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Carbothermal Reduction of Titania in Different Gas Atmospheres

MOHAMMAD A.R. DEWAN, GUANGQING ZHANG, and OLEG OSTROVSKI

The synthesis of titanium oxycarbide by carbothermal reduction of titania was studied in hydrogen, argon, and helium in isothermal and temperature programmed reduction experiments in a tube reactor with continuously flowing gas. In the temperature range of 1000 °C to 1500 °C, the reduction rate increased with increasing temperature. Formation of titanium oxycarbide started at 1200 °C in all three gases. The reduction was the fastest in hydrogen. Formation of titanium oxycarbide in hydrogen was close to completion in 120 minutes at 1300 °C, 60 minutes at 1400 °C, and less than 30 minutes at 1500 °C. The reduction in argon and helium had similar rates and reached 90 to 95 pct after a 300-minute reduction at 1400 °C to 1500 °C. Faster carbothermal reduction of titania in hydrogen than in argon and helium was attributed to involvement of hydrogen in the reaction. Hydrogen reduced titania to titanium suboxides and reacted with carbon, forming methane, which reduced titanium suboxides to titanium oxycarbide. Titanium oxycarbide synthesized in hydrogen for 180 minutes at 1300 °C contained 13 mol pct TiO. At 1500 °C, oxygen concentration decreased to a degree corresponding to 1.4 mol pct TiO. In the titanium oxycarbide produced by a 300-minute reduction at 1600 °C, the TiO content was 0.6 mol pct.

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I. INTRODUCTION

TITANIUM carbide has high-temperature strength retention, excellent oxidation resistance, a low thermal expansion coefficient, high wear resistance, a high melting point, and light weight.^[1] This advanced engineering material is used in the metalworking, electrical, electronic, automotive, and refractory industries. Titanium carbide is similar to titanium metal in appearance and behavior and has higher corrosion resistance.^[2]

Titanium carbide is commercially produced primarily by the reduction of titania by carbon in a temperature range between 1700 °C and 2100 °C. Other methods include synthesis of TiC from metallic titanium and carbon; chemical reaction between TiCl₄, H₂, and C; self-propagating high-temperature synthesis; reaction of titanium sulfide with carbon; reaction of titanium hydride with carbon; chemical vapor deposition; and the sol-gel method.^[3] These methods are currently under development or have limited applications.

Production of titanium carbide is expensive. The cost of high-quality TiC powder is a major factor hindering wide application of titanium carbide. Therefore, developing a more efficient and less expensive process for titanium carbide is an attractive way to expand the application of this advanced material.

Titanium carbide and oxycarbide can be chlorinated at temperatures of 200 °C to 500 °C,^[4] which are much

lower than temperatures of conventional chlorination of rutile, which are in the range of 800 °C to 1100 °C. Energy-efficient conversion of titania to titanium oxycarbide will stimulate development of low-temperature chlorination processes.

It is established that the kinetics of carbothermal TiO₂ reduction is affected by the reaction temperature, molar TiO₂/C ratio, TiO₂ grain size, and initial bulk density.^[1,5,6] Gas atmosphere also has a strong effect on the TiO₂/C reactivity^[6,7] and the rate of TiO₂ reduction by methane containing gas.^[8,9] However, published data on the effect of gas compositions on the TiO₂ carbothermal reduction and their interpretation are to some extent conflicting.

Vodop'yanov *et al.*^[7] came to the conclusion that carbothermal reduction of titania to TiC is the fastest in the CO gas atmosphere. This contradicts experimental results and calculations conducted by Zhang and Ostrovski,^[8] which showed that Ti₂O₃ formed in the course of TiO₂ reduction, rather than being reduced further to TiC or titanium oxycarbide, was oxidized by CO to Ti₃O₅, when CO concentration in an Ar-CO gas atmosphere was more than 10 vol pct. Chou and Lin^[6] studied carbothermal reduction of TiO₂ in a helium atmosphere and observed the decreasing reduction rate and declining reaction yield (measured as TiC/TiO₂ ratio) with increasing helium flow rate.

The effect of gas atmosphere on the carbothermal reduction was studied more thoroughly in the reduction of manganese oxides.^[10,11] It was established that the rate of carbothermal reduction of manganese ore is faster in helium than in argon^[10,11] and faster in hydrogen than in helium.^[11] This was explained by the higher diffusion coefficient of CO in helium and hydrogen in comparison with argon (by a factor of 4) and by involvement of hydrogen in the reduction process.

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This article investigates carbothermal reduction of titania in hydrogen, argon, and helium. The aim of this article is to establish the effects of temperature and gas composition on the extent, rate, and mechanisms of carbothermal reduction of TiO_2 and the optimal conditions for synthesis of titanium oxycarbide.

II. EXPERIMENTAL

Titania powder ($\text{TiO}_2 > 99.9$ pct, size $< 5 \mu\text{m}$) and synthetic graphite ($< 20 \mu\text{m}$) were mixed with distilled water (70 wt pct of solid mixture) and carboxymethyl cellulose (CMC, 0.3 wt pct). Addition of CMC ensured uniform mixing of titania and graphite. The mixture was dried at 120°C overnight. The titania-graphite mixture had a titania-to-graphite molar ratio of 1:4.5. The mixture was pressed into pellets in a uniaxial hydraulic press by applying 20 kN of pressure for 2 minutes. The pellets with a mass of about 1.5 g were 8 mm in diameter and about 12 mm in length.

Reduction of titania 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 system were presented elsewhere.^[8] The gases used in the investigation were of 99.999 pct purity. The outlet gas was analyzed online by an infrared $\text{CO}/\text{CO}_2/\text{CH}_4$ 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, Siemens D5000, Siemens, Aktiengesellschaft, Germany). Oxygen and carbon contents in reduced samples were determined using LECO*

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

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 dioxide removed in the course of reduction. The reduction curves were calculated based on gas composition and oxygen content in 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 extent of reduction 90 pct, the error was about 0.1 pct, which gives 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 is 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 a heating rate of $3^\circ\text{C}/\text{min}$.

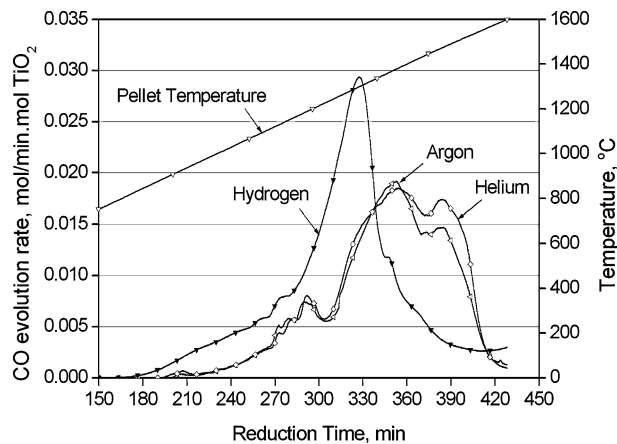


Fig. 1—Temperature programmed reduction of titania in different gas atmospheres. The furnace temperature was ramped from 350°C to 1620°C at $3^\circ\text{C}/\text{min}$.

Figure 1 compares the rate of generation of CO in reduction experiments in different gas atmospheres. Generally, reduction of titania in hydrogen started at a lower temperature and achieved a higher peak reduction rate at a lower temperature than in argon and helium.

When reduction was carried out in hydrogen, CO evolution started at about 800°C . At 1324°C , a maximum CO evolution rate of $0.0293 \text{ mol}/\text{min}\cdot\text{mol TiO}_2$ was achieved. The rate sharply decreased after 1324°C , and the reduction was completed at about 1500°C . Reduction in argon and helium started at about 850°C . The maximum CO evolution rates in both inert gases corresponded to the same temperature of 1360°C and had similar values— $0.018 \text{ mol}/\text{min}\cdot\text{mol TiO}_2$ in argon and $0.019 \text{ mol}/\text{min}\cdot\text{mol TiO}_2$ in helium. The major reduction peak overlapped with another peak at 1460°C , with a CO evolution rate at $0.017 \text{ mol}/\text{min}\cdot\text{mol TiO}_2$ in argon and $0.015 \text{ mol}/\text{min}\cdot\text{mol TiO}_2$ in helium. The origin of the second peak is unclear; it was not observed when the reduction was carried out in hydrogen.

To identify the phase changes during titania reduction, the TPR experiments were stopped at different temperatures, and the samples were analyzed by XRD. Figure 2 represents the XRD patterns of samples reduced to different temperatures in hydrogen. The phases found in a sample reduced to 915°C included Ti_8O_{15} and unreduced titania. In a sample reduced to 975°C , the only phase identified by XRD was Ti_4O_7 . Ti_4O_7 and Ti_3O_5 phases were found at 1035°C . They were further converted into a mixture of Ti_3O_5 and Ti_2O_3 at 1165°C . At 1324°C , TiO_xC_y was formed, with Ti_2O_3 as the residual suboxide. In the sample subjected to reduction in hydrogen with temperature ramping to 1600°C , only titanium oxycarbide was present in addition to residual graphite.

The XRD patterns of samples obtained in reduction of titania in argon are presented in Figure 3. The XRD spectra of samples reduced in helium were very similar to those reduced in argon. When the temperature was

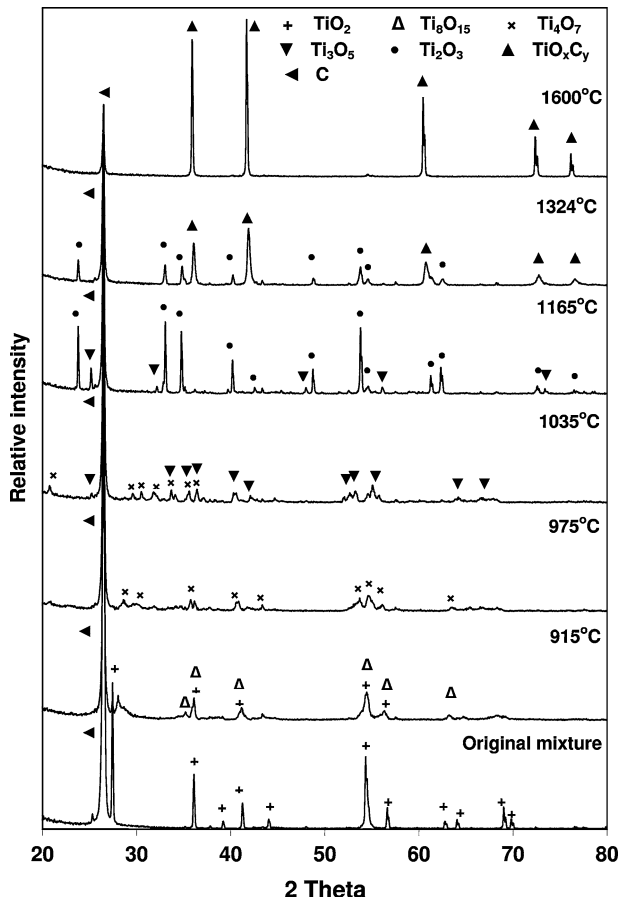


Fig. 2—XRD patterns of samples in the progress of temperature-programmed reduction in hydrogen. The furnace temperature was ramped from 350 °C at 3 °C/min.

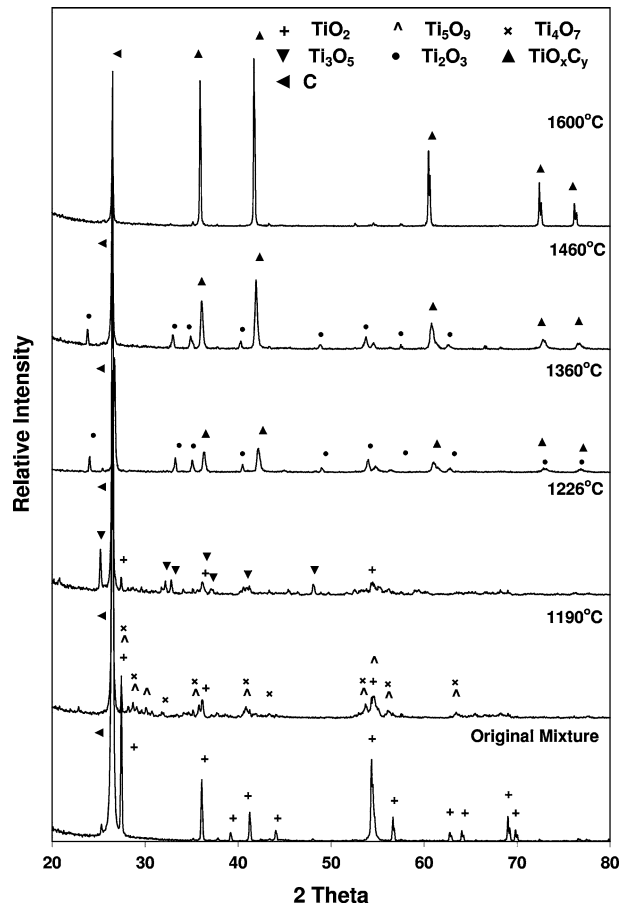


Fig. 3—XRD patterns of samples in the progress of temperature-programmed reduction in argon. The furnace temperature was ramped from 350 °C at 3 °C/min.

ramped to 1190 °C, Ti_5O_9 and Ti_4O_7 were identified in addition to unreacted titania. A further increase in temperature to 1226 °C resulted in formation of Ti_3O_5 , while unreacted titania was still detectable. At 1360 °C, when the reduction was the fastest, TiO_xC_y and Ti_2O_3 were identified. The same phases were present in the samples further reduced with increasing temperature to 1460 °C, which corresponded to the second maximum in the reduction rate. Finally, when the temperature was ramped to 1600 °C, all titania was converted to TiO_xC_y .

B. Isothermal Reduction

The extent of reduction of titania in hydrogen in the temperature range of 1000 °C to 1500 °C is presented in Figure 4. The XRD spectra of samples reduced at different temperatures for 300 minutes are presented in Figure 5. Carbothermal reduction of titania was very slow at 1000 °C and 1100 °C. After a 300-minute reduction at 1000 °C, titania was reduced to Ti_2O_3 and Ti_3O_5 with the extent of reduction of 19 pct. Only Ti_2O_3 was detected in the sample reduced at 1100 °C, with an extent of reduction of 29 pct. Increasing the temperature to 1200 °C resulted in a significant increase of the rate and extent of reduction, which

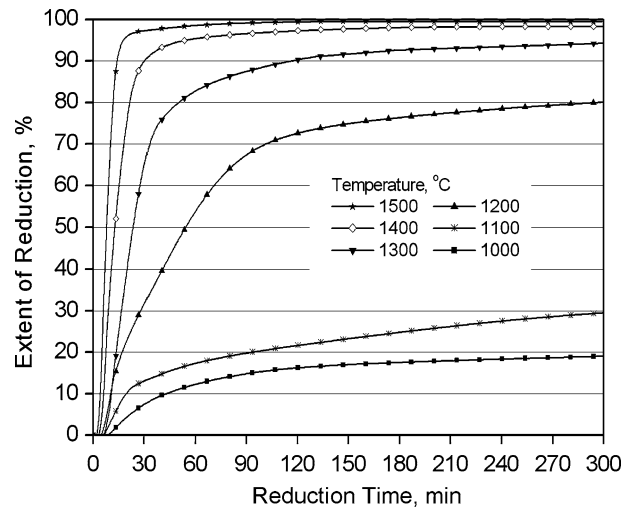


Fig. 4—Effect of temperature on extent of reduction in hydrogen.

reached 80 pct after 300 minutes of reaction. A significant amount of TiO_xC_y was formed, and Ti_2O_3 was almost undetectable in the reduced sample. The reduction was further enhanced by increasing the temperature to 1300 °C to 1500 °C. At 1300 °C, the formation

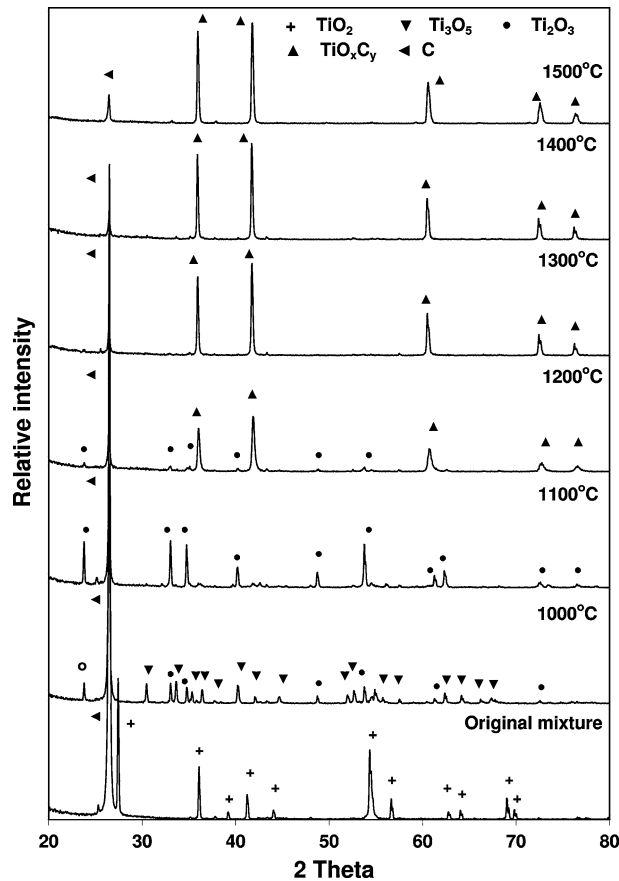


Fig. 5—XRD patterns of samples reduced in hydrogen for 300 min at different temperatures.

of titanium oxycarbide was completed in about 120 minutes, with an extent of reduction of 91 pct. The reduction period was shortened to 60 minutes at 1400 °C, and the reduction extent reached 96 pct. At 1500 °C, titania was converted to titanium oxycarbide in less than 30 minutes, corresponding to the extent of reduction of 97 pct.

Reduction curves obtained in argon at different temperatures are presented in Figure 6. Figure 7 shows the XRD patterns of the samples reduced for 300 minutes. When carbothermal reduction was carried out in argon, formation of titanium oxycarbide was significantly slower. After a 300-minute reduction at 1000 °C, an extent of reduction calculated from CO evolution was only 4 pct. The XRD analysis in argon detected Ti_8O_{15} and Ti_9O_{17} in addition to unconverted TiO_2 . Titania was partially reduced to Ti_2O_3 and Ti_3O_5 at 1100 °C with an extent of reduction of 23 pct. Titanium oxycarbide was detected at 1200 °C, at which the extent of reduction was 37 pct, with Ti_2O_3 as the main phase of the reduced sample. Unreduced TiO_2 was still detectable at this temperature. Further increasing the reduction temperature to 1300 °C increased the extent of reduction to 57 pct, and the reduction product contained TiO_xC_y and Ti_2O_3 . The reduction was strongly enhanced by increasing the temperature to 1400 °C to 1500 °C. At 1400 °C, the extent of reduction

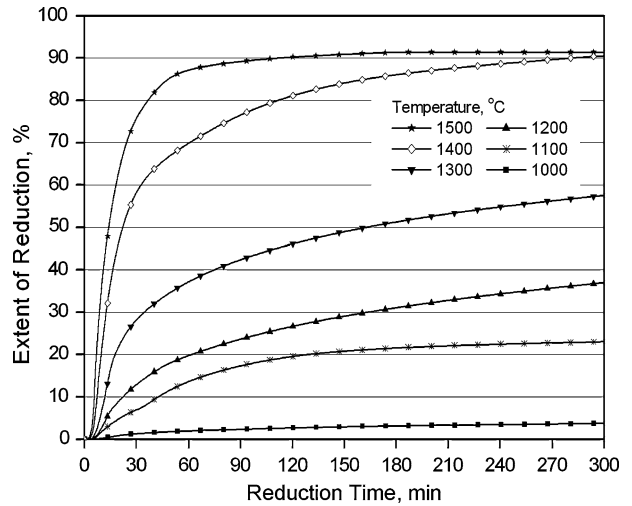


Fig. 6—Effect of temperature on extent of reduction in argon.

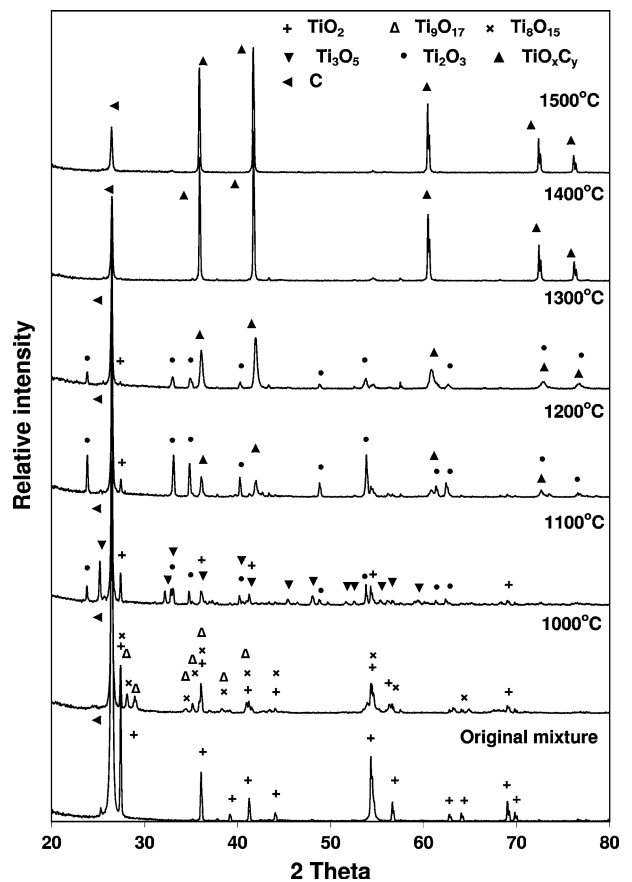


Fig. 7—XRD patterns of samples reduced in argon for 300 min at different temperatures.

continued to rise with increasing reduction time, reaching 90 pct in 300 minutes. In experiments at 1500 °C, the extent of reduction reached 90 pct in 100 minutes. After 300 minutes of reduction, the final composition of the reduced samples was almost the same as at 1400 °C, with the extent of reduction of 91 pct.

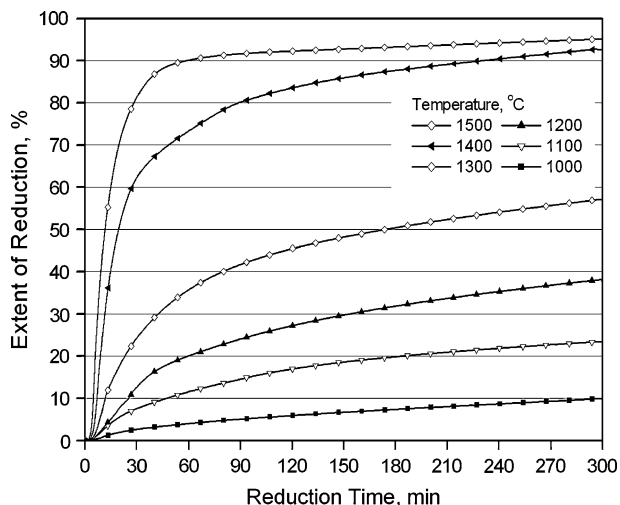


Fig. 8—Effect of temperature on extent of reduction in helium.

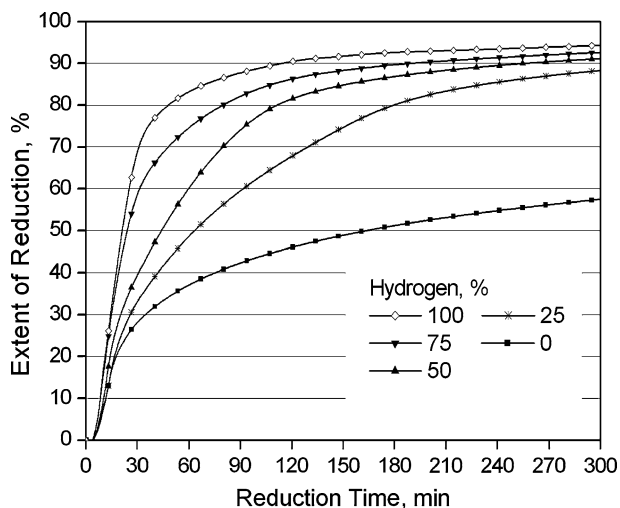


Fig. 9—Reduction of titania in argon-hydrogen gas mixtures with different hydrogen contents at 1300 °C.

Carbothermal reduction curves of titania at different temperatures in helium are presented in Figure 8. The reduction curves are similar to those in argon. Phases detected in samples reduced at the same temperatures in these two gases were also identical. The extent of reduction achieved was 90 pct in 230 minutes at 1400 °C and 60 minutes at 1500 °C. The final extent of reduction after 300 minutes was 93 pct at 1400 °C and 95 pct at 1500 °C.

The effect of hydrogen content in the H₂-Ar and H₂-He gas mixture on the carbothermal reduction of titania was examined at 1300 °C. The reduction curves obtained in experiments in the hydrogen-argon gas mixtures with different hydrogen contents are presented in Figure 9. In pure argon, an extent of reduction was 57 pct after a 300-minute reduction. The addition of 25 vol pct hydrogen significantly increased the rate and extent of reduction. The final extent of reduction increased to 88 pct. A further increase in hydrogen content to 50 to 100 vol pct consistently accelerated the reduction process.

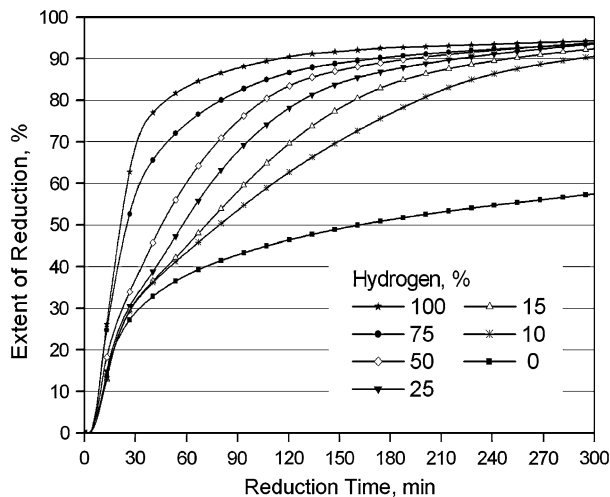


Fig. 10—Reduction of titania in helium-hydrogen gas mixtures with different hydrogen contents at 1300 °C.

A similar effect of hydrogen was observed in the carbothermal reduction of titania in the hydrogen-helium mixtures (Figure 10). An addition of 10 vol pct hydrogen into helium resulted in an increase in the extent of reduction from 57 to 90 pct. Further increasing the hydrogen content consistently accelerated the reduction process. The reduction curves obtained in experiments with 25 and 75 vol pct hydrogen in helium were close to those obtained in the hydrogen-argon gas mixtures with the same level of hydrogen.

C. Phase Development in the Progress of Reduction

In the reduction experiments at 1300 °C in hydrogen, argon, and helium, samples reduced to different extent were analyzed by XRD. The XRD patterns of samples reduced in hydrogen and argon are presented in Figures 11 and 12, respectively. The XRD spectra of samples reduced in helium were similar to those obtained in argon. After 10 minutes of reduction in hydrogen, titania was reduced to Ti₃O₅ and Ti₂O₃. No unreduced TiO₂ was detectable. In the sample reduced for 20 minutes, titanium oxycarbide was observed while Ti₂O₃ was the main component. Conversion of Ti₂O₃ into titanium oxycarbide was completed in 120 minutes.

After 20 minutes of reduction in argon and helium, the main phases were Ti₃O₅ and Ti₂O₃. TiO_xC_y was observed in samples reduced in either inert gas after 20 minutes of reduction. After 30 minutes of reduction, almost all Ti₃O₅ was reduced to Ti₂O₃ and TiO_xC_y. Conversion of Ti₂O₃ to TiO_xC_y was completed after 180 minutes of reduction. Further reduction involved slow replacement of oxygen in oxycarbide by carbon. The TiO and TiC form a solid solution with structural parameters changing slightly with the solution composition. The XRD patterns of TiO-TiC solutions of different composition were very close to one another.

Table I presents the extent of reduction and composition of samples reduced at different temperatures for various times in hydrogen. The titanium oxycarbide

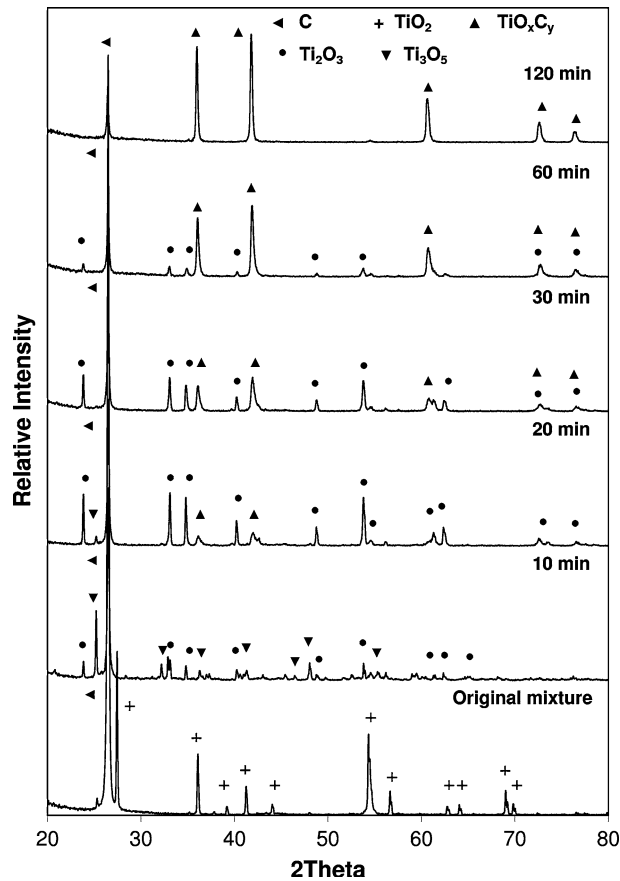


Fig. 11—XRD patterns of samples reduced in hydrogen at 1300 °C for different times.

composition was calculated only for samples reduced in hydrogen, in which no titanium suboxides were detected by XRD. The titanium oxycarbide produced at 1300 °C in a 120-minute reduction experiment contained 18 mol pct TiO. The TiO content decreased to 13 and 11 mol pct with increasing reduction time to 180 and 240 minutes, respectively. At 1400 °C, the titanium oxycarbide contained up to 27 mol pct TiO after 30 minutes of reduction and 3.4 mol pct after 180 minutes. At 1500 °C, titanium oxycarbide with 9.6 mol pct TiO was obtained after 20 minutes of reduction. The TiO content was reduced to 1.4 mol pct after 180 minutes and 1.0 mol pct after 300 minutes. The oxygen content in the titanium oxycarbide decreased with either extending reduction time or increasing reduction temperature. Increasing reduction temperature was more effective than extending reduction time. Further increasing the reduction temperature to 1600 °C increased the extent of reduction to 99.7 pct, with a corresponding titanium oxycarbide composition of $\text{TiO}_{0.006}\text{C}_{0.994}$.

IV. DISCUSSION

Analysis of phases in the progress of carbothermal reduction showed that titania was reduced through the Magneli phases to Ti_2O_3 , and then Ti_2O_3 was further

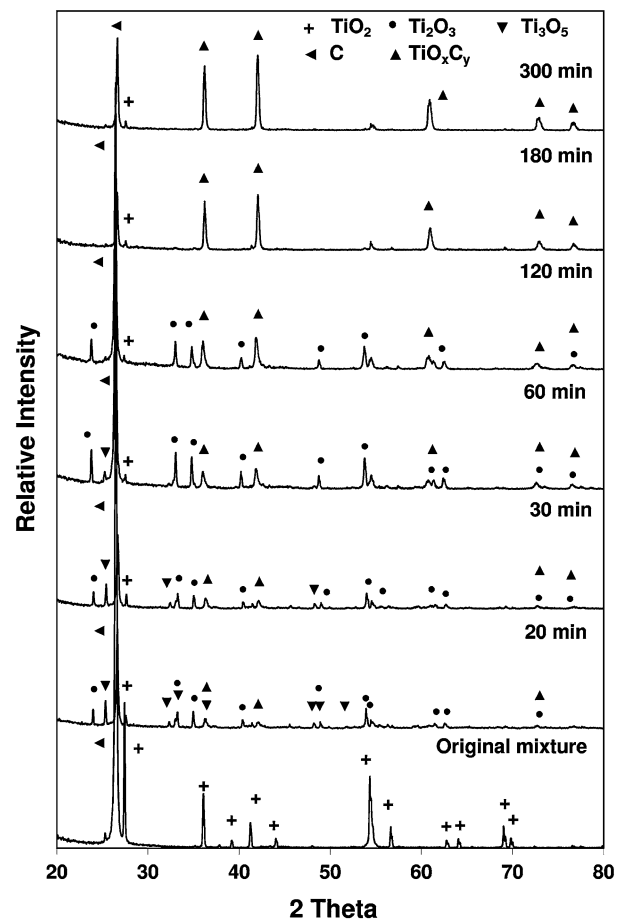
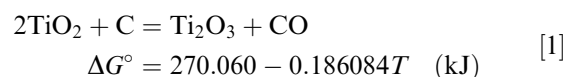


Fig. 12—XRD patterns of samples reduced in argon at 1300 °C for different times.

Table I. Extent of Reduction and Composition of Titanium Oxycarbide of Samples Reduced in Hydrogen

Reduction Temperature, °C	Reduction Time, Min	Extent of Reduction, Pct	Composition
1300	120	91.2	$\text{TiO}_{0.18}\text{C}_{0.82}$
1300	180	93.7	$\text{TiO}_{0.13}\text{C}_{0.87}$
1300	240	95.3	$\text{TiO}_{0.11}\text{C}_{0.89}$
1400	30	86.4	$\text{TiO}_{0.27}\text{C}_{0.73}$
1400	60	95.6	$\text{TiO}_{0.088}\text{C}_{0.912}$
1400	120	97.6	$\text{TiO}_{0.048}\text{C}_{0.952}$
1400	180	98.3	$\text{TiO}_{0.034}\text{C}_{0.966}$
1500	20	95.2	$\text{TiO}_{0.096}\text{C}_{0.904}$
1500	30	96.8	$\text{TiO}_{0.064}\text{C}_{0.936}$
1500	60	98.5	$\text{TiO}_{0.030}\text{C}_{0.970}$
1500	180	99.3	$\text{TiO}_{0.014}\text{C}_{0.986}$
1500	300	99.5	$\text{TiO}_{0.010}\text{C}_{0.990}$
1600	300	99.7	$\text{TiO}_{0.006}\text{C}_{0.994}$

reduced to a solid TiO-TiC solution. Reduction reactions can be presented as follows:



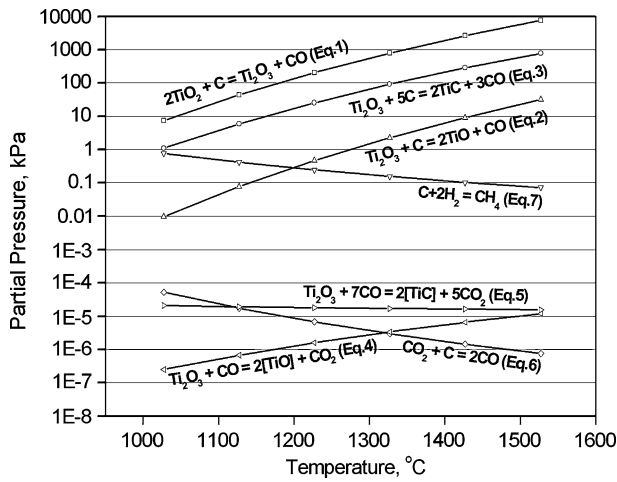
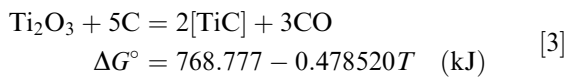
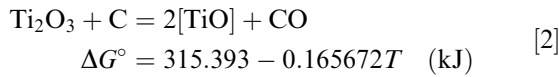


Fig. 13—Equilibrium partial pressure of CO for Reactions [1] through [3], CO₂ for Reactions [4] through [6] (calculated with $P_{\text{CO}} = 1$ kPa), and CH₄ for Reaction [7] ($P_{\text{H}_2} = 100$ kPa).



The standard Gibbs free energy changes of the reactions were calculated using data from the *NIST-JANAF Thermochemical Tables*^[12] in the range of 1027 °C to 1527 °C. The equilibrium partial pressures of CO from Reactions [1] through [3] are plotted in Figure 13. The reduction of titania to Ti₂O₃ thermodynamically is much easier than the Ti₂O₃ further reduction to TiO and TiC. The formation of TiC is more favorable than TiO. This is consistent with the experimental results.

The rate of carbothermal reduction of titania was affected by the gas atmosphere. Figure 14 compares the rates of carbothermal reduction of titania at 1400 °C in different gas atmospheres. Except the slow final reduction stage, the reduction rate in hydrogen was much higher than in inert argon and helium. Overall, the rates of reduction in helium and argon were about the same.

In the solid-state carbothermal reduction, the reaction is executed by the transfer of carbon from the graphite phase to the oxide phase, and of oxygen from the oxide phase to graphite.

In argon and helium, Reactions [2] and [3] proceed through the following reactions:

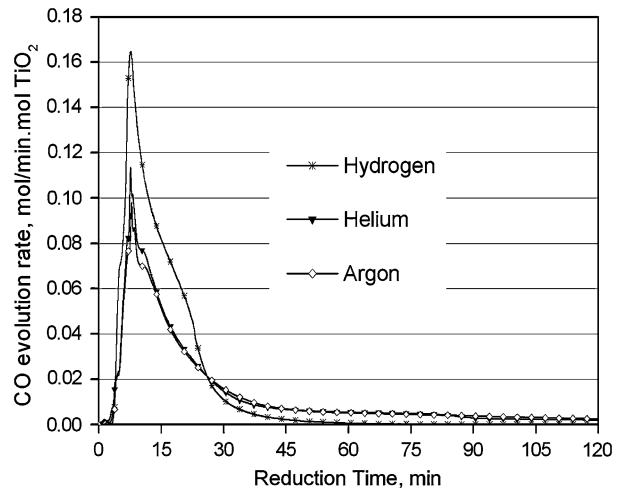
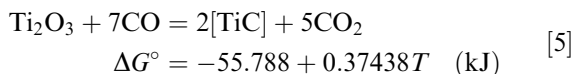
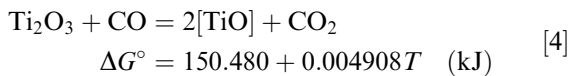
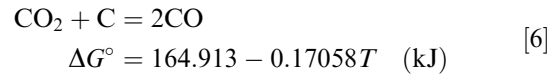
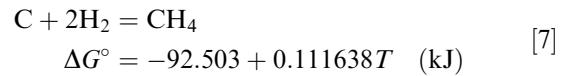


Fig. 14—Effect of gas atmosphere on CO evolution at 1400 °C.

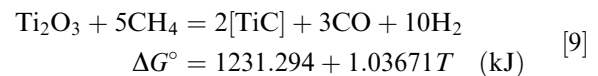
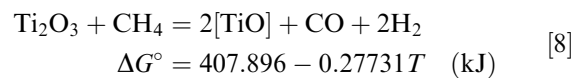
The CO₂ formed in Reactions [4] and [5] is then converted back to CO by the Boudouard reaction:



When the reduction of titania is carried out in hydrogen or hydrogen containing gas, hydrogen is involved in reduction reactions. First, hydrogen reduces titania to its suboxides,^[8] which accelerates the overall reduction process. This role of hydrogen is effective in the early stage of reduction until titania is reduced to Ti₂O₃. Second, methane can be formed by the reaction of hydrogen and carbon:



The methane can act as a reductant reducing titanium oxide to oxycarbide:



Formation of the reaction intermediates CH₄ or CO₂ in the carbothermal reduction does not change the thermodynamics of related reduction reactions, but affects the reaction kinetics. Assuming a CO partial pressure of 1 kPa and H₂ partial pressure of 100 kPa, the equilibrium partial pressures of CO₂ in Reactions [4] through [6] and the equilibrium partial pressure of CH₄ in Reaction [7] were calculated and plotted in Figure 13. The concentration of CH₄ is by four to five orders higher than that of CO₂. This explains why the

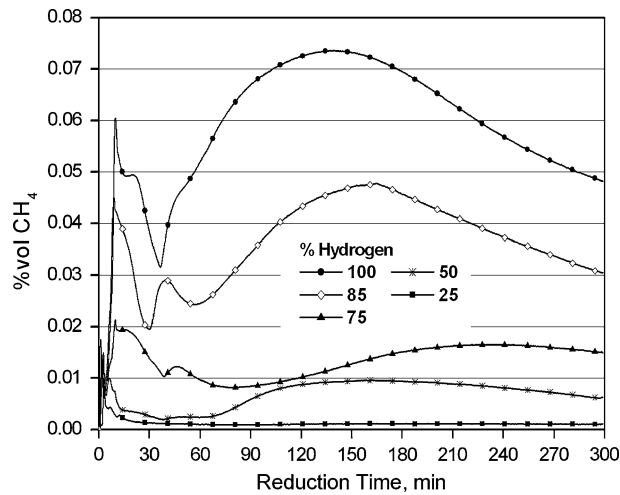


Fig. 15—Concentration of CH₄ in the off-gas in the process of carbothermal reduction of titania in hydrogen-argon mixtures at 1300 °C.

carbothermal reduction was much faster in hydrogen than in argon and helium.

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 800 ppm. The observed change of methane content during reduction with hydrogen content in the hydrogen-argon mixtures is presented in Figure 15. Increasing the partial pressure of hydrogen increases the equilibrium partial pressure of methane and enhances the reduction of titania.

V. CONCLUSIONS

The carbothermal reduction of titania was strongly affected by temperature and gas composition. The reduction rate increased with increasing temperature and hydrogen partial pressure. The reduction rates in argon and helium were similar.

The formation of titanium oxycarbide started at 1200 °C in all gases. The formation of the titanium oxycarbide in hydrogen was completed in 120 minutes

at 1300 °C, 60 minutes at 1400 °C, and less than 30 minutes at 1500 °C. In argon and helium, a higher temperature and longer reaction time were needed.

The oxygen content of titanium oxycarbide can be decreased by extending the reduction time and increasing the reduction temperature. The reduction temperature had a stronger effect than the reduction time. After reduction at 1600 °C in hydrogen for 300 minutes, the titanium oxycarbide contained only 0.6 mol pct TiO.

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