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The effects of metallic Si additions on the synthesis of β -SiC powders using a sol-gel method

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Single phase β -SiC powders were synthesized using SiO₂/C hybrid precursors with and without the addition of metallic Si powders. The SiO₂/C hybrid precursors with various C/Si mole ratios (1.6-4.0) were prepared by a sol-gel process using tetraethyl orthosilicate and phenol resin as starting materials. Fine β -SiC powders were synthesized by the carbothermal reduction of the SiO₂/C hybrid precursor with and without the addition of metallic Si powders in the temperature range between 1250 °C-1800 °C under a vacuum atmosphere. Single phase β -SiC powders were obtained by the carbothermal reduction of the SiO₂/C hybrid precursor with a C/Si mole ratio of 1.6 above 1600 °C under a vacuum atmosphere. It was found that the addition of metallic Si powders to the the SiO₂/C hybrid precursor with excess carbon reduced the temperature for the synthesis of single phase β -SiC powders to as low as 1350 °C. The particle sizes of synthesized β -SiC powders from the metallic Si powder added SiO₂/C hybrid precursor with excess carbon were less than 1 µm, in which fine β -SiC powders appeared to be slightly aggregated.

Keywords: Synthesis, SiC powder, Sol-gel, carbothermal.

Introduction

Silicon carbide (SiC) is the most widely applied non-oxide ceramic in industry due to its good thermo-mechanical properties such as high melting point, high temperature strength, high wear resistance, high chemical resistance, and high thermal shock resistance. In addition, SiC of high purity has been recently noticed as an attractive material for high power, high frequencies, and high temperature electronic applications, since SiC has unique physical and chemical properties such as a wide band gap, high thermal conductivity, high breakdown voltage, and high forward current density even under severe conditions [1]. For an increase in the industrial applications of SiC, the importance of SiC powders as starting materials with highly controlled properties is becoming increased. SiC powders have been mainly produced on an industrial scale by a carbothermal reduction process using SiO₂ and carbon (petroleum coke) known as the Acheson Process [2]. However, hexagonal β-SiC powders produced by the Acheson process are not adequate for advanced industrial applications without further purification processes. A number of other processes have been studied to synthesize fine and high purity SiC powders, which have included gas phase reaction methods, thermal decomposition of organic silicon compounds, and pyrolysis of hybrid precursors containing C

and Si sources. Although fine β -SiC powders of high purity were synthesized by gas phase reaction methods and thermal decomposition of organic silicon-carbon compounds using polycarbosilane, tetramethyldisilane, methyltriclorosilane (MTS), and other combined gas phases containing Si and C sources [3-6], applications of β -SiC powders synthesized by these methods have been quite limited due to expensive raw materials and low productivity.

Therefore, since mixing procedures of Si and C sources in the liquid state could also produce a highly intimate Si/ C source mixture homogeneously, a pyrolysis method using Si/C hybrid precursors has been studied to fabricate fine β-SiC powders of high purity. The sol-gel process has known to be a widely used process to fabricate homogeneous hybrid precursors with a highly intimate C/Si source mixture. In these processes, alkoxides and colloidal solutions were used as Si sources and phenol resin, pitch, and ethylene glycol were used as carbon sources [7-16]. Cubic SiC (β -SiC) powders not containing any residual SiO₂ and carbon were synthesized after the carbothermal reduction of the hybrid precursors prepared with a proper C/Si mole ratio. The particle sizes of β -SiC powders fabricated by this method were in the range of 25 nm-500 nm depending on the starting materials and the carbothermal reduction temperature. It was reported that the carbothermal reduction of a hybrid precursor consisting of SiO₂ and carbon commonly required to be proceeded above 1600 °C to fabricate high purity β -SiC powders without residual SiO₂ and carbon [7, 9, 10, 11, 14-16]. However, a decrease in the carbothermal reduction temperature of SiO₂-carbon hybrid precursors was not achieved in the previous studies.

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In this study, we attempted to reduce the carbothermal reduction temperature to fabricate β -SiC powders by the addition of metallic Si powders to SiO₂/C hybrid precursors. TEOS and novolac type phenol resin were used as starting materials for silicon and carbon sources to fabricate the SiO₂/C precursor by a sol-gel process. Metallic Si powders were added to the SiO₂/C hybrid precursor prepared by the sol-gel process. β -SiC powders were synthesized by the carbothermal reduction of SiO2/C hybrid precursors with and without the addition of Si powders in the temperature range between 1250-1800 °C under a vacuum atmosphere. A comparative study between SiO₂/C hybrid precursors with and without the addition of metallic Si powders was performed to clarify the effect of the addition of metallic Si powder on the synthesis of β -SiC powders by a carbothermal reduction of SiO₂/C hybrid precursors.

Experimental

The raw materials used in this study included tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich), Si powder (99.5% purity, -325 mesh, Alfa Aesar), novolac type phenol resin (Kolong Co., Korea) and p-toluenesulfonic acid (p-TSA, 98.5%, Sigma Aldrich) as shown in Table 1. Ethanol of analytical grade and deionized water were used as the solvent and precipitation reagent, respectively. Since the carbonization treatment of phenol resin plays an important role in the synthesis of silicon carbide powders, thermo gravimetric (TG) and differential scanning calorimetry (DSC) analysises were carried out to characterize the thermal behavior of the phenolic resin in a N₂ atmosphere. Fig. 1 shows the TG and DSC curves obtained at a heating rate of 10 °C·minutes⁻¹. The complete pyrolysis temperature and carbon content of the phenolic resin used in this study are about 1000 °C and 48 wt.%, respectively. The molar ratios of carbon to the silicon used for silicon/carbon hybrid precursors in this study were 1.6, 2.5, 3.0 and 4.0. TEOS was mixed with the phenol resin solution in ethanol and then continuously stirred (400 rpm) to gelation with heating at 40 °C. p-TSA solution (30 wt% in water) used as a catalyst for hydrosis was added in to the TEOS/ phenolic resin solution during the mixing process. The molar ratio of p-TSA to TEOS and water to TEOS used in this study was 0.07 and 4, respectively. The silicon/carbon hybrid gels were dried at 60 °C for 12 h in an oven. The dried hybrid gels were pyrolyzed to make the SiO₂/C hybrid precursor for the synthesis of SiC at 1000 °C for 0.5 h

Table 1. Characteristics of the stating materials used in this study

Materials	Supplier	Remark	Purity
Tetraethyl Orthosilicate	Aldrich	TEOS	98%
Toluene sulfonic acid solution	n Aldrich	p-TSA	98.5%
Novolac type Phenol Resin	Kolong	SPR	Carbon contents > 55%
Si	Aldrich		99.8% 325mesh (45 µm)



Fig. 1. The thermal behaviors of the phenol resin used in this study in a N_2 atmosphere.

in a N₂ atmosphere. The dried gel and hybrid precursor were characterized using Fourier transform infrared spectroscopy (FT-IR; spectrum100, Perkin Elmer, Precisely). The SiO₂/C hybrid precursors with Si/C mole ratios of 2.5, 3.0, and 4.0 were mixed with Si powders. The amounts of Si powder were calculated for the complete reaction with the residual carbon that is resulted after completing the carborization process of the hybrid precursors with C/Si mole ratios of 2.5~4.0. The hybrid precursors with and wihout Si powders were pyrolized in the temperature range of 1250-1800 °C for 1 h under a vacuum atmophere of 10^{-1} torr (1.33 × 10⁷ µPa). The synthesized silicon carbide powders were characterized using an X-ray diffractometer (XRD; D-8, Buker), Fourier transform infrared spectroscopy (FT-IR; spectrum100, Perkin Elmer, Precisely) and scanning electron microscopy (SEM).

Results and Discussion

Fig. 2. shows FT-IR spectra of the phenol resin, dried hybrid gel, SiO₂/C hybrid precursor and synthesized SiC powders synthesized using the gel with Si/C mole ratio of 1.6 and 2.5 at various temperatures. Most of the absorption peaks in the dried gel powders as well as the hybrid prcursor cured at 1000 °C consisted of those of the amorphous silica from Si-O bonds (1050-1250 cm⁻¹ and 800 cm⁻¹) and phenol resin from O-H bonds $(3100-3600 \text{ cm}^{-1})$, benzene ring (1605, 1587, and 1493 cm⁻¹) and C-O bonds (1200 cm⁻¹) regardless of the composition of the hybrid gel. Similar results were observed in previous studies [7, 8, 16]. As the pyrolyzing temperayerature of the hybrid precursor and hybrid precursor with the addition of Si powders for the carbothermal reduction was increased, the FT-IR spectra for silica and phenol resin became obscure and the FT-IR spectra for the Si-C bonds at 796 cm⁻¹ appeared. FR-IR spectra for silica and phenol resin disappearred or were almost negligible only after completing the carbothermal reaction of the hybrid precursors with and without Si powder above 1600 °C and 1450 °C, respectively. The FT-IR spectra for Si-Si bonds are not observed 1800°C

1450°C

1350°C

1250°C

precursoi gel

Phenolresin

2000

Wave number (cm⁻¹)

1400°C

1350°C

1250°C Precursor gel

Phenolresin

2000

3000

3000

Transimittance (arb. unit)

4000

Fransimittance (arb. unit)

4000

(a)

1000

(b)

1000



in the powder obtained by pyrolizing the hybrid precursor with Si powder.

Fig. 3. shows XRD patterns for powders synthesized from the hybrid precursor with a C/Si mole ratio of 1.6 in the temperature range of 1250 °C-1800 °C. No crystalline phase was detected in powders pyrolized at 1250 °C and a crystalline phase started to be synthesized at 1350 °C, which was mainly indentified as the cubic β -SiC phase (3C-SiC). With an increase in the pyrolysis temperature from 1350 °C to 1800 °C, peaks for the unreacted amorphous carbon phase progressively decreased and the crystallinity of synthesized β -SiC was increased. The β -SiC powders of high crystallinity were synthesized using a hybrid precursor with a C/Si mole ratio of 1.6 at 1800 °C. Similiarly,



Fig. 3. X-ray diffraction patterns of powders fabricated by the carbothermal reduction of the SiO₂/C hybrid precursor with a C/Si mol ratio of 1.6 in the temperature range between 1250-1800 °C for 1 h under a vacuum atmosphere of 10^{-1} torr($1.33 \times 10^7 \mu$ Pa).

in previous studies, it has been reported that single phase fine β -SiC powders were obtained by pyrolyzing C/SiO₂ hybrid precursors prepared by a sol-gel process using silicon and carbon sources in the liquid state above 1600 °C [7, 9, 11, 15, 16]. In addition, the colors of β -SiC powders synthesized using the hybrid precursor with a C/Si mole ratio of 1.6 varied with the pyrolisis temperature. With an increase in the pyrolysis temperature from 1550 °C to 1800 °C, the colors of synthesized β -SiC powders were changed from black at 1550 °C to yellowish green color at 1800 °C by progressing the carbothermal reaction in the hybrid precursor.

Fig. 4 shows SEM micrography of the powders pyrolized from the hybrid precursor with a C/Si mole ratio of 1.6 at 1350 °C, 1450 °C, 1600 °C and 1800 °C. The powders pyrolized at 1350 °C and 1450 °C consisted of very fine β -SiC particles which were appeared to be aggregated particles as shown in Fig. 4(a) and (b). The particle size of the fine β -SiC powders was less than 300 nm. The unreacted amorphous SiO₂ and carbon particles were seemed to be included in particle agglomerates. The powders pyrolized at 1600 °C and 1800 °C have bi-modal particle size distributions as shown in Fig. 4(c) and (d). The powders consist of β -SiC particles with sizes of 2-5 µm and less than 400 nm. The particle size of the synthesized fine β -SiC powders are sligtly increased by increasing the pyrolisis temperature from 1600 °C to 1800 °C.

Fig. 5 shows the XRD patterns of the powders synthesized from the hybrid precursor with a C/Si mole ratio of 2.5/ Si powder mixture in the temperature range of 1300 °C-1450 °C. The powders pyrolized at 1300 °C consist of mainly of cubic β -SiC (3C- β -SiC), Si, and unreacted



Fig. 4. Scanning electron micrographs of β -SiC powders synthesized by the carbothermal reduction of the SiO₂/C hybrid precursor with a C/Si mol ratio of 1.6 at the temperatures of (a) 1350 °C, (b) 1450 °C, (c) 1600 °C, and (d) 1800 °C for 1h under a vacuum atmosphere of 10^{-1} torr (1.33 × 10⁷ µPa).



Fig. 5. X-ray diffraction patterns of powders fabricated by the carbothermal reduction of the metallic Si powder added SiO₂/C hybrid precursor with a C/Si mol ratio of 2.5 in the temperature range between 1300-1450 °C for 1h under a vacuum atmosphere of 10^{-1} torr (1.33 × 10⁷ µPa).

amorphous carbon. For the powders pyrolized to 1350 °C, only the β -SiC phase was detected without any of the amorphous carbon and Si while the β -SiC phase with a low crystallinity had begun to be synthesized in the powder synthesized using the hybrid precursor (C/Si mole ratio = 1.6) as shown in Fig. 3. With a further increase in the pyrolysis temperature of the hybride precursor (C/Si mole ratio = 2.5)/Si powder mixture, the crystallinity of the synthesized β -SiC phase was increased as shown in Fig. 5. A diffraction peak at the shoulders of the main peak for the (111) plane of cubic β -SiC ($2\theta = 35.6^{\circ}$) is detected, which was also reported in powders synthesized by pyrolizing hybrid precursors using ethylsilicate and phenol resin [7, 11, 15, 16]. It is known that such a diffraction peak resulted from the stacking faults existing in the cubic lattice in synthesized β -SiC powders [17, 18]. The β -SiC powder synthesized at 1300 °C was a dark green color which changed to a yellowish green color with an increase in the pyrolysis temperature above 1400 °C. The change in the color of β -SiC powders synthesized in this study seems to mainly depend on the amounts of unreacted carbon in the pyrolized powders. From these results, it was found that the addition of metallic Si powders to the hybrid precursor with a C/Si mole ratio higher than 1.6 promoted the carbothermal reaction to synthesize β -SiC, resulting in a considerable decrease in the carbothermal reduction



Fig. 6. X-ray diffraction patterns of powders fabricated by the carbothermal reduction of the metallic Si powder added SiO₂/C hybrid precursor with C/Si mol ratios of 2.5~4.0 at 1300 °C for 1 h under a vacuum atmosphere of 10^{-1} torr ($1.33 \times 10^{7} \mu$ Pa).

temperature of the SiO₂/C hybrid precursors prepared by the sol-gel process. Fig. 6 shows XRD patterns of the powders pyrolized using the hybrid precursors (C/Si mole ratios of 2.5, 3.0, and 4.0)/ Si powder mixture at 1300 °C.

The XRD peaks show Si peaks along with β -SiC peaks and unreacted amorphous carbon. The intensity of Si peaks was increased with the C/Si mole ratio in the hybrid precursor since the amount of Si powders added to the hybrid precursor was increased with the C/Si mole ratio in the hybrid precursor. In addition, there was not a big difference in the unreacted carbon contents in the powders pyrolized. The increase in the amounts of metallic Si powders as well as the excess carbon in the hybrid precursor did not further accelerate the carbothermal reaction at 1300 °C. The reactions between Si and C was not a dominent reaction to synthesize β -SiC powders in the hybrid precursor/ Si powder mixture at 1300 °C although the reaction between Si and C was a highly exothermic reaction at that temperature.

Fig. 7 shows SEM micrography of β -SiC powders synthesized from the hybrid precursor (C/Si mole ratio = 2.5)/ Si powder mixture at 1350 °C and 1450 °C. However, the large Si particles used in the hybrid precursor/Si powder mixture were not observed in SEM micrography, which is consistent with XRD results. As shown in Fig. 7, the powders synthesized at 1350 °C and 1450 °C consisted of fine β -SiC particles. It was found that the sizes of synthesized β -SiC particles were much increased compared with those synthesized using the hybrid precursor with a C/Si mole ratio of 1.6. The particle sizes of β -SiC powders synthesized at 1350 °C were less than 1 µm, and appeared





Fig. 7. Scanning electron micrographs of β -SiC powders fabricated by the carbothermal reduction of the metallic Si powder added SiO₂/C hybrid precursor with a C/Si mol ratio of 1.6 (a) at 1300 °C and (b) 1450 °C for 1h under a vacuum atmosphere of 10^{-1} torr (1.33 × $10^7 \mu$ Pa).

to be slighly aggregated. With an increase in the pyrolysis temperature from 1350 °C to 1450 °C, the particle size of synthesized β -SiC powders was slightly increased and particle aggregation became a little more noticeable as shown in Fig. 7(b).

From these results, it was obvious that the addition of metallic Si powders into SiO₂/C hybrid precursors with excess carbon contents could reduce the temperature to synthesize β -SiC powders from SiO₂/C hybrid precursors which were prepared by a sol-gel process using TEOS and phenol resin. In the SiO₂-C hybrid precursors, it is known that β -SiC powders are synthesized by the carbothermal reduction of SiO₂, which is expressed by the following reaction (1):

$$SiO_2 + 3C = SiC + 2CO_g$$
(1)

However, it has been reported that the direct solid state reaction (1) is not the predominent reaction reponsible for the synthesis of β -SiC. SiO₂ prefers to be dissociated into gaseous SiO and CO with a reaction with carbon, and gaseous SiO reacts with C sequentially to form β -SiC phase. For the reaction mechanism of the carbothermal



Fig. 8. Gibbs free energy changes calculated for the reactions to synthesize β -SiC from SiO₂-C system, Si-C system, and Si-SiO₂-C system in the temperature range between 1280-1600 °C.

reaction in the SiO₂-C precursors, the following two stepwise reactions involving the gaseous SiO formation as an intermediate phase proceed for the synthesis of β -SiC [7, 9, 10, 14]:

$$SiO_2 + C = SiO_g + CO_g$$
(2)

$$SiO_g + 2C = SiC + CO_g$$
(3)

The overall reaction for the above reactions (2) and (3) is expressed as reaction (1).

Fig. 8 shows the Gibbs free energy changes of the overall reaction (1) in SiO₂-C system in the temperature range between 1200 °C and 1800 °C. The Gibbs free energy changes of reaction (1) appear to be positive below 1525 °C as shown in Fig. 8, which are in good agreement with the experimental results obtained in this study. For the SiO₂-Si-C system used in this study, the reaction mechanisms to synthesize β -SiC become more complicated since the following reaction (4) between Si and C has to be considered additionally:

$$Si + C = SiC$$
 (4)

As shown in Fig. 8, the calculated Gibbs free energy changes of reaction (4) in the temperature range between 1200 °C and 1600 °C are always negative. Although the reaction mechanisms in the Si-C system has not been known in detail at a temperature below the melting temperature of Si, gaseous SiO as an intermediate phase would be involved to synthesize β -SiC in reaction (4) in the following twostepwise reactions:

$$\mathrm{Si} + 1/2\mathrm{O}_2 = \mathrm{SiO}_{\mathrm{g}} \tag{5}$$

$$\operatorname{SiO}_{g} + C = \operatorname{SiC} + 1/2\operatorname{O}_{2} \tag{6}$$

However, the synthesis of β -SiC in the SiO₂-Si-C system is thermodynamically more favorable compared to that in the SiO₂-C system in the temperature range of 1200 °C-1600 °C according to the following overall reaction (7):

$$Si + SiO_2 + 4C = 2SiC + 2CO_g$$
⁽⁷⁾

Although the yield of β -SiC synthesized from reation (4) in the SiO₂-Si-C system used in this study was not precisely analyzed, about 50% of β -SiC is expected to be synthesized through reaction (4) from the hybrid precursor(C/S mole ratio = 2.5/Si powder mixture. The calculated Gibbs free energy changes of reaction (7) for the synthesis of β -SiC from the SiO₂-Si-C system are much lower than those of reaction (1) in the temperature range of 1200 °C-1600 °C, which becomes negative above 1350 °C as shown in Fig. 8. These calculated Gibbs free energy changes of reaction (7) seem to be relatively consistent with the experimental results in this study. Since reaction (4) is the highly exothermic reaction, the temperature of the hybrid precursor with the excess carbon/Si powder mixture is expected to be locally increased during the carbothermal reaction, which may accelerate the reaction between SiO₂ and C even at a low temperature. From the above suggested, the reaction mechanism in the hybrid precursor with the excess carbon/Si powder mixture, single phase β -SiC powders could be synthesized even at a temperature as low as 1350 °C in this study.

Conclusions

Single phase β -SiC powders were synthesized using SiO₂/C precursors prepared by a sol-gel process, in which commercially-available TEOS and phenol resin were used as starting materials. Single phase β -SiC powders were obtained by pyrolyzing the SiO₂/C hybrid precursor with a C/Si mole ratio of 1.6 at a temperature above 1600 °C under a vacuum atmosphere. However, it was found that single phase β -SiC powders could be synthesized at a temperature as low as 1350 °C by pyrolyzing metallic Si powders added to the SiO₂/C hybrid precursor with excess carbon under a vacuum atmosphere. The addition of metallic Si powders to the SiO₂/C hybrid precursor with excess carbon seemed to accelerate the reaction between SiO2 and carbon in the hybrid precursor by providing large amounts of latent heat through the reaction between Si and C. The particle sizes of synthesized β -SiC powders using the SiO₂/C hybrid precursor with the excess carbon/Si powder mixture were less than 1 μ m, in which fine β -SiC powders appeared to be slightly aggregated.

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