SYNTHESIS OF SILICON CARBIDE BY CARBOTHERMAL REDUCTION OF QUARTZ IN H_2-Ar GAS MIXTURES

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ABSTRACT

This article examines the synthesis of silicon carbide by carbothermal reduction of quartz in H_2, Ar and their mixtures. The quartz was crushed to less than 70 µm, uniformly mixed with graphite and pressed into pellets with carbon/silica molar ratio of 3.6. Reduction was studied in isothermal and temperature programmed experiments in a tube reactor in continuously flowing gas atmosphere. The reduction rate increased with increasing H_2 partial pressure and temperature. Silicon carbide began to form at 1200 °C inreduction in H_2. The conversion of quartz to silicon carbide at 1400 °C was completed in 270 minutes. This period was reduced to 140 minutes at 1500 °C and 70 minutes at 1600 °C. In the carbothermal reduction of quartz in Ar, the conversion of quartz to silicon carbide started at 1300 °C, and was incomplete after 270 minutes at 1500 °C.

The faster reduction rate in H_2 containing gas was attributed to the involvement of H_2 in the reactions. At high temperatures, 1400-1600 °C, quartz was directly reduced by H_2 to silicon monoxide.

KEYWORDS: *Carbothermal reduction, silicon carbide, quartz, hydrogen, methane.*

1 INTRODUCTION

SiC is commercially produced primarily by carbothermal reduction of quartz usingcarbonaceous materials (petroleum coke, anthracite coal, bituminous coal and carbon black)at temperatures above 2000 °C. Carbothermal reduction is the primary chemicalprocess practiced commercially for the synthesis of many ceramic materials, including SiC.The overall reduction reaction can be written as

$$SiO_2\ (s) + 3C\ (s) = SiC\ (s) + 2CO\ (g) \qquad (1)$$

$$AG° = 598.18 - 0.3278\ T\ (kJ)$$

The Gibbs free energy change with temperature of Reaction (1) and other reactions in thispaper was calculated using HSC Chemistry 6.1 in the range of 1000 to 2000 °C [1]. The standard Gibbs free energy of the above reaction decreases with increasing temperature and becomes zero at 1525 °C. However, the reaction can take place at lower temperatures when the CO partial pressure is significantly lower than atmospheric pressure. It is generally accepted that SiC is synthesized through intermediate silicon monoxide (SiO) [2]:

$$C\ (s) + SiO_2\ (s) = SiO\ (g) + CO\ (g) \qquad (2)$$

$$AG° = 668.07 - 0.3288\ T\ (kJ)$$

$$SiO\ (g) + 2C\ (s) = SiC\ (s) + CO\ (g) \qquad (3)$$

$$AG° = -78.89 + 0.0010\ T\ (kJ)$$

The standard Gibbs free energy of Reaction (3) is negative in the examined temperature range, therefore the overall reaction of SiC formation is defined by the reaction of SiO formation. It is well established that the kinetics of carbothermal reduction of SiO_2 is affected by temperature [3], molar SiO_2/C ratio [4], carbon and SiO_2 particle size [5], and initial bulk density [6]. The effect of gas atmosphere on the carbothermal reduction of silica has been studied to a lesser extent. The SiC formation will stop when the CO partial pressure in Reaction (1) reaches the equilibrium value. CO has to diffuse out of the reactant mixture for further reaction to take place.

Recent work demonstrated that the gas atmosphere has a strong effect on the kinetics of the carbothermal reductions of manganese oxides [7], titania [8] and alumina [9]. Data obtained by Terayama and Ikeda [10] for the carbothermal reduction of MnO showed that MnO is reduced much faster in helium than in Ar. Similar results were obtained by Yastreboff et al. [11] in reduction of MnO, manganese ore, and ferromanganese slag.

This study investigated the carbothermal reduction of quartz in Arand H_2 containing gas. The aim of this article was to establish the effects of temperature and gas composition on the extent, rate, and mechanisms of carbothermal reduction of quartz.

2 EXPERIMENTAL

Quartz powder (particle size < 70 µm) was obtained by crushing quartz lumps in a 6 inch agate pulversiver in a Rocklabs ring mill. The agate was made of grey silica to minimise contamination of the quartz sample. Quartz powder and synthetic graphite (< 45µm, Sigma-Aldrich Co. Ltd, Germany) were mixed with distilled water (80 wt% of solid mixture) in a plastic jar with zirconia balls for 8 hours. The quartz–graphite mixture had aC/SiO_2 molar ratio of 3.6. Water was removed by heating the mixture at 120 °C for 48 hours. Then the mixture was pressed into pellets in a uniaxial hydraulic press by applying 20 KN of load for 2 minutes. The pellets with a mass of approximately 1 g were 8 mm in diameter and about 14 mm in height.

Reduction of quartz by graphite in Ar,H_2, and Ar-H_2 gas mixtures was studied in a laboratory fixed bed reactor heated in an electric vertical tube furnace. A pellet was loaded at the bottom of the inner reactor tube at the room temperature, and then heated to a desired temperature by inserting the reactor into the furnace preheated to a designated temperature for isothermal reduction experiments. Reaction was stopped after certain duration by raising the reactor above the furnace hot zone and cooling down. While in the temperature programmed reduction experiments, the reactor was loaded in the hot zone and heated with the furnace from 300 °C to 1600 °C at 3 °C /min. The gases used in the investigation were of 99.999% purity. The total gas flow rate was maintained at 1.0 NL/min at 1 atm. After reduction, the reduced pellets were weighed and analyzed.

During reduction experiments, the outlet gas composition was continuously monitored by an infrared CO/CO_2/CH_4 analyzer (Advanced optima AO2020, ABB, Ladenburg, Germany) connected ещ a computer. The gas concentrations were recorded every 5 seconds.

The original mixture and reduced samples were analyzed by X-ray diffraction (XRD, MMA, GBC Scientific Equipment, Braeside, Australia). The fine powder of a sample after grinding was scanned at a speed of 0.02° s^{-1} and step size 0.02° with CuK radiation generated at 35 kV and 28.6 mA. The oxygen content in the reduced samples was determined by LECO TC-436 DR Nitrogen/Oxygen Determinator (LECO Corporation, St. Joseph, U.S.A.).

The extent of reduction was defined as a fraction of oxygen in quartz removed in the course of reduction. Oxygen was removed in the form of CO, CO_2 and SiO. The main oxygen-containing product was CO, as CO_2 was converted to CO by the Boudouard reaction, and SiO reacted with graphite forming SiC. Using the CO and CO_2 concentrations in the off gas, the extent of reduction was calculated using Eq. (4).

$$X' = \frac{1}{n_{O-i}}\int_0^t \frac{GFR}{22.4}\left(C_{V-CO} + 2\times C_{V-CO_2}\right)dt \qquad (4)$$

where X' is the conversion of silica based on CO and CO_2 concentrations, % at time t;$C_{V-CO}$is the concentration of CO and $C_{V-CO_2}$the concentration of CO_2, vol %;GFR is the gas flow rate, NL/min;$n_{O-i}$is the initial content of oxygen in quartz, mol; and t is the reaction time, min.

More accurate extent of reduction was obtained using residual oxygen content in a reacted sample determined by LECO oxygen analysis. The conversion of $SiO_2$was obtained using Eq. (5).

$$X = \frac{100}{n_{O-i}}\left(n_{O-i} - n_{O-LECO}\right) \qquad (5)$$

where X is the conversion of silica at the end of reduction, %; n_{O-LECO} is the content of oxygen in the reacted sample, mol.

Plots of the extent of reduction X versus the reaction time t were obtained by normalizing the final extent of reduction from on-line gas analysis (Eq. (4)) to the values determined using LECO analyzer.

3 RESULTS

3.1 TEMPERATURE PROGRAMMED REDUCTION

Temperature programmed reduction experiments were carried out in a temperature range from 300 to 1600 °C, with heating rate of 3 °C/min. The extent of reduction of quartz in different gas atmospheres at various temperatures is presented in Figure 1. Reduction rate in pure Ar was low at temperatures below 1500 °C. The extent of reduction was below 30.0% at 1500 °C; itincreased to 89.0% when the temperature was increased to 1600 °C. Addition of 10 vol % H_2 to Ar significantly increased the reduction rate. The reduction of quartz was close to completion at 1600 °C. Further increasing of H_2 content in the Ar-H_2 gas mixture to 100 vol % accelerated the reduction.

To identify the changes of phase composition during the carbothermal reduction of quartz, the temperature programmed reduction experiments were stopped at different temperatures, and the samples were analyzed by XRD. Figure 2 presents the XRD patterns of the samples reduced to different temperatures in Ar. In a sample heated to 1200 °C, the only phases identified by XRD were quartz and graphite as in the original mixture. A weak peak of β-SiC was observed in the XRD spectrum of a sample heated to 1300 °C, at 2θ = 35.66o (d = 2.516 Å). Cristobalite was identified in samples heated to 1500 °C and 1600 °C, as a result of the transformation of quartz to cristobalite which took place above 1470 °C. With increasing temperature to 1600 °C, the amount of β-SiC significantly increased, with graphite and a small amount of cristobalite as residual reactants.

Figure 3 presents the XRD patterns of the samples heated to different temperatures in H_2. There was no visible change up to 1100 °C. When the temperature was increased to 1200 °C, a small amount of β-SiC was identified. With the increase of temperature, the peak intensity of β-SiC in the reduced sample became stronger, corresponding to the decrease of quartz peaks intensities. In the sample subjected to reduction until 1600 °C, only β-SiC was present besides a small amount of residual graphite; no cristobalite phase was detected by the XRD analysis. These results indicate that carbothermal reduction in H_2 was faster than in Ar; it can be suggested that the rate of quartz reduction was faster than its transformation to crystobalite.

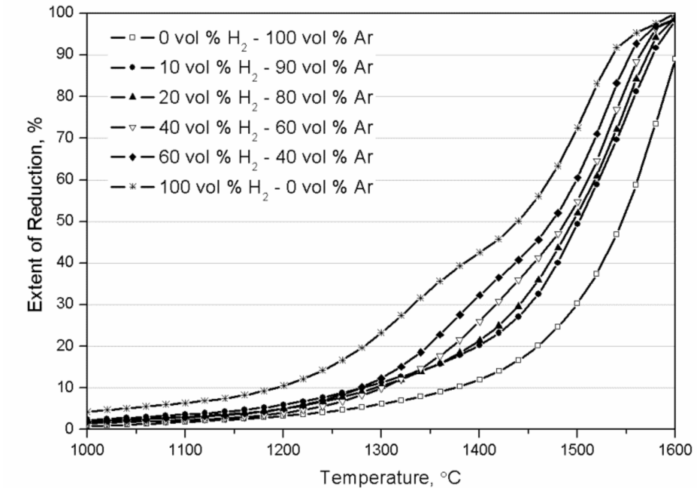

Figure 1: Effect of H_2 content in the Ar-H_2 gas mixtures on the reduction of quartz in the temperature programmed reduction experiments.

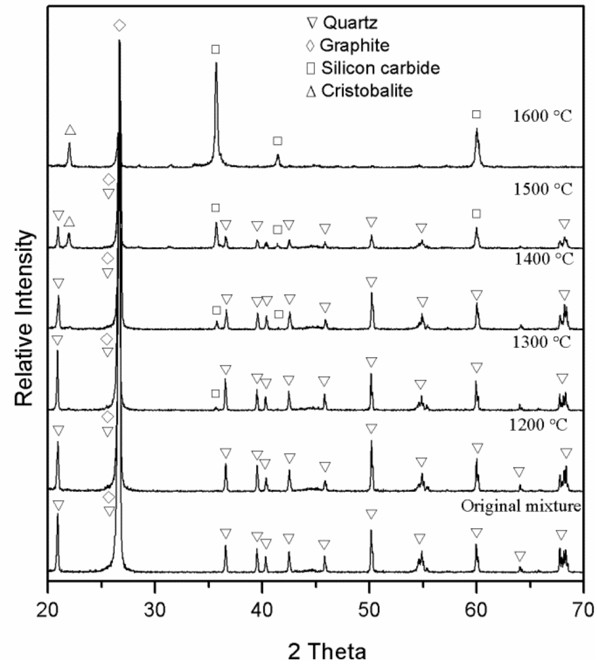

Figure 2: XRD patterns of samples in the progress of temperature programmed reduction in pure Ar.

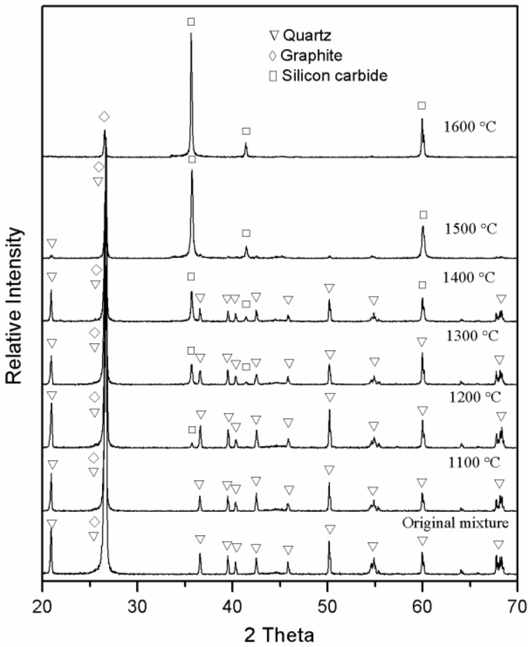

Figure 3: XRD patterns of samples in the progress of temperature programmed reduction in pure H_2.

3.2 ISOTHERMAL REDUCTION

The extent of reduction of quartz in Ar in isothermal experiments at different temperatures from 1200 to 1600 °C is presented in Figure 4. Carbothermal reduction of quartz in Ar was very slow below 1400 °C. After reduction at 1200 °C, only a small amount of quartz was reduced with the extent of reduction of 7.8% after 270 min reaction. The extent of reduction increased to 12.6 and 27.7% at 1300°C and 1400 °C, respectively. Increasing temperature to 1500 °C resulted in a significant increase of the reduction rate, and the extent of reduction after 270 min reaction reached 85.9%. The reduction was further enhanced by increasing temperature to 1600 °C, where the formation of SiC was close to completion in about 75 minutes, with the extent of reduction of 99.3% as determined from oxygen analysis in the reduced sample using LECO analyser.

The reduction curves obtained in H_2 at different temperatures are shown in Figure 5. The carbothermal reduction in H_2 was significantly faster than in Ar at 1200–1500 °C. The extent of reduction at 1200 °C after 270 minutes reached 36.0 %, which is higher than the extent of reduction reached at 1400 °C in Ar. Further increasing temperature to 1400 °C enhanced SiC formation, when the extent of reduction 98.5 % (270 min reaction). In the experiment at 1500 °C, the extent of reduction reached 99.1 % in 140 minutes. The reduction was almost completed (99.6 %) in 70 minutes at 1600 °C.

The effect of H_2 content in the Ar-H_2 gas mixtures on the carbothermal reduction of quartz was examined at 1400 °C. The reduction curves are presented in Figure 6. The extent of reduction in pure Ar was only 27.7 % after reduction for 270 minutes. The addition of 10 vol % H_2 to Ar significantly increased the reaction rate. The final extent of reduction increased to 67.7 %. Further increasing H_2 content consistently accelerated the reduction process.

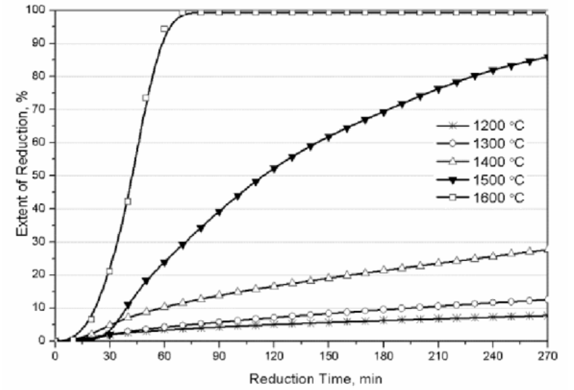

Figure 4: Effect of temperature on the reduction of quartz in Ar.

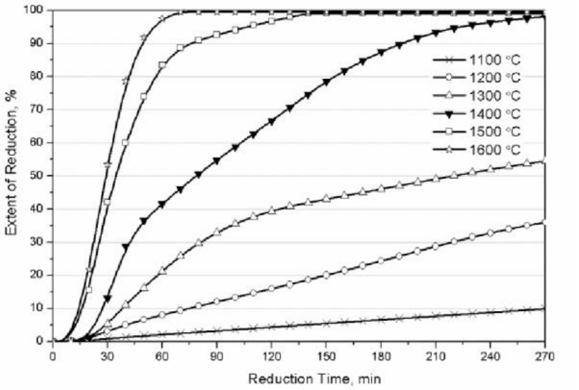

Figure 5: Effect of temperature on the reduction of quartz in H_2.

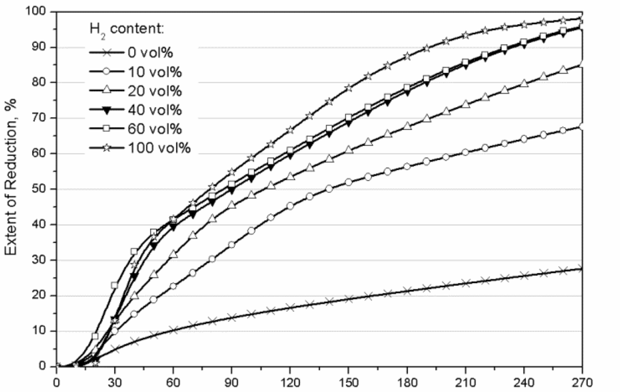

Figure 6: Reduction of quartz in Ar-H_2 gas mixtures with different H_2 contents at 1400 °C.

4 DISCUSSION

Gas atmosphere had a pronounced effect on the carbothermal reduction of quartz. Figure 7compares the rate of generation of CO in the temperature programmed reduction experiments in different gas atmospheres. In general, the reduction curves in H_2 containing gases include two peaks. With the increase of H_2 content in the inlet gas, both CO peaks shifted towards lower temperatures. When the H_2 content was increased to 100 vol %, the two CO peaks appeared at 1321 °C and 1508 °C, respectively. In the reduction in Ar, only one peak was observed on the reduction curve which did not reach maximum in the studied temperature range (up to 1600 °C).

It is well recognised that the carbothermal reduction of silica involves gaseous intermediate SiO. When the reduction of quartz is carried out in Ar, SiO is initially formed at the contact points of graphite and quartz particles following the solid-solid Reaction (2), and then SiO is further reacts with carbon to form SiC following Reaction (3). SiO can also be generated by Reaction (6) which, with the decrease in the contact area between quartz and graphite, becomes a major reaction for the SiO formation. CO_2 formed in Reaction (6) is converted back to CO by Boudouard Reaction (7) which is highly favoured thermodynamically within the temperature range of isothermal reduction experiments of this investigation.

$$SiO_2\ (s) + CO\ (g) = SiO\ (g) + CO_2\ (g) \qquad (6)$$

$$C\ (s) + CO_2\ (g) = 2CO\ (g) \qquad (7)$$

When the reduction is carried out in the H_2-Ar gas mixture, H_2reacts with carbon forming CH_4 (Reaction (8)), which reacts with SiO_2 forming SiO (Reaction (9)).

$$C\ (s) + 2H_2\ (g) = CH_4\ (g) \qquad (8)$$

$$SiO_2\ (s) + CH_4\ (g) = SiO\ (g) + CO\ (g) + 2H_2\ (g) \qquad (9)$$

In the presence of carbon, H_2 can also directly reduce silica (Reactions (10) and (11)).

$$SiO_2\ (s) + H_2\ (g) = SiO\ (g) + H_2O\ (g) \qquad (10)$$

$$H_2O\ (g) + C\ (s) = H_2\ (g) + CO\ (g) \qquad (11)$$

Formation of the reaction intermediates CO_2, CH_4 or H_2O in the carbothermal reduction does not change the thermodynamics of Reactions (2) and (3) or the overall Reaction (1), but affects the reaction mechanism and kinetics. The equilibrium partial pressures of SiO in Reactions (2), (6), (9) and (10) calculated assuming CO partial pressure of 1 KPa, H_2 partial pressure of 100 kPa and CH_4 partial pressure of 0.05 KPa, are plotted in Figure 8. For Reactions (6) and (10), it is also assumed that the equilibrium partial pressure of CO_2 or H_2O on the quartz particle is the same as that of SiO. The assumption is made based on the understanding that SiO and CO_2 or SiO and H_2O were formed simultaneously on the quartz particles by Reactions (6) or (10), then diffused to the graphite particles where SiO formed SiC (Reaction (3)), while CO_2 and H_2O were converted to CO (Reaction (7)), and H_2 and CO (Reaction (11)), respectively. Although differences exist between the diffusivities of SiO and CO_2 or H_2O, it is expected that the partial pressures of SiO and CO_2 or H_2O on the quartz surface were of the same order. This figure also presents the partial pressure of intermediate CH_4 formed by Reaction (8) and partial pressures of CO_2 and H_2O on the graphite particle following Reactions (7) and (11) with the same assumptions.

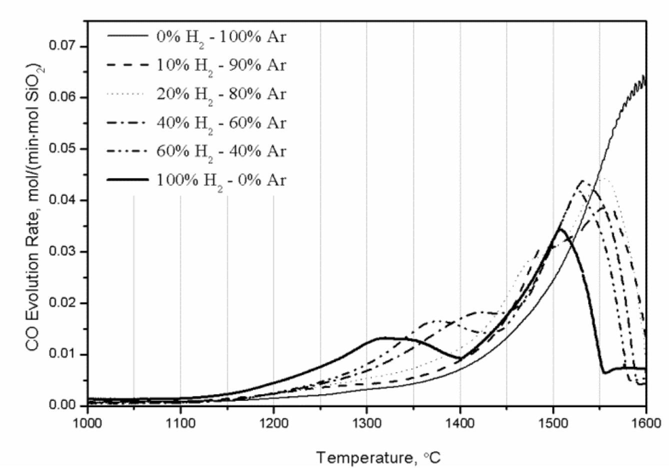

Figure 7: CO evolution rate in the temperature programmed reduction of quartz in different gas atmospheres.

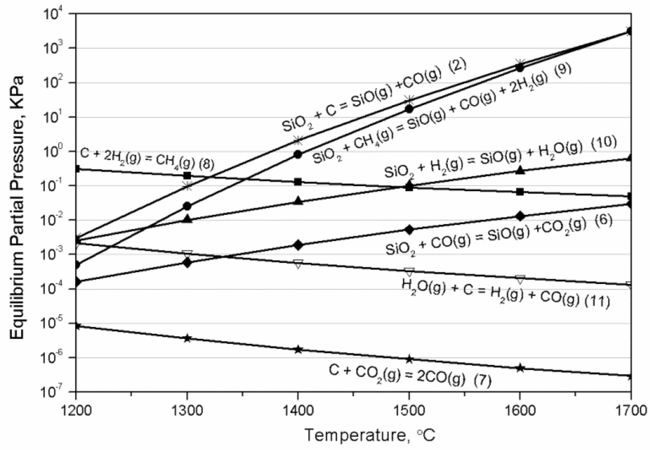

Figure 8: Equilibrium partial pressure of SiO for Reactions (2), (6), (9) and (10) calculated with P_{CO} = 1 KPa, P_{H2} = 100 KPa and P_{CH4} = 0.05 KPa; equilibrium partial pressure of CO_2 for Reaction (7) calculated with P_{CO} = 1 KPa; equilibrium partial pressure of CH_4 for Reaction (8) calculated with P_{H2} = 100 KPa; equilibrium partial pressure of H_2O for Reaction (11) calculated with P_{H2} = 100 KPa and P_{CO} = 1 KPa. It is assumed that $P_{CO2} = P_{SiO}$ for Reaction (6) and $P_{H2O} = P_{SiO}$ for Reaction (10).

According to Figure 8, CO_2 has a negligible partial pressure when solid carbon is present, meaning that Reaction (7) is practically irreversible in the studied temperature range. Reaction (6) generates SiO and CO_2 at ppm level at 1200 °C (under assumption that CO concentration was 1 vol %), which makes reduction of quartz in Ar at 1200 °C negligible. With the increase in temperature, the partial pressures of SiO and CO_2 significantly increase, and reach 100s ppm level. This explains why carbothermal reduction of quartz in Ar needs high temperatures.

The partial pressures of SiO and H_2O generated by Reaction (10) are always more than one order of magnitude higher than those of SiO and CO_2 generated by Reaction (6) (Figure (8)), which explains the faster reduction of quartz in H_2. However, it should be noted that at temperature slower than 1200 °C, Reaction (10) is not feasible, as the equilibrium partial pressure of H_2O at the surface of graphite particle is higher than that at the quartz particle. Therefore the direct reduction by H_2at relatively low temperatures can be limited by the removal of H_2O by Reaction (11).

Formation of CH_4 in the reduction experiments in H_2 was confirmed experimentally by analyzing the off-gas composition. The observed CH_4 concentrations in the temperature programmed reduction of quartz in H_2 containing gas are presented in Figure 9. The CH_4 concentration was close to zero when H_2 content was below 40 vol %, due to the lower generation rate of CH_4 by Reaction (8) than consumption rate by Reaction (9). When the H_2-Ar gas mixture contained more than 40 vol %H_2, generation of CH_4 was faster than its consumption; CH_4 in the off-gas was detected at the level of hundreds ppm, as shown in Figure 9. Increasing the partial pressure of H_2 increased the equilibrium partial pressure of CH_4 and enhanced the reduction rate of SiO_2. CH_4 stability decreases with increasing temperature (Figure 8); its concentration in reduction experiments at temperatures > 1400 °C was very low (Figure 9).

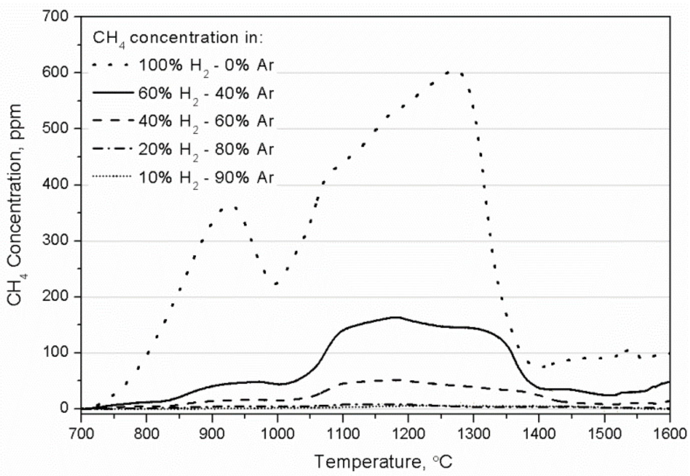

Figure 9: Concentration of CH_4 in the progress of temperature programmed reduction in the Ar–H_2 gas mixtures with different H_2 contents.

Based on the analysis above, it can be concluded that synthesis of SiC from quartz and graphite in pure Ar was initiated by Reactions (2) and (3) and then proceeded by the SiO-CO-CO_2 path through Reactions (6), (7) and (3). In the synthesis of SiC in the H_2 containing gas atmosphere, this path plays a less significant role. Instead, it proceeds by the SiO-H_2-CH_4 path through Reactions (8), (9) and (3) and/or SiO-H_2-H_2O path through Reactions (10), (11) and (3). The measured partial pressure of CH_4 was very low at temperatures above 1400 °C; it can be expected that the SiO-H_2-CH_4 pathdominated at low temperatures, while at high temperatures SiC synthesis occurs by the SiO-H_2-H_2O path. These reduction mechanisms also explain two peaks in the CO evolution curves observed in the reduction in H_2–Ar gas mixtures as shown in Figure 7. The low temperature peak can be attributed to the formation of SiC by the SiO-H_2-CH_4 path. The SiO-H_2-H_2O path is the major mechanism in the formation of SiC at high temperatures.

5 CONCLUSIONS

Carbothermal reduction of quartz was strongly affected by the gas atmosphere and temperature. The reduction rate increased with increasing H_2partial pressure and temperature. SiC began to form at 1200 °C in H_2. The conversion of quartz to SiC at 1400 °C was completed in 270 minutes. This period was reduced to 140 minutes at 1500 °C and 70 minutes at 1600 °C. In the carbothermal reduction of SiO_2 in Ar, the conversion of quartz to SiC started at 1300 °C, and was incomplete after 270 minutes at 1500 °C.

The faster reduction rate in H_2 containing gas was attributed to the involvement of H_2 in the reactions. Quartz was directly reduced by H_2 to SiO; CH_4 formed by reacting H_2 with graphite also accelerated reduction of quartz to SiC.

6 ACKNOWLEDGMENTS

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