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Carbothermal reduction of silica in nitrogen and nitrogen-hydrogen mixture

Abstract

Carbothermal reduction of silica was investigated in a fixed bed reactor at 1300-1650 °C in nitrogen at 1-11 atm pressure and in hydrogen-nitrogen mixtures at atmospheric pressure. Samples were prepared from silica-graphite mixtures in the form of pellets. CO evolution in the reduction process was monitored using an infrared sensor; oxygen, nitrogen and carbon contents in reduced samples were determined by LECO analyses. Phases formed in the reduction process were analysed by XRD. Silica was reduced to silicon nitride and silicon carbide; their ratio was dependent on reduction time, temperature and nitrogen pressure. Reduction products also included SiO which was removed from the pellet with the flowing gas. In the temperature-programmed experiments, reduction of silica started below 1300 °C; the reduction rate increased with increasing temperature. Silicon carbide was the major product at the early stage of reduction; a fraction of silicon nitride increased with increasing reaction time. Maximum silicon nitride to carbide ratio (68.0/9.8 specifically for 720 min) in the reduction of silica in nitrogen at atmospheric pressure was observed at 1450 °C. Further increase in temperature decreased Si₃N₄/SiC ratio. When nitrogen pressure was 11 atm, maximum Si₃N₄/SiC ratio of 71.4/13.3 was observed at 1550-1600 °C. Increasing nitrogen pressure increased reduction and nitridation rates and suppressed SiO loss under otherwise the same conditions.

Keywords

silica, nitrogen, hydrogen, carbothermal, mixture, reduction

Disciplines

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**CARBOTHERMAL REDUCTION OF SILICA IN NITROGEN
AND NITROGEN-HYDROGEN MIXTURE**¹Xiaohan Wan, ²Guangqing Zhang, ¹Oleg Ostrovski, ³Hal Aral¹School of Materials Science and Engineering, the University of New South Wales,
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Wollongong, NSW 2522, Australia³Institute for Sustainability and Innovation, Victoria University, Werribee, VIC 3030, Australia**ABSTRACT**

Carbothermal reduction of silica was investigated in a fixed bed reactor at 1300-1650°C in nitrogen at 1-11 atm pressure and in hydrogen-nitrogen mixtures at atmospheric pressure. Samples were prepared from silica-graphite mixtures in the form of pellets. CO evolution in the reduction process was monitored using an infrared sensor; oxygen, nitrogen and carbon contents in reduced samples were determined by LECO analyses. Phases formed in the reduction process were analysed by XRD. Silica was reduced to silicon nitride and silicon carbide; their ratio was dependent on reduction time, temperature and nitrogen pressure. Reduction products also included SiO which was removed from the pellet with the flowing gas.

In the temperature-programmed experiments, reduction of silica started below 1300°C; the reduction rate increased with increasing temperature. Silicon carbide was the major product at the early stage of reduction; a fraction of silicon nitride increased with increasing reaction time. Maximum silicon nitride to carbide ratio (68.0/9.8 specifically for 720 min) in the reduction of silica in nitrogen at atmospheric pressure was observed at 1450°C. Further increase in temperature decreased Si₃N₄/SiC ratio. When nitrogen pressure was 11 atm, maximum Si₃N₄/SiC ratio of 71.4/13.3 was observed at 1550-1600°C. Increasing nitrogen pressure increased reduction and nitridation rates and suppressed SiO loss under otherwise the same conditions.

KEYWORDS: Silica, carbothermal reduction, silicon nitride, silicon carbide.

1. INTRODUCTION

Silicon nitride has been extensively studied as an advanced ceramic material for high temperature application due to its excellent high temperature properties: high strength and hardness, resistance to creep, oxidation, and thermal shock [1-3]. There are several routes to produce silicon nitride. Commercial Si₃N₄ is manufactured by direct nitridation, Si-diimide processing, and carbothermal reduction/nitridation. Carbothermal reduction/nitridation process has some advantages which include cheaper raw materials, low level of impurities and solid state conversion. This process is examined in the present work.

Zhang and Cannon [4] reported a significant SiO₂ reduction at the reaction temperature above 1425°C. Liou and Chang [5] observed that SiO₂ reduction slowed down after a period time when the temperature was higher than 1450°C. They suggested that the reactant surface was gradually covered with the solid product what caused the decline of reduction rate. Boundary temperature for the silicon nitride synthesis above which silicon carbide is formed is of particular interest. Various values of this temperature were reported: 1450°C [6], 1500°C [7], 1510-1550°C [8], and 1590°C [9]. These differences may be due to kinetic considerations [6], impurities in reaction system [4, 10-13], and error margins in experimental methods.

Generally carbothermal synthesis of silicon nitride is conducted in nitrogen gas atmosphere [9, 10, 13-17]. Some experimental works have been carried out with different gas atmosphere including a gas mixture with 95% N₂ and 5% H₂ [18-20]. Henry and Jack [9] examined the effect of nitrogen partial pressure p_{N_2} in the N₂-Ar gas mixture with atmospheric total pressure. They reported that to avoid formation of SiC minimum $p_{N_2} = 0.45$ atm was needed. Ekelund and Forslund [14] studied the effect of nitrogen pressure at elevated p_{N_2} up to 6 MPa. Increase in N₂ pressure to 2 MPa resulted in the greatest yield of Si₃N₄.

Analysis of literature shows that data on carbothermal synthesis of silicon nitride are limited and inconsistent. This paper examines effects of reaction temperature, hydrogen addition, and nitrogen pressure on the carbothermal reduction/nitridation synthesis of silicon nitride.

2. EXPERIMENTAL

Silica-graphite mixture was mixed with addition of 0.3 wt% carboxymethylcellulose. The C to SiO₂ molar ratio was 4.5. The powder mixture was loaded into a die with 8 mm diameter and pressed at 20 kN for 2 min into a pellet with mass of ~0.8 g.

Carbothermal reduction/nitridation was conducted in nitrogen or the hydrogen-nitrogen mixture. Brooks mass flow controllers (model 5850E; Brooks Instruments, Hatfield, PA) were used to control the gas flow rate. An infrared CO/CO₂/CH₄ sensor (Advanced Optima Uras 14; ABB, Ladenburgh, Germany) was employed to analyse concentrations of CO, CO₂, and CH₄ in the off gas.

In the temperature-programmed reduction experiment, the furnace temperature was ramped from 1300°C to 1600°C at a ramping rate of 3 °C/min. The CO content was monitored continuously during the heating period.

Phases in samples after reaction were examined 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 and nitrogen contents were detected by LECO TC 600 Nitrogen/Oxygen Determinator. The carbon contents of the reduced samples were analysed by LECO SC-444 DR Carbon/Sulphur Determinator.

The extent of reduction (x_{SiO_2}) of silica was defined as fraction of oxygen removed from SiO₂ by the reduction. The extent of nitridation, defined as Si₃N₄ yield ($y_{Si_3N_4}$), was calculated as the fraction of Si in the form of Si₃N₄. Similarly, the extent of carburisation, defined as SiC yield (y_{SiC}), was calculated as the fraction of Si in the form of SiC.

3. RESULTS

3.1. Effect of temperature on reduction/nitridation of silica

The effect of temperature on reduction/nitridation of silica was investigated in the temperature range 1425-1500°C in the N₂-H₂ gas mixture (10 vol% H₂) with gas flow rate 1 L/min at 1 atm pressure. Fumed silica-graphite mixture was employed with a molar C/SiO₂ ratio of 4.5. Figure 1 presents the conversion of SiO₂ with reaction time. The rate of SiO₂ reduction increased with increasing temperature. Complete SiO₂ reduction at 1425°C was reached for about 420 min. The reduction completion time decreased to 300 min at 1450°C, 180 min at 1475°C and 120 min at 1500°C.

Table 1 presents elemental composition of the reduced samples, weight loss of the samples, calculated extent of reduction of silica and the yields of Si₃N₄, SiC and SiO. The weight loss was calculated by the mass difference between an initial and reacted sample divided by the mass of an

initial pellet.

XRD analysis showed that fumed silica was not totally amorphous; weak quartz peaks were observed in the XRD spectra. Silica peaks were not seen in XRD spectra of reduced samples, which included α - Si_3N_4 , β - Si_3N_4 , SiC and excess C. α - Si_3N_4 was the dominant phase of silicon nitride; the relative content of β - Si_3N_4 showed a tendency to decrease with increasing temperature. The relative intensity of β -SiC peak was also observed to decrease with increasing temperature. The intensity of the graphite peak dropped with increasing temperature. Carbon was consumed by the reduction reactions and reaction with H_2 .

Table 1: Effect of temperature on the composition of samples after 720 min silica reduction/nitridation

Temperature, °C	Weight loss, %	O, wt%	N, wt%	C, wt%	x_{SiO_2} , %	$y_{\text{Si}_3\text{N}_4}$, %	y_{SiC} , %	y_{SiO} , %
1400	55.0	0.66	22.8	32.5	98.9	62.7	16.9	19.3
1450	61.1	0.66	28.6	20.9	99.1	68.0	9.8	21.2
1500	68.1	0.54	31.6	8.5	99.4	61.7	14.7	23.0
1550	72.0	0.48	31.7	5.15	99.5	54.3	16.6	28.6

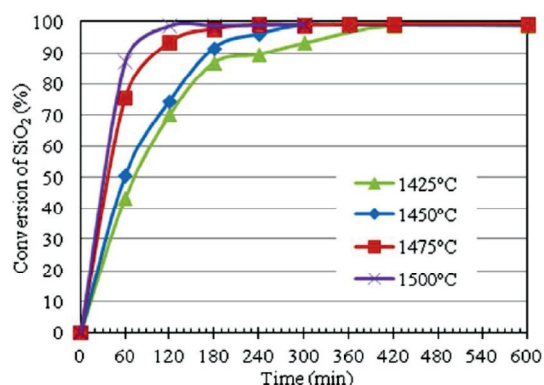


Figure 1: Effect of temperature on conversion of fumed SiO_2 in 10 vol% H_2 –90 vol% N_2 mixture at atmospheric pressure. C/ SiO_2 molar ratio was 4.5; gas flow rate was 1 L/min

Weight loss increased with increasing temperature. According to the overall Reaction (1) of Si_3N_4 formation, the theoretical weight loss in 100% conversion of SiO_2 to Si_3N_4 equals to 32.7% for the mixture with C/ SiO_2 molar ratio of 4.5; a theoretical weight loss of 49.1% corresponds to 100% conversion of SiO_2 to SiC according to Reaction (2):



The experimental weight loss shown in table 1 was much higher than the theoretical values. Typically the weight loss is due to loss of SiO, CO, and CO_2 gases purged by flowing gas. SiO loss (y_{SiO}) increased with an increase in temperature from 1400°C to 1550°C. At a higher reduction temperature, SiO had a higher partial pressure due to increased rate of SiO_2 reduction; a higher amount of SiO is purged away by flowing gas. The carbon content (C wt%) dropped from 32.5% at 1400°C to 5.15% at 1550°C, which was consistent with the decline of C peak intensity shown in figure 2.

The SiO_2 conversion (x_{SiO_2}) was close to 100% for all samples after 720 min reduction. Residual oxygen (< 0.7 wt%) in the reduced samples was attributed to unreduced SiO_2 in table 1, although contamination of the reduced products by oxygen in air when samples were taken from the reactor cannot be excluded.

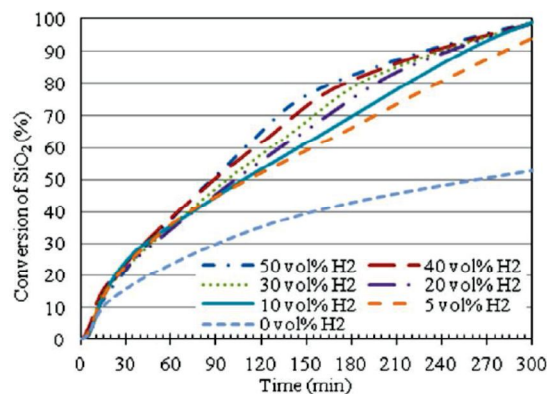


Figure 2: Effect of hydrogen addition in nitrogen on conversion of fumed SiO_2 . C/SiO_2 molar ratio was 4.5; gas flow rate was 1 L/min; reaction temperature was 1450 °C

The nitrogen content (N wt%) increased with increasing temperature. However Si_3N_4 yield was not directly in proportion to the N wt% value, as the sample weight changed. The greatest Si_3N_4 yield of 68.0% was obtained at 1450°C; it decreased to 54.3% with increasing temperature to 1550°C, which is consistent with thermodynamic analysis (Si_3N_4 is less stable at high temperatures). At a lower temperature of 1400°C, the level of $y_{\text{Si}_3\text{N}_4}$ of 62.7% was slightly lower than that reached at 1450°C due to slower rate of Si_3N_4 formation. The change in SiC yield followed a trend opposite to that of Si_3N_4 . The lowest yield of SiC of 9.8% was attained at 1450°C, at which the Si_3N_4 yield was the highest.

3.2. Effect of hydrogen addition on reduction/nitridation of silica

It was reported that carbothermal reduction of stable oxides of manganese, chromium and titanium in hydrogen is faster than in inert gas atmospheres [21-24]. The effect of hydrogen addition on the carbothermal synthesis of silicon nitride was examined by adding H_2 to N_2 from 5 vol% to 50 vol%. The experiments were carried out with fumed silica-graphite mixture with C/SiO_2 molar ratio of 4.5 at 1450°C at atmospheric pressure. The gas flow rate was 1 L/min. The SiO_2 conversion with time is presented in figure 2.

Addition of H_2 significantly enhanced the kinetics of SiO_2 reduction. After 300 min reaction, SiO_2 conversion was increased from 53% in N_2 to 94% in 5 vol% H_2 -95 vol% N_2 mixture. The rate of SiO_2 reduction increased with further increase in H_2 content from 5 vol% to 50 vol% although with a lower increment.

No silica was detected in samples reduced in N_2 - H_2 gas atmosphere by the XRD analysis, although the cristobalite peak ($2\theta = 21.95^\circ$) was detected in the sample reduced in N_2 . The XRD patterns of the samples reduced in H_2 containing gases were all similar except the significant decrease in the strength of the graphite peak at $2\theta = 26.50^\circ$, which can be explained by reaction of graphite with hydrogen with formation of methane. The rate of CH_4 formation increased with increase in H_2 content in the gas mixture. The relative intensity of Si_3N_4 peaks increased with addition of 5 vol% of H_2 , and then changed only marginally. α - Si_3N_4 was the main phase of silicon nitride, although β - Si_3N_4 was also detected. β -SiC peaks at $2\theta = 35.63^\circ$ were observed in all the

reacted samples.

There was a significant increase in the weight loss, from 29.8 % to 49.4 % when 5 vol% of H₂ was added to nitrogen. The weight loss kept increasing with increasing H₂ content which was partially attributed to the increased SiO loss (y_{SiO}).

Besides SiO, CO and CO₂ purged away by flowing gas, consumption of C by reacting with H₂ to form CH₄ also contributed to the weight loss; the carbon content in the reduced samples decreased from 44.9% in the reduction in N₂ to 21.1% in the reduction in gas containing 50 vol% H₂. This result is consistent with a sharp decrease in the relative intensity of C peak at $2\theta = 26.50^\circ$ with increasing H₂ content. The nitrogen and silicon nitride contents in the reduced samples increased with increasing H₂ content in the gas mixture from 0 vol % to 40 vol% and decreased when hydrogen content increased further to 50 vol%. Increasing H₂ content in the gas mixture was beneficial to the kinetics of SiO₂ reduction, however, it also decreased the N₂ partial pressure which was detrimental to the formation of Si₃N₄. Similar results were reported by Henry and Jack [9]. They used N₂-Ar gas to control the N₂ partial pressure, and reported 0.5 atm of p_{N_2} was the minimum to ensure the high Si₃N₄ yield. The greatest yield of Si₃N₄ was obtained at 10 vol% of H₂.

The highest yield of silicon carbide of 42.8% was obtained in the experiment in N₂. When 10 vol% of H₂ was added to the gas, the SiC yield of 23.1% was the lowest. Increasing H₂ content above 10 vol% resulted in an increase in y_{SiC} up to 37.2%. The best selectivity of Si₃N₄ to SiC ($y_{\text{Si}_3\text{N}_4}/y_{\text{SiC}}$) was obtained in reduction in gas containing 10 vol % H₂.

3.3. Effect of nitrogen pressure on reduction/nitridation of silica

It is expected from Reaction (1), that increasing nitrogen pressure promotes silicon nitride formation. It is also expected that Si₃N₄ will be more stable at elevated N₂ pressure; therefore Si₃N₄ can be produced at higher temperatures with a higher rate. Experiments with fumed silica mixed with graphite in the molar ratio of C/SiO₂ of 4.5 were carried in nitrogen with gas flow rate 1 L/min at pressure of 11 atm in the temperature range of 1450°C to 1650°C for 60 min.

Table 2 shows the elemental composition, weight loss, extent of reduction and yield of silicon nitride and silicon carbide. The reduction rate of SiO₂ increased with increasing temperature.

The sample reduced at 1450°C contained 19.3 wt% of oxygen which corresponds to the extent of reduction of 39.3%. The oxygen content decreased to 13.1 wt%, while the extent of reduction increased to 64.1% at 1500°C. Further increasing temperature to 1550°C decreased oxygen content to 3 wt%, and SiO₂ conversion increased to 95.3%. The data also confirmed that the conversion of SiO₂ was complete in 60 min at 1600°C and 1650°C.

Table 2: Carbothermal synthesis of silicon nitride in nitrogen under pressure 11 atm

Temperature, °C	Weight loss, %	O, wt%	N, wt%	C, wt%	x_{SiO_2} , %	$y_{\text{Si}_3\text{N}_4}$, %	y_{SiC} , %	y_{SiO} , %
1450	18.5	19.3	4.4	49.5	39.3	23.6	12.5	3.2
1500	29.3	13.1	8.0	48.5	64.1	37.3	21.7	5.1
1550	40.0	2.0	17.4	47.0	95.3	69.2	14.9	11.2
1600	42.7	0.30	18.8	47.1	99.3	71.4	13.3	14.6
1650	45.5	0.33	4.1	56.2	99.4	13.3	70.2	15.9

Both α -Si₃N₄ and β -Si₃N₄ were detected in the reduced samples by XRD, with α -Si₃N₄ being the main form of Si₃N₄. SiC was in the form β -SiC. Si₃N₄ peaks were observed in all experiments after 60 min reaction; strength of Si₃N₄ increased while the strength of SiC peaks decreased with

increasing temperature from 1450°C to 1600°C. At 1650°C, however, the Si₃N₄ peaks were significantly weaker, while SiC peak became stronger.

The yield of Si₃N₄ was 23.6 % in reduction at 1450°C (table 2). It increased to 37.3 % at 1500°C, 69.2 % at 1550°C, and reached the maximum at 1600°C. The yield of SiC at 1450°C was relatively low, 12.5 % due to a low SiO₂ conversion. It increased to 21.7 % at 1500 °C, however, decreased with further increasing temperature until 1600°C at which the yield was 13.3 %. Further increase in temperature to 1650°C reversed the above trend. Up to 70.2 % of Si was in the form SiC, while Si₃N₄ yield was only 13.3 %. The weight loss in reduction increased from 18.5 % to 45.5 % with increasing temperature from 1450°C to 1650°C. The loss of SiO also increased from 3.2 % to 15.9 %. An increase in the weight loss was consistent with increased SiO₂ reduction rate with increasing reaction temperature.

The effect of N₂ pressure in the range 7-11 atm on carbothermal synthesis of Si₃N₄ was further investigated in 60 min reduction experiments at 1600°C. Table 3 presents the elemental composition of the reduced samples and the extent of reduction and Si distribution between different phases.

Table 3: Effect of nitrogen pressure on carbothermal synthesis of silicon nitride at 1600 °C

p _{N₂} , atm	Weight loss, %	O, wt%	N, wt%	C, wt%	x _{SiO₂} , %	y _{Si₃N₄} , %	y _{SiC} , %	y _{SiO} , %
7	46.1	0.37	12.0	50.1	99.2	43.0	45.4	10.8
9	43.1	0.27	16.2	48.8	99.4	61.0	25.5	12.9
11	42.7	0.30	18.8	47.1	99.3	71.4	13.3	14.6

Reduction of SiO₂ was close to completion in all experiments with N₂ pressure in the range 7-11 atm. The major difference between the samples reduced under different N₂ pressures was the distribution of Si between nitride and carbide: the yield of Si₃N₄ increased from 43.0 % to 71.4 % while the yield of SiC decreased from 45.4 % to 13.3 % when the N₂ pressure was increased from 7 atm to 11 atm. The greatest selectivity of Si₃N₄ to SiC was obtained in the case of 11 atm of N₂ pressure.

The weight loss slightly decreased from 46.1 % to 42.7 % while the SiO loss increased from 10.8 % to 14.6 % with the increase in N₂ pressure from 7 atm to 11 atm. The decreased weight loss with increasing N₂ pressure was attributed to higher nitride yield at higher pressure which increased the content of nitrogen in the reduced sample.

Increase of SiO loss can be related to the increased the partial pressure with increasing total pressure. This factor suppresses the reduction of SiO₂.

1.1. Phase development in the process of reduction/nitridation of silica

Figure 3 shows changes of silicon distribution among different compounds in the process of reduction of fumed silica (C/SiO₂ molar ratio of 4.5) at 1450 °C. Reduction was conducted in the gas mixture of 10 vol% H₂-90 vol% N₂ with the total flow rate of 1 L/min.

In the early stage of reduction, both α-Si₃N₄ and β-Si₃N₄ peaks were detected by XRD analysis, but β-SiC was the main phase in the reduction product. With further progress of the reaction, SiC was converted to Si₃N₄; SiC peaks increased till about 360 min and then decreased to a minor peak at 840 min. Si₃N₄ peak intensity kept increasing along the process. At 300 min SiO₂ was almost depleted. At the end of 840 min reaction, about 82.4 % of Si was converted into Si₃N₄. Formation rate of SiC was greater than that of Si₃N₄ until approximately 120 min reaction. Then the content of SiC started to drop to almost zero by the end of 840 min reaction. There was

approximately 18 % of Si loss in the form of SiO.

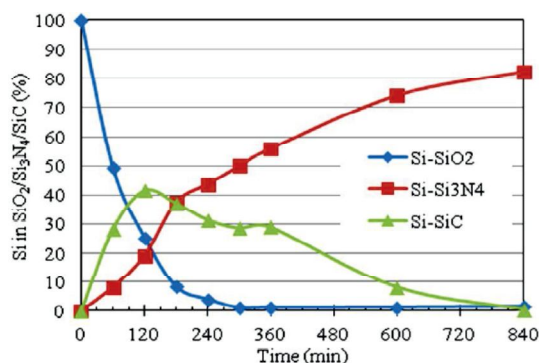


Figure 3: Silicon distribution between SiO₂, Si₃N₄, and SiC in fumed silica reduced in the 10 vol % H₂-90 vol% N₂ gas mixture at 1450°C. Gas flow rate was 1 L/min; C/SiO₂ molar ratio was 4.5

2. DISCUSSION

In carbothermal reduction of silica, both silicon nitride and carbide were formed under given experimental conditions. The standard Gibbs free energy of Reactions (1) and (2) is equal to zero at 1547°C and 1515°C, respectively. At higher temperatures, these reactions are expected to be spontaneous under standard conditions ($p_{\text{CO}}=1$ atm and $p_{\text{N}_2}=1$ atm). In practice, the CO partial pressure is much lower than the standard pressure (1 atm). Therefore, Reactions (1) and (2) can start at a lower temperature. According to the results of the temperature-programmed reduction of fumed silica, SiO₂ conversion commences before the reaction temperature reaches 1300°C.

Calculations of CO partial pressure for reactions (1) and (2) for $p_{\text{N}_2} = 0.9$ atm considering 10 vol% H₂-90 vol % N₂ gas mixture at total pressure 1 atm, showed that at temperatures below 1433 °C, calculated $p_{\text{CO}(1)}$ is slightly higher than $p_{\text{CO}(2)}$. It means that at these temperatures Si₃N₄ is thermodynamically more stable in comparison with SiC, although the difference is only 0.0313 atm at 1400°C. At temperatures above 1433°C, $p_{\text{CO}(1)}$ is smaller than $p_{\text{CO}(2)}$, indicating that SiC is more stable than Si₃N₄ at these temperatures. At 1450°C, $p_{\text{CO}(2)}$ is by 0.0281 atm higher than $p_{\text{CO}(1)}$. Compared to equilibrium CO partial pressures for reactions (1) and (2), the difference between $p_{\text{CO}(1)}$ and $p_{\text{CO}(2)}$ is quite small. This explains that there was not a sharp boundary temperature for a preferential formation of Si₃N₄ or SiC under given experimental conditions (figure 1, table 1). At 1550°C, although $p_{\text{CO}(1)} = 0.989$ atm is smaller than $p_{\text{CO}(2)} = 1.46$ atm, the potential to form Si₃N₄ is still significant. It should be noted that the actual CO partial pressure cannot be higher than 1 atm for the reaction conducted under atmospheric pressure. The equilibrium CO partial pressure higher than 1 atm indicates a strong thermodynamic potential for reaction to occur.

Carbothermal reduction of oxides proceeds through the gas phase. Thus, reaction (2) for SiC formation can be presented as a sum of reactions (3) and (4):



Reduction of SiO₂ involves carbon transfer from a C particle to SiO₂ in the form of CO and

oxygen transfer from silica to graphite in the form of CO₂. Equilibrium partial pressure of CO₂ for Reaction (3) is very low; for p_{CO}=0.1 atm, at temperatures 1450-1600°C, it is in the range (3.5-4.2)×10⁻⁶ atm. At such low CO₂ partial pressure, the reduction rate can be controlled by the mass transfer of CO₂ from SiO₂ to C and chemical reaction of carbon gasification [21-24].

Addition of hydrogen to the reaction gas atmosphere can change the reduction mechanism. H₂ can be directly involved into SiO₂ reduction according to reactions (5) and (6).



Equilibrium H₂O partial pressure for Reaction (5) increases with increasing temperature and H₂ partial pressure and decreasing SiO partial pressure. Assuming SiO partial pressure in the range from 0.01 to 0.1 atm and fixing the H₂ partial pressure at 0.1 atm, equilibrium p_{H₂O} is in the range of 3×10⁻⁶ to 3×10⁻⁵ atm at 1550°C, which is comparable with CO₂ partial pressure for reaction (3). Reaction (5) followed by Reaction (6) also explains higher C consumption with higher concentration of H₂ in reducing gas. Hydrogen reacting with carbon forms methane by reaction (7), which can reduce silica by reaction (8):



The equilibrium p_{CH₄} of reaction (7) increases with decreasing temperature and increasing H₂ partial pressure. In the experimental temperature range, calculated CH₄ partial pressure (p_{H₂}=0.5 atm) is (1-2)×10⁻⁴ atm, which is significantly higher (by more than the order in magnitude) than the equilibrium p_{CO₂} for reaction (3) and p_{H₂O} for reaction (5). H₂ addition reduces N₂ partial pressure when the total pressure is kept constant. The N₂ partial pressure is a significant factor for Si₃N₄ formation. It is seen in table 2 that the highest Si₃N₄ yield and selectivity of Si₃N₄ to SiC were obtained with 10 vol% of H₂ addition. H₂ content higher than 10 vol% led to decreased N₂ partial pressure. The SiC yield increases while Si₃N₄ yield decreases with increasing H₂ content in gas beyond 10 vol%. Conversion of SiC to Si₃N₄ according to reaction (9) is the only route of Si₃N₄ formation after SiO₂ is completely reduced according to figure 3.



The equilibrium p_{N₂} increases with increase in temperature, meaning that conversion of SiC to Si₃N₄ by reaction (9) is favoured at lower temperature. At 1400°C, reaction (9) spontaneously starts when p_{N₂} is higher than 0.64 atm. When temperature increases to 1650°C, p_{N₂} has to be above 6.92 atm to ensure Si₃N₄ formation by reaction (9). At the experimental temperature of 1450°C, the equilibrium p_{N₂} calculated using data from the NIST-JANAF thermochemical tables [25] is 1.08 atm. However, Si₃N₄ was detected in samples reduced in the N₂ gas with p_{N₂} = 0.9 atm (table 1). A possible reason is that the thermodynamic data are not accurate at high temperatures.

Equilibrium N₂ partial pressure calculated using the thermodynamic data from Thermochemical Data of Elements and Compounds [26] are different with values found using data

from [25]. When data of Binnewies and Milk [26] were used, calculated equilibrium partial pressure of nitrogen for reaction (9) of conversion of SiC to Si₃N₄ by was found 0.42 atm at 1450 °C and 0.7 atm at 1500 °C. These data explain why Si₃N₄ was formed at temperatures above 1450 °C.

Addition of H₂ can activate conversion of SiC to Si₃N₄ by the nitridation reaction (10).



3. CONCLUSIONS

In the process of carbothermal reduction in nitrogen and N₂-H₂ gas mixture, silica was converted to silicon nitride and silicon carbide with no a clear temperature boundary defining stability of these compounds. SiO₂ reduction rate increased with increasing temperature. The highest Si₃N₄/SiC ratio was observed at 1450 °C in the N₂-H₂ gas mixture with 10 vol% H₂.

Hydrogen addition to nitrogen promotes the silica conversion rate by changing the reduction mechanisms. H₂ can be directly involved into the reduction or/and by forming CH₄ by reacting with C. The maximum Si₃N₄ to SiC ratio was obtained with addition of 10 vol% H₂ at 1450 °C. Higher H₂ addition led to lower N₂ partial pressure with a negative effect on Si₃N₄ formation. Increasing nitrogen pressure increased reduction and nitridation rates. The maximum Si₃N₄/SiC ratio was observed at 1550-1600 °C under a N₂ pressure of 11 atm. Of the silicon 71.4 % was converted to Si₃N₄, and the remainder mostly formed SiC and trace residual SiO₂. The Si₃N₄ grade was shown to be pressure dependent.

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