} + (5 - 3x + 3y)\mathrm{CH_4} + (1.5z)\mathrm{N_2} = 3(x[\mathrm{TiO}] + y[\mathrm{TiC}] + z[\mathrm{TiN}]) + (5 - 3x)\mathrm{CO} + 2(5 - 3x + 3y)\mathrm{H_2} \quad [6]$$

$$\begin{aligned}\Delta G_6 &= x\Delta G^\#_{\mathrm{TiO}} + y\Delta G^\#_{\mathrm{TiC}} + z\Delta G^\#_{\mathrm{TiN}} + 3RT\ln\frac{(a_{\mathrm{TiO}})^x(a_{\mathrm{TiC}})^y(a_{\mathrm{TiN}})^z P_{\mathrm{CO}}^{5/3-x}P_{\mathrm{H_2}}^{2(5/3-x+y)}}{P_{\mathrm{CH_4}}^{5/3-x+y}P_{\mathrm{N_2}{}^{z/2}}}\\ &= x(784.0 - 0.549\,T) + y(2019.1 - 1.69T) + z(1298.9 - 1.12T)\\ &\quad + 3RT\ln\frac{(a_{\mathrm{TiO}})^x(a_{\mathrm{TiC}})^y(a_{\mathrm{TiN}})^z P_{\mathrm{CO}}^{5/3-x}P_{\mathrm{H_2}}^{2(5/3-x+y)}}{P_{\mathrm{CH_4}}^{5/3-x+y}P_{\mathrm{N_2}}^{z/2}}\end{aligned}$$

where $\Delta G^\#_{\mathrm{TiO}}$ and $\Delta G^\#_{\mathrm{TiC}}$ are the standard Gibbs free energy change for formation of TiO and TiC by reaction of Ti_3O_5 with CH_4; $\Delta G^\#_{\mathrm{TiN}}$ is the Gibbs free energy change for formation of TiN by reaction of Ti_3O_5 with CH_4 and N_2. Intermediate CO or CH_4 in the carbothermal reduction does not change the thermodynamics of the overall reaction [2].

Figure 9 presents the calculated equilibrium partial pressures of CO_2 for reactions [3] and [4] and that of CH_4 for reaction [5], assuming that titanium oxycarbonitride is an ideal solution containing 15 mol pct TiO, 10 mol pct TiC, and 75 mol pct TiN ($TiO_{0.15}C_{0.10}N_{0.75}$); the partial pressures of H_2, N_2, and CO in the gas phase were assumed at 50 kPa, 50 kPa, and 1 kPa, respectively. The equilibrium partial pressure of CO_2 for reduction Reaction [3] is low, close to 10^{-4} kPa. The equilibrium partial pressure of CO_2 for the Boudouard reaction [4] is equal to 1.42×10^{-7} kPa at 1423 K (1150 °C) and 3.7×10^{-8} kPa at 1573 K (1300 °C). The equilibrium partial pressure of CH_4 is 2 to 3 orders higher than that of CO_2 for reaction [3].

Rankin and Wynnyckyj[15] demonstrated that the rate of carbothermal reduction reactions can be controlled by the intrinsic gas phase diffusion of the intermediate CO_2 between the oxide and graphite particle when the CO_2 partial pressure is low. The diffusion control in the gas phase for solid–solid reactions is expected when a partial pressure of intermediate gaseous species is below 10^{-2} kPa.[15] This is the case of intermediate CO_2, for which the equilibrium partial pressure with Ti_3O_5 and $TiO_{0.15}C_{0.10}N_{0.75}$ is near 10^{-4} kPa in the temperature range examined in this article. However, for carbothermal reduction/nitridation in the H_2-containing gases, the

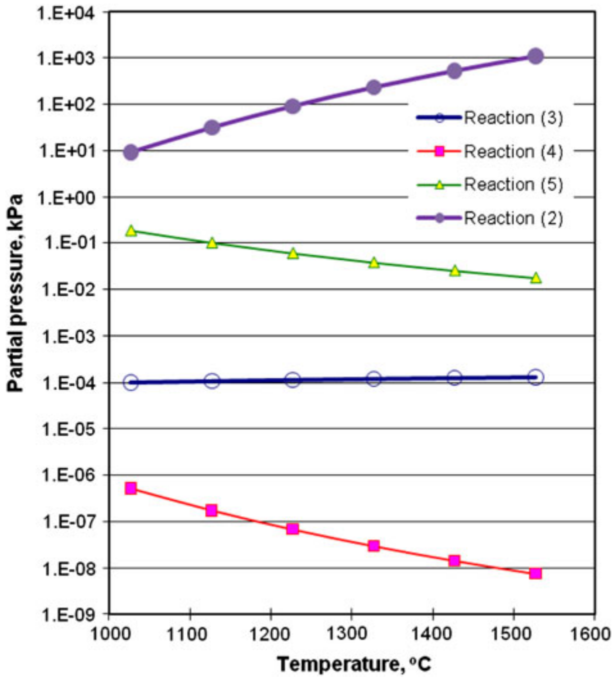

Fig. 9—Equilibrium partial pressure of CO_2 for reactions [3] and [4], CH_4 for reaction [5], and CO for reaction [2] calculated for an ideal $TiO_{0.15}C_{0.10}N_{0.75}$ solution. Partial pressures of H_2, CO, and N_2 are assumed at 50 kPa (reaction [5]), 1 kPa and 50 kPa (reactions [3] and [4]), respectively.

partial pressure of intermediate CH_4 is well above 10^{-2} kPa. Therefore, under the experimental conditions described in this work, the carbothermal reduction in pure nitrogen or its mixtures with an inert gas was controlled by the diffusion of CO_2 from oxide particles to graphite, and a reduction in a hydrogen-nitrogen mixture was controlled by the intrinsic kinetics of a reduction reaction (reduction of Ti_3O_5 by CH_4).

A change in N_2 concentration in the He-H_2-N_2 gas mixture (constant H_2 content at 50 vol pct) had a strong effect on X,X_N, and the reduction rate (Figure 8 and Table IV). A significant difference in the reduction behavior of titania in the H_2-He gas mixture (0 vol pct N_2) and H_2-He-N_2 gas mixture with only 5 vol pct N_2 is a manifestation of the fact that the conversion of titania to oxycarbonitride is more favorable thermodynamically and kinetically than that to oxycarbide. TiN is a more stable titanium compound compared with TiC and TiO. The equilibrium temperature for TiN formation by carbothermal reduction of Ti_3O_5 under standard conditions is 1493 K (1220 °C), which is 116 K and 347 K lower than those of TiC and TiO, respectively. The nitrogen partial pressure in reduction experiments was much higher than the partial pressure of CH_4 or CO, which are reaction intermediates in formation of TiC. These thermodynamic and kinetic parameters are favorable for the TiN formation and explain the high TiN fraction in titanium oxycarbonitride.

V. CONCLUSIONS

The gas composition had a strong effect on the carbothermal reduction/nitridation of titania to titanium oxycarbonitride. The reduction was the fastest in the H_2-N_2 gas mixture, and it was slower in pure nitrogen and the slowest in the Ar-N_2 gas.

Increasing temperature resulted in formation of titanium oxycarbonitride with higher TiC content.

The carbothermal reduction of solid oxides proceeds through the gas phase. In the reduction in inert atmosphere, titanium oxide was reduced by CO with the formation of CO_2, which was converted to CO by the Boudouard reaction. The equilibrium partial pressure of CO_2 produced in the reduction reaction is low, close to 10^{-4} kPa. At such a low CO_2 partial pressure, carbothermal reduction reactions can be controlled by the intrinsic diffusion of the intermediate CO_2 between the oxide and graphite particles.

Hydrogen was involved in the carbothermal reduction reactions. After reduction in hydrogen-containing gas, titanium oxides were reduced by methane, which was formed by the reaction of hydrogen with carbon. The equilibrium partial pressure of CH_4 was 2 to 3 orders higher than that of CO_2. This finding explains why the carbothermal reduction was faster in hydrogen than in argon and helium. Partial replacement of N_2 by H_2 also increased the diffusivity of gas species in the gas phase, however, with an insignificant effect on the reaction kinetics.

The addition of hydrogen to the gas atmosphere in the process of carbothermal synthesis of titanium oxycarbonitride has a positive effect on the reaction kinetics; it reduces the reaction temperature and time.

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