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Synthesis of Silicon Carbide Powders from Methyl-Modified Silica Aerogels

Kyoung-Jin Lee ¹, Yanggu Kang ^{1,2}, Young Hun Kim ³, Se Won Baek ³ and Haejin Hwang ^{1,*}

¹ Department of Materials Science and Engineering, Inha University, 100 Inha-ro, Incheon 22212, Korea; legna211@naver.com (K.-J.L.); kykang1006@komexcarbon.co.kr (Y.K.)

² KOMEX, Ansung, Gyeonggi 17604, Korea

³ Basic Materials & Chemicals R&D, LG Chem, 188 Munji-ro, Yuseong-gu, Daejeon 34122, Korea; zerok@lgchem.com (Y.H.K.); hector@lgchem.com (S.W.B.)

* Correspondence: hjhwang@inha.ac.kr; Tel.: +82-32-860-7521

Received: 3 August 2020; Accepted: 3 September 2020; Published: 4 September 2020

Abstract: β -silicon carbide (SiC) powders were synthesized by the carbothermal reduction of methyl-modified silica aerogel/carbon mixtures. The correlations between the phase evolution and morphologies of the SiC powders and the C/SiO₂ ratio were investigated. At a C/SiO₂ ratio of 3, β -SiC formed at 1425 °C and single-phase SiC powders were obtained at 1525 °C. The methyl groups (-CH₃) on the silica aerogel surfaces played important roles in the formation of SiC during the carbothermal reduction. SiC could be synthesized from the silica aerogel/carbon mixtures under lower temperature and C/SiO₂ ratios than those needed for quartz or hydrophilic silica. The morphology of the SiC powder depended on the C/SiO₂ ratio. A low C/SiO₂ ratio resulted in β -SiC powder with spherical morphology, while agglomerates consisting of fine SiC particles were obtained at the C/SiO₂ ratio of 3. High-purity SiC powder (99.95%) could be obtained with C/SiO₂ = 0.5 and 3 at 1525 °C for 5 h.

Keywords: silicon carbide (SiC); silica (SiO₂); aerogel; surface methyl (-CH₃) group; carbothermal reduction

1. Introduction

Silicon carbide (SiC) is a typical non-oxide ceramic material that forms covalent bonds in structural units. Because of its strong covalent bonds and chemical stability, SiC exhibits excellent properties at temperatures up to 1400 °C such as a high hardness, wear resistance, corrosion resistance, and strength [1,2]. Other notable features of SiC are high thermal and electrical conductivities. Based on these excellent mechanical and electronic properties, SiC has been actively studied in various fields with respect to different applications such as for gas turbine components, heat exchangers, high temperature gas filters, power devices, heat dissipation substrates, and catalyst support materials.

The SiC ceramics can be fabricated by sintering SiC powders or preceramic polymers [3–5] at high temperature because of the covalent nature of the Si-C bond and low self-diffusion coefficient [6]. Single crystals of SiC for power device applications can be grown from SiC powder compacts by physical vapor transport (PVT) or sublimation epitaxial growth (SEG) [7,8]. The defects (stacking faults and dislocations) in SiC single crystals, sinterability, microstructure, and properties of sintered SiC strongly depend on the purity, morphology, size, and distribution of the SiC starting powders [9–12].

Various techniques have been developed for the synthesis of high-quality SiC powders such as the carbothermal reduction of silica (SiO₂) [13–15], direct carbonization [16,17], the thermal decomposition of preceramic polymers [18], and chemical vapor deposition (CVD) [19,20]. The synthesis of α -SiC using the carbothermal reduction of SiO₂ is the most common technique, which is characterized by

relatively low-cost processing (inexpensive starting materials) and can be easily scaled up [21,22]. The carbothermal reaction can be expressed as follows:

A C/SiO₂ powder mixture with a stoichiometric C/SiO₂ ratio above 3 is required for the reaction to obtain SiO₂-free SiC powder [23]. Because gaseous silicon monoxide (SiO) species may form and the SiC particles grow based on the reaction of SiO and C [24], the morphology and characteristics of the SiC powder obtained using carbothermal reduction strongly depend on starting the starting material, that is, SiO₂ and C, as well as on the reaction conditions.

Parmentier et al. synthesized SiC powders with high specific surface areas through the carbothermal reaction of mesoporous MCM-48 silica and pyrolytic carbon using the chemical vapor infiltration of propylene [25]. Meng et al. proposed a novel sol-gel process to obtain SiO₂ xerogels containing carbon nanoparticles [26]. They fabricated nanostructured α -SiC powder at 1650 °C using the carbothermal reduction of the precursor powder mentioned above.

In our previous study [27], we developed a novel technique for the synthesis of silica aerogel powders with spherical shapes using emulsion polymerization from water glass. The synthesized silica aerogels were highly porous (~95% porosity), and their surfaces were modified to contain methyl groups (-CH₃). When the surface-modified silica aerogel is employed as a starting material for the carbothermal reduction to synthesize SiC powder, the covalent bonds of Si-C and the high surface energy, owing to mesoporous nature of the silica aerogels, can accelerate the conversion of silica to SiC. In addition, the use of the surface-modified silica aerogel is expected to produce a spherical SiC powder. To our knowledge, there has been no attempt to use silica aerogels containing surface methyl groups to synthesize SiC powder.

This study focuses on the synthesis of spherical β -SiC powders through the carbothermal reduction of surface-modified SiO₂ aerogels. The effects of the surface methyl groups (-CH₃) and mesoporous structure of the silica aerogel on the carbothermal reduction reaction were investigated for different SiO₂/C ratios. The synthesized SiC powders were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Materials and Methods

2.1. Preparation of Silica Aerogel

Silica aerogel and carbon black (Raven425, Birla Carbon, Seoul, Korea) were used as starting materials for the carbothermal reduction. Silica aerogel powders were prepared from water glass (silica content, 28–30 wt.%; SiO₂/Na₂O = 3.52:1; Young IL Chemical, Incheon, Korea) and n-hexane (95%, Samchun Pure Chemicals, Pyeongtaek, Korea) using an emulsion polymerization technique. The detailed procedure is described elsewhere [27]. Silica aerogel and carbon black were mixed in n-hexane using an ultrasonic bath. Homogeneous slurry was obtained after 10 min and dried at 100 °C in an electric oven. The C/SiO₂ molar ratios were 0, 0.5, 1, 2, and 3. The SiO₂/C powder mixture was poured into an alumina (Al₂O₃) boat, which was placed inside a tube furnace under a constant argon flow (100 sccm). The carbothermal reduction was performed at 1450–1525 °C for 1 and 5 h. The synthesized powders were further heat-treated at 800 °C for 1 h in air to remove residual carbon black.

2.2. Evaluation

To measure tap density, 0.2 g of the silica aerogel powder was placed in a 5 mL cylinder (9 mm in diameter) and tapped 1000 times using a tapping density tester (TAP-2S, Logan Instruments Co., Somerset, NJ, USA). Fourier transform infrared (FT-IR) spectroscopy (FTS-165, Bio-Rad, Hercules CA, USA) was used to confirm the surface chemical structure of the aerogels in the wave number range of 400–4000 cm⁻¹. The powder was mixed with potassium bromide (KBr) and pressed to form a sample

disk for FT-IR measurements. The phases of the obtained powders were identified using XRD (D/MAX 2200V/PC, RIGAKU Co., Ltd., Tokyo, Japan) with Ni-filtered $\text{CuK}\alpha$ radiation. The thermogravimetry (TG) and differential thermal analysis (DTA) (Diamond TG/DTA Lab System, Perkin Elmer) was performed in air up to 800 °C at a heating rate of 5 °C · min⁻¹ to investigate the thermal behavior of the silica aerogel powder. The carbon, hydrogen, and oxygen contents in the starting silica aerogel and synthesized SiC powders were determined using an elemental analyzer (EA, Thermo EA1112, Thermo Fisher Scientific, Waltham, MA, USA) and an oxygen–nitrogen analyzer (EMGA-920, Horiba, Japan), respectively. The surface area, pore volume, and mean pore size of the starting silica aerogel powder were measured using Brunauer–Emmett–Teller (BET) equipment (0.01 < p/p0 < 1; ASAP 2010; Micrometrics, Norcross, GA, USA). The equipment is used to measure the amount of nitrogen that is adsorbed as the pressure changes. Before N₂ adsorption, the powder sample was degassed at 200 °C. The microstructures of the obtained powder samples were examined using field-emission SEM (FESEM, S-4300, Hitachi, Japan).

3. Results and Discussion

Some of the physical properties of the starting silica aerogel powder are listed in Table 1. The silica aerogel has a highly porous structure with mesopores, and its surface was modified by methyl groups (-CH₃). The Fourier transform infrared spectra of the starting silica aerogel powder are shown in Figure 1. The absorption peaks near 1100, 800, and 460 cm⁻¹ were assigned to the asymmetry, symmetry, and bending modes of Si-O-Si, respectively [28,29]. These peaks are characteristic peaks showing a typical silica aerogel network structure. By contrast, the peaks at 1260 and 850 cm⁻¹ indicate the presence of a Si-C bond, while the peaks at 2900 and 1450 cm⁻¹ are due to C-H stretching [30,31]. Thus, it can be inferred that the silica aerogel was modified into a hydrophobic form by the surface methyl groups (-CH₃). A N₂ adsorption–desorption isotherm of the starting silica aerogel powder is shown in Figure 2. N₂ absorption sharply increases near the high relative pressure (Type IV adsorption–desorption isotherm), which indicates that the silica aerogel is mesoporous [32,33].

Table 1. Some physical properties of the starting silica aerogel powder.

	Tap Density, g·cm ⁻³	Porosity, % §	BET Surface Area, m ² ·g ⁻¹	Pore Volume, cm ³ ·g ⁻¹	Pore Diameter, nm
Silica aerogel	0.12	94.5	730	2.35	12.89

§ porosity = ((1-tap density)/ ρ_{SiO_2}) × 100, ρ_{SiO_2} = 2.19 g·cm⁻³.

Figure 1. FT-IR spectra of the starting silica aerogel powder. The inset is an SEM image of the starting silica aerogel powder.

Figure 2. N₂ adsorption–desorption isotherm (a) and pore size distribution of the starting silica aerogel powder (b).

The TG was carried out to quantitatively analyze the presence and content of surface carbon in the silica aerogel powder. The TG curves are illustrated in Figure 3. Weight loss was observed in two temperature regions. The weight loss of ~0.5% observed from room temperature to 200 °C is due to the release of physically adsorbed water or the evaporation of residual solvents on the surface of the silica aerogel. On the other hand, the weight loss of 11.8% in the temperature range of 300 to 800 °C is due to the combustion of the surface methyl group ($-\text{CH}_3$). It is assumed that the DTG peak and sharp weight loss at ~475 °C can be attributed to the oxidation of the surface methyl groups ($-\text{CH}_3$) of hydrophobic silica aerogel particles [34]. The silica aerogel, which is chemically modified by surface methyl groups, exhibits a hydrophobic–hydrophilic transition upon heating in air, which is due to the oxidation of $-\text{CH}_3$. The EA analysis revealed that the carbon and hydrogen contents of the silica aerogel powder were 11.78 and 3.04 wt.%, respectively. This value (11.78 wt.% of carbon) corresponds to ~0.70 mol% of SiO_2 . Therefore, the actual C/ SiO_2 ratios are 0.70, 1.30, 1.88, 3.06, and 4.23 for the nominal C/ SiO_2 ratios of 0, 0.5, 1, 2, and 3, respectively.

Figure 3. TG and its derivative curves for the silica aerogel powder.

Figure 4 illustrates the XRD patterns of the powder samples synthesized from SiO_2 -C mixtures with various C/ SiO_2 ratios at 1525 °C for 1 h. The powder samples obtained at C/ SiO_2 ratios of 0 and 0.1 are α -cristobalite that formed from amorphous silica. This indicates that the carbothermal

reduction did not proceed under these two conditions. This is reasonable because the C/SiO₂ ratios of 0 and 0.1 are much lower than the stoichiometric value (3). On the other hand, in the powder sample synthesized from the SiO₂-C mixture with a C/SiO₂ ratio of 0.3, the α -cristobalite peak intensity was decreased and peaks corresponding to β -SiC appeared. At a C/SiO₂ ratio of 0.5, all peaks due to α -cristobalite disappeared and single-phase β -SiC powder was obtained. Three peaks (35.5°, 41.5°, and 59.9°) are attributable to various β -SiC facets, and the small peak observed at 34.0° is due to stacking faults in β -SiC. This result is unexpected because the C/SiO₂ ratio of 0.5 is also much lower than the stoichiometric ratio required for the carbothermal reduction of silica. Generally, a C/SiO₂ ratio above the stoichiometric value is required for the carbothermal reduction of silica [14,23,26]. Thus, the result observed in Figure 4 strongly suggests that the surface methyl groups, which modify the silica aerogel particles, represent an efficient carbon source for the carbothermal reduction.

Figure 4. XRD patterns of the powder samples synthesized under various C/SiO₂ ratios at 1525 °C.

Figure 5 illustrates the XRD patterns of the powder samples synthesized from the SiO₂-C mixture with a C/SiO₂ ratio of 0.5 at various reduction temperatures for 1 h. At 1450 °C, the powder sample consists of β -SiC and α -cristobalite. As the reduction temperature increases, the peak intensity of α -cristobalite gradually decreases, while that of β -SiC increases. Based on Figure 5, it can be inferred that a reduction at 1525 °C is required to synthesize a single-phase β -SiC at a C/SiO₂ ratio of 0.5.

We calculated the equilibrium compositions for the carbothermal reduction reaction as a function of temperature in a previous study. The results indicated that β -SiC forms at temperatures above 1516 °C [35]. Based on the XRD analysis (Figure 5), β -SiC formed at 1450 °C, which is ~70 °C lower than the temperature obtained from the thermodynamic calculation (1516 °C). This discrepancy can be attributed to the enhanced reactivity between silica and carbon or the increased surface energy (nano-size effect) [36,37]. In this study, surface methyl groups are the carbon source, which are bonded to the silica aerogels at the atomistic level. Therefore, it can be expected that the carbothermal reaction proceeds in a highly reactive state. In addition, the high mesopore volume and high specific surface area of the silica aerogels allow the nano-size effect on the conversion of silica to SiC [25]. The thermodynamic calculation of the carbothermal reduction of silica considering the surface energy contribution indicates that the formation temperature for SiC can be reduced to 1410 °C [35].

To confirm that the surface methyl groups of the silica aerogel were the carbon source for the carbothermal reduction of silica, the surface methyl groups were removed by calcining the silica aerogel at 600 °C for 3 h in air. The resulting hydrophilic silica aerogel powder was mixed with carbon black, and the carbothermal reduction was performed as described in Section 2. For comparison,

a commercial quartz powder was purchased from Junsei (extra pure, Japan) and used for an additional carbothermal reduction experiment.

Figure 5. XRD patterns of the powder samples synthesized from the $\text{SiO}_2\text{--C}$ mixtures with the C/SiO_2 ratio of 0.5 at various reduction temperatures.

Figure 6 illustrates the XRD patterns of the powder samples synthesized from the hydrophobic silica aerogel, aerogel without surface methyl groups (hydrophilic silica aerogel), and quartz powders. The carbothermal reductions of the hydrophobic silica aerogel (Figure 6a,b) and other samples (Figure 6c,d) were performed at 1525 and 1550 °C, respectively. As described above, the powder sample synthesized from the hydrophobic silica aerogel containing surface methyl groups was single-phase $\beta\text{-SiC}$, although the C/SiO_2 ratio was 0.5 and the reduction temperature was 1525 °C. By contrast, the XRD analysis indicates that the powder sample synthesized from the hydrophilic silica aerogel is $\alpha\text{-cristobalite}$. Characteristic peaks corresponding to the crystalline $\beta\text{-SiC}$ phase could not be observed. This phenomenon suggests that the surface methyl groups play important roles in the enhancement of the carbothermal reduction reaction of silica. With respect to quartz, $\alpha\text{-cristobalite}$ remained in the synthesized powder, although the reduction temperature and C/SiO_2 ratio were higher than those of the hydrophobic silica aerogel.

A schematic illustration of the proposed carbothermal reduction reaction mechanism for silica aerogels is shown in Figure 7. The surface of the hydrophobic silica aerogel was modified to contain methyl groups. During the carbothermal reduction of the aerogel, the C-H bonds were broken, whereas the tetrahedral environments of silicon and carbon were maintained. It can be inferred that amorphous hydrogenated SiC or hydrogenated Si-C-O (silicon oxycarbide) has a cristobalite form at temperatures between 1000 and 1400 °C [38]. During this process, condensation reactions between $-\text{Si}(\text{CH}_3)_3$ and neighboring $-\text{Si}(\text{CH}_3)_3$ groups occur, which lead to the formation of CH_4 and H_2 from the consumed CH_3 groups [39]. Above 1400 °C, SiC particles nucleate and grow toward the inside of the silica aerogel particles via a gas-phase reaction between SiO and CO, as has typically been observed for the carbothermal reduction of silica. It appears that the surface methyl groups not only act as the carbon source but also serve as a template for the formation of the SiC particles [40–42]. As observed in Figures 6 and 7, the SiC particles maintained the spherical morphology of the silica aerogel powder.

Figure 8 shows the SEM images of the silica aerogel and $\beta\text{-SiC}$ powders synthesized from the $\text{SiO}_2\text{--C}$ mixtures at various reduction temperatures. The C/SiO_2 ratio was 0.5. Based on Figure 8a, the starting silica aerogel had spherical morphology and significant aggregation cannot be observed. The particle size was estimated to be 5 to 10 μm . An interesting feature can be observed in Figure 8b–e, that is, the synthesized $\beta\text{-SiC}$ powders exhibit spherical morphology, regardless of the reduction temperature.

Figure 6. XRD patterns of the powder samples synthesized from (a) the hydrophobic silica aerogel (C/SiO_2 ratio of 0.5), (b) the hydrophobic silica aerogel (C/SiO_2 ratio of 3), (c) the hydrophilic silica aerogel (C/SiO_2 ratio of 1), and (d) the quartz (C/SiO_2 ratio of 3).

Figure 7. Surface structure of the hydrophobic silica aerogel used in this study.

The particle size and morphology of the SiC powder samples obtained at different C/SiO_2 ratios were analyzed using SEM. Figure 9 shows the SEM images of the β -SiC powders synthesized from SiO_2 -C mixtures with C/SiO_2 ratios of 0.5 and 3. The carbothermal reduction was performed at 1525 °C for 1 h. The comparison of Figure 9a,b shows that the morphology of the SiC particles was completely different. At a C/SiO_2 ratio of 0.5, the SiC particles were spherical. By contrast, a high C/SiO_2 ratio of 3 yielded an agglomerated structure consisting of fine SiC particles. In addition, nanofiber-like SiC was observed between the fine SiC particles. The BET specific surface areas of the SiC powders prepared using C/SiO_2 ratios of 1 and 3 were estimated to be 6.4 and 12.7 m^2/g , respectively. This shows that the specific surface areas increase with the C/SiO_2 ratio. These results suggest that the C/SiO_2 ratio affects the nucleation and growth mechanisms during the synthesis of SiC powder.

To elucidate the effect of the porous structure of the SiC on oxidation, the oxygen content in the SiC powder samples was determined using an oxygen–nitrogen analyzer. The oxygen contents in the SiC powder prepared at 1525 °C for 5 h with C/SiO_2 ratios of 0.5 and 3 were 0.36 and 0.05 wt.% for the samples after the heat treatment in air, respectively. Almost-pure SiC powders were obtained when the C/SiO_2 ratio was 3.

Figure 8. SEM images of (a) the starting spherical silica aerogel and b-SiC powders synthesized from the SiO₂–C mixtures at (b) 1450 °C, (c) 1475 °C, (d) 1500 °C, and (e) 1525 °C for 3 h. The C/SiO₂ ratio was 0.5.

Figure 9. SEM images of the SiC powders synthesized from SiO₂–C mixtures with C/SiO₂ ratios of (a) 0.5 and (b) 3 at 1525 °C for 1 h. The powder samples were heat-treated in air at 1000 °C for 1 h after reduction.

The overall carbothermal reduction reaction for silica, which is a solid (SiO₂)–solid (C) reaction, is shown in Equation (1). At low temperature, the carbothermal reduction reaction can be written in as follows [43]:

At a high temperature and high P_{SiO}/P_{CO} ratio, whisker- or nanofiber-like SiC can be grown on the SiC nuclei based on Equation (4), which is similar to the CVD of SiC [35,44]. The SiC particles obtained through Equation (3) serve as nucleation sites for Equation (4).

The morphologies of the SiC particles differ, as shown in Figure 9a,b, which indicates that the formation mechanisms for the SiC particles differ. At a C/SiO₂ ratio of 0.5, the morphologies of the synthesized SiC particles are similar to that of the starting silica aerogel, suggesting that the SiC formation mechanism relies on Equation (1), that is, the solid–solid reaction. The solid SiO₂ particles directly react with carbon from the surface methyl groups, whereby spherical SiC powder was observed at a C/SiO₂ ratio of 0.5.

The molar ratio of carbon in the SiO₂–C mixture is of great importance because the CO gas that is produced by Equations (1) or (2) was sufficiently supplied. The high C/SiO₂ ratio (3) leads to an

increase in the partial pressure of gaseous species, such as SiO(g) and CO(g); consequently, SiC particles form and grow, as illustrated in Equations (3) and (4). The nanofiber-like SiC observed in Figure 9b might be due to the reaction expressed in Equation (4).

4. Conclusions

β -SiC powders were synthesized by the carbothermal reduction of methyl-bearing surface-modified silica aerogel/carbon mixtures. Based on the XRD analysis, single-phase β -SiC was synthesized at 1525 °C from the silica aerogel/carbon mixture with a C/SiO₂ ratio of 3. The surface methyl groups that are covalently bonded to the silica aerogel serve as a carbon source for the carbothermal reduction reaction; therefore, the formation temperature for SiC is lower. The direct bond between silicon and carbon atoms in the surface methyl group results in the enhanced kinetics of the carbothermal reduction reaction. The results show that the C/SiO₂ ratio plays an important role in both the reduction of the formation temperature for SiC and the control of the morphology of the synthesized SiC particles. At a C/SiO₂ ratio of 0.5, SiC maintains the original spherical morphology of the silica aerogels. By contrast, agglomerates with fine SiC particles were synthesized from the SiO₂-C mixture at a C/SiO₂ ratio of 3. This phenomenon can be attributed to different formation mechanisms for SiC, which depend on the silica–carbon ratio of the starting silica/carbon mixture. Almost pure SiC powder (99.95%) was obtained when the silica aerogel/carbon mixture at a C/SiO₂ ratio of 3 was reduced at 1525 °C for 5 h.

Author Contributions: Conceptualization, K.-J.L. and H.H.; methodology, Y.K., Y.H.K. and S.W.B.; analysis, K.-J.L., Y.K. and Y.H.K.; writing—original draft preparation, K.-J.L. writing—review and editing, H.H.; supervision, H.H.; project administration, H.H. and S.W.B. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by LG Chem. This research was supported by the Ministry of Trade, Industry & Energy (MOTIE), Korea Institute for Advancement of Technology (KIAT), through the Encouragement Program for The Industries of Economic Cooperation Region (P0002149).

Conflicts of Interest: The authors declare no conflict of interest.

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