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Processing of porous silicon carbide with toughened strut microstructure

Jung-Hye EOM, Young-Wook KIM† and Masaki NARISAWA*

Department of Materials Science and Engineering, The University of Seoul, 90, Jeonnong-dong, Dongdaemun-ku, Seoul 130–743, Korea
***Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, 1–1, Gakuen-cho, Naka-Ku, Sakai, Osaka 599–8531**

Porous SiC ceramics were fabricated by the carbothermal reduction of polysiloxane-derived SiOC containing hollow microspheres followed by sintering. The effect of the Al_2O_3–Y_2O_3–CaO (AYC) content on the microstructure and flexural strength of the porous SiC ceramics were investigated. The growth of large platelet α-SiC grains increased with increasing additive content due to enhanced grain growth and the $\beta \rightarrow \alpha$ phase transformation of SiC. In situ toughened microstructures consisting of large platelet grains and fine equiaxed grains were obtained when 10 or 20 wt% AYC was added. The porosity generally decreased with increasing the additive content, whereas the flexural strength increased. The typical flexural strength of the porous SiC ceramics sintered with 10 wt% AYC was 61 MPa at a porosity of 44%.

Key-words : Porous ceramics, SiC, Microstructure, Strength

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Silicon carbide (SiC) is a difficult material to sinter because of the covalent nature of its bond. Therefore, sintering additives, such as metals, oxides, and non-oxides, are usually added to densify SiC ceramics.[1)–3)] Among the compositions investigated as sintering additives, Al_2O_3–Y_2O_3–CaO (AYC) was found to be most effective in the development of an in situ-toughened microstructure at low temperatures[4)] as well as the crystallization of the grain boundary phases.[5)] In addition, the SiC ceramics sintered with AYC additives showed crack healing ability after heat-treatment at 1100°C for 1 h in air.[6)]

Recently, a novel processing route for fabricating porous SiC ceramics from carbon-filled polysiloxane was reported.[7),8)] The process consisted of three steps: (i) the pyrolysis of polysiloxane at 1100°C, which involves the loss of the organic material and the conversion of polysiloxane to an amorphous Si–O–C material (SiOC); (ii) the carbothermal reduction of SiOC and C at 1450°C, which converts the mixture to a SiC ceramic with the concomitant evolution of CO gas; and (iii) liquid-phase sintering of the SiC ceramic at high temperatures with the aid of oxide additives. The use of polysiloxane to fabricate porous SiC ceramics has potential advantages of a low-cost polymer processing, such as extrusion, and the easiness of porosity control.[7),9)]

The reported microstructure of porous SiC ceramics consisted mainly of an equiaxed grain structure.[10)–18)] Monolithic SiC ceramics with a toughened microstructure showed better mechanical properties than ceramics with an equiaxed microstructure.[1),19)] Similarly, the monolithic SiC ceramics, in situ-toughened microstructure would help improve the mechanical properties and structural reliability of porous SiC ceramics. Therefore, this study examined the possible development of an in situ-toughened microstructure in porous SiC ceramics using the AYC additive and processing strategy with polysiloxane.

† Corresponding author: Y.-W. Kim; E-mail: ywkim@uos.ac.kr

The following raw materials were used: a polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan), carbon black (~45 nm, Corax MAF, Korea Carbon Black Co., Ltd., Inchon, Korea), β-SiC (~0.27 μm, Ultrafine grade, Betarundum, Ibiden Co. Ltd., Ogaki, Japan), hollow microspheres (~20 μm, 461DE20, Expancel, Sundsvall, Sweden), Al_2O_3 (~0.3 μm, 99.9% pure, Sumitomo Chemical Co., Tokyo, Japan), Y_2O_3 (~0.75 μm, 99.9% pure, H.C. Starck GmbH & KG, Goslar, Germany), and CaO (~4 μm, 99.9% pure, Kojundo Chemical Laboratory Co., Sakado, Japan) powders. SiC was used as an inert filler, while the oxides were used as sintering additives. The inert filler was added to minimize shrinkage during sintering[20)] and accelerate SiC grain growth via a solution–reprecipitation mechanism. The microspheres were hollow poly(methyl methacrylate) spheres with diameters ranging from 15 to 25 μm.

Five batches of powder were prepared (**Table 1**). The ratio of polysiloxane, carbon black and beta-SiC was fixed based on the previous results that produce porous SiC ceramics with no secondary phase by X-ray diffraction and with excellent strength.[8),9),20)] The microsphere content was fixed at 5 wt%. Each batch was mixed for 24 h in a polyethylene jar containing ethanol and SiC balls. The milled powder mixture was dried and pressed uniaxially under 28 MPa to produce rectangular bars. The compacts formed were cross-linked by heating them to 200°C in air. The cross-linked samples were then pyrolyzed at 1100°C for 1 h in argon at a heating rate of 1°C/min to convert the polysiloxane to silicon oxycarbide. The pyrolyzed specimens were heated further to 1450°C in argon and held at that temperature for 1 h. This step brought about the carbothermal reduction of the polysiloxane-derived SiOC. The samples were then sintered at 1950°C for 4 h in argon. The heat treatment at 1450°C and sintering at 1950°C were performed in a graphite furnace.

The bulk density of each porous ceramic was calculated from its weight-to-volume ratio. The cell and grain morphology was

Table 1. Batch composition of porous SiC ceramics

Sample	Batch composition (wt%)						
	Polysiloxane†	Carbon black‡	β-SiC*	Hollow microspheres§	Al_2O_3	Y_2O_3	CaO
AYC1	54.18	8.49	31.33	5	0.60	0.20	0.20
AYC2	53.60	8.40	31.00	5	1.20	0.40	0.40
AYC5	51.87	8.13	30.00	5	3.00	1.00	1.00
AYC10	48.99	7.68	28.33	5	6.00	2.00	2.00
AYC20	43.22	6.78	25.00	5	12.00	4.00	4.00

†YR3370, GE Toshiba Silicones Co. Ltd., Tokyo, Japan.
‡Corax MAF, Korea Carbon Black Co., Ltd., Inchon, Korea.
*Ultrafine, Betarundum, Ibiden co. Ltd., Ogaki, Japan.
§461DE20, Expancel, Sundsvall, Sweden.

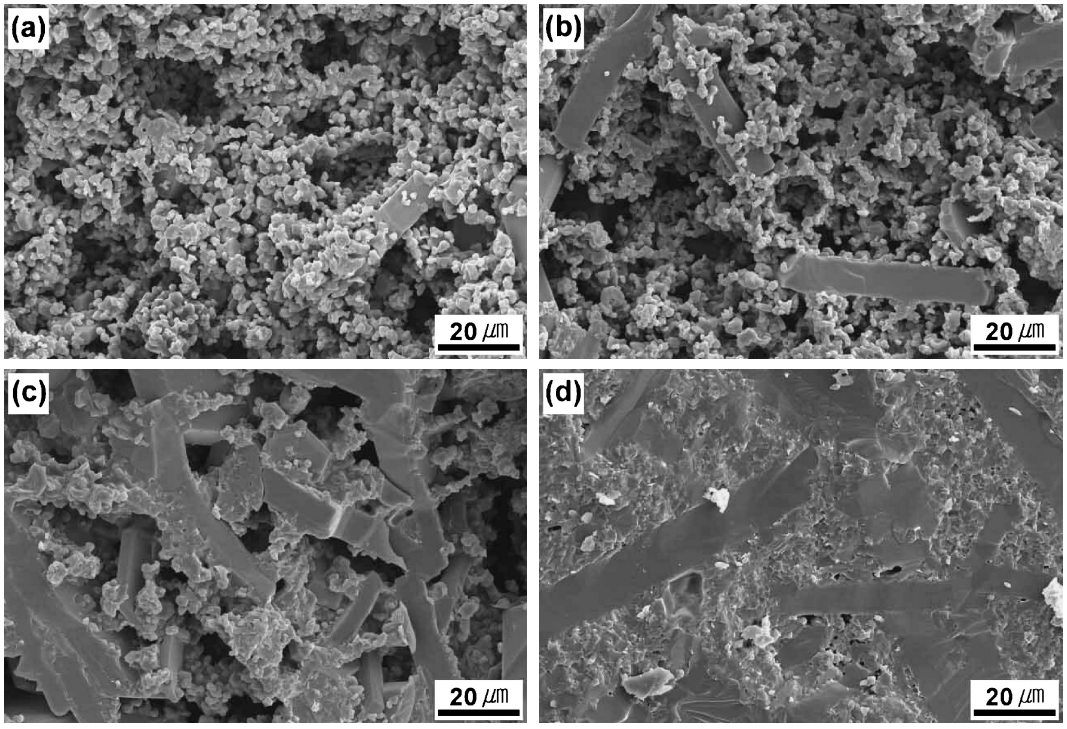

Fig. 1. Typical fracture surfaces of the porous SiC ceramics sintered at 1950°C for 4 h in argon: (a) AYC1, (b) AYC5, (c) AYC10, and (d) AYC20 (refer to Table 1).

examined by scanning electron microscopy (SEM). X-ray diffraction (XRD) was performed on the ground powders using Cu Kα radiation. The porosity was determined from the ratio of the bulk density to the true density. For the flexural strength measurements, bar-shaped samples were cut and polished to a size of 4 × 5 × 30 mm. Bend tests were performed at a crosshead speed of 0.5 mm/min using a four-point method with inner and outer spans of 10 and 20 mm, respectively.

XRD of the specimens showed that all specimens consisted of β- and α-SiC, indicating the occurrence of the $\beta \rightarrow \alpha$ phase transformation of SiC during sintering. However, the intensity of the peaks for α-SiC increased with increasing AYC content. The $\beta \rightarrow \alpha$ phase transformation rate was increased by adding higher amounts of AYC. This confirms that the $\beta \rightarrow \alpha$ phase transformation of SiC occurred via a solution–reprecipitaion mechanism, as reported for Si_3N_4.[21]

Figure 1 shows typical fracture surfaces of the porous SiC ceramics sintered at 1950°C for 4 h. A bimodal microstructure consisting of large platelet grains and small equiaxed grains was obtained in all specimens. However, an increase in the AYC content led to a change in the microstructure from mostly equiaxed to in situ-toughened. Extra large platelet grains, as large as 80–120 μm, were observed in the AYC20 specimen. The growth of extra large grains can be understood by the following. The particle size of the SiC filler was ~0.3 μm whereas the particle size of polysiloxane-derived SiC was 10–50 nm.[22] Therefore, the bimodal distribution of SiC particles accelerated the growth of the larger SiC grains.[23] The eutectic liquid of the AYC system appears at ~1400°C[24] and has low viscosity compared to other additive systems, such as Al_2O_3–Y_2O_3 and AlN–Y_2O_3. This is supported by the low temperature densification (1750°C) of SiC with AYC.[4,23] Since a low viscosity reduces the activation energy for diffusion, a faster grain growth rate would be expected in the specimen containing AYC composition as a sintering additive. XRD indicated the occurrence of the $\beta \rightarrow \alpha$ phase transformation of SiC. The formation of the large platelet grains from the equiaxed grains is observed frequently in liquid-phase-sintered SiC ceramics after sintering or

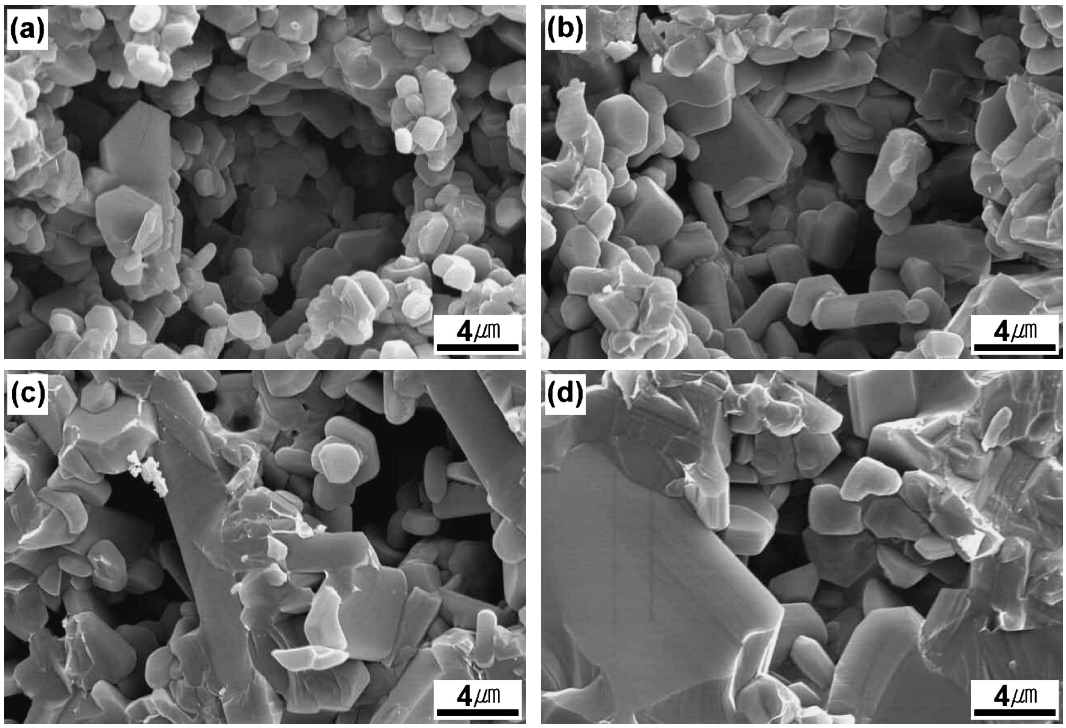

Fig. 2. Typical grain morphology of the porous SiC ceramics sintered at 1950°C for 4 h in argon: (a) AYC2, (b) AYC5, (c) AYC10, and (d) AYC20 (refer to Table 1).

annealing at temperatures >1900°C due to the $\beta \rightarrow \alpha$ phase transformation of SiC.[1),19)] Overall, a toughened strut microstructure had developed as a result of the enhanced grain growth due to the bimodal distribution of SiC, the low viscosity of the liquid phase, and the $\beta \rightarrow \alpha$ phase transformation of SiC. The change in microstructure with increasing additive content was attributed to the difference in the mass transport and $\beta \rightarrow \alpha$ phase transformation during sintering. These results also suggest that a limited amount of liquid phase in the presence of pores suppresses grain growth and the $\beta \rightarrow \alpha$ phase transformation of SiC during sintering or annealing at high temperatures due to a deficiency of the rapid mass transport path.

Tanaka et al.[25)] reported enhanced grain growth in porous SiC ceramics prepared from β- and α-SiC powder mixtures containing AlB_2 and sintered at 2200°C. However, the mean grain size in those ceramics was smaller than 10 μm. They also observed a few very large grains (~100 μm) when pure β-SiC was used as the starting powder. The additive composition in the present study led to the growth of large platelet grains at lower temperature (1950°C) due to the low viscosity of the liquid phase formed during sintering. Therefore, sintering additive chemistry and content played an important role in the grain growth and microstructural development in these materials.

Fine and well-distributed open cells and porous struts in the cellular structure were produced in the specimens sintered with 1–5 wt% of the additive (Figs. 1 and **2**). The primary cells (cells replicated from hollow microspheres) had an almost spherical morphology, indicating that the shape of the hollow microspheres was retained in the polysiloxane-carbon black-SiC-additives compact up to its decomposition temperature. When 5 wt% of microspheres were added and sintered at 1950°C, the cell size was smaller than 20 μm, and there were no large voids in the bulk. As shown in Fig. 2, the pore morphology changed from spherical to irregular with increasing additive content. The enhanced grain growth with increasing additive content is responsible for the change in pore morphology from spherical to irregular.

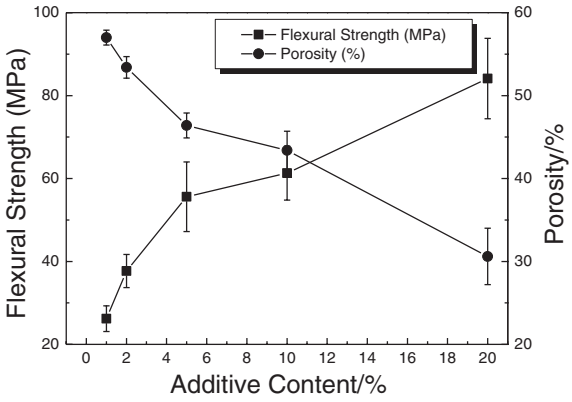

Fig. 3. Porosity and flexural strength of the porous SiC ceramics as a function of the additive content.

Figure 3 shows the flexural strength and porosity of the porous SiC ceramics as a function of the additive content. The strength increased with increasing additive content, whereas the porosity decreased with increasing additive content. This tendency has been observed in many other porous ceramics[26)–28)] and attributed to the higher probability of pore coalescence at the higher porosity under load. Pore coalescence leads to a larger defect size, resulting in lower strength. Comparison of the strength value reported and the present data is shown in **Fig. 4**. As shown, the typical flexural strengths of porous, polysiloxane-derived SiC ceramics with an equiaxed microstructure were reported to be 48 MPa at 45% porosity[8)] and 42 MPa at 49% porosity.[20)] A flexural strength of 28 MPa at 44% porosity was

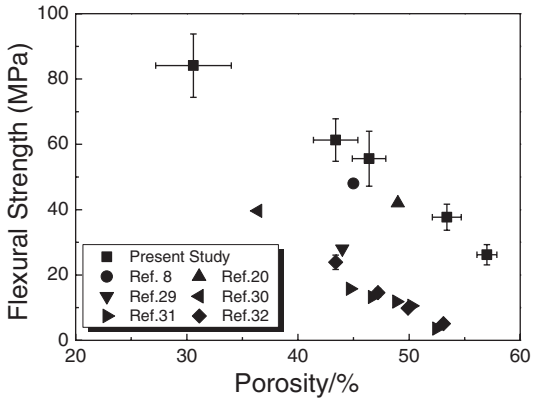

Fig. 4. Flexural strength of porous SiC ceramics as a function of porosity.

reported for reaction-bonded porous SiC ceramics.[29] Some further lower strengths were also reported in oxidation-bonded[30] and reaction-bonded porous SiC ceramics.[31),32] In contrast, typical strengths of the AYC5 and AYC10 specimens with a toughened microstructure were 56 MPa at 47% porosity and 61 MPa at 44% porosity, respectively. Figure 4 clearly shows that the present strength data obtained in the porous SiC ceramics with toughened microstructure was superior to the other data obtained from the ceramics with equiaxed microstructure. Figure 2(c) shows that the large platelet grains are well bonded with surrounding small equiaxed grains. It means that the large platelet grains act as a nail or bolt reinforcing the strut of the porous ceramics. Further improvement in the mechanical properties can be achieved by controlling the strut microstructure of the porous ceramics.

In summary, porous SiC ceramics with toughened struts were fabricated by the carbothermal reduction of polysiloxane-derived SiOC containing hollow microspheres, followed by sintering with Al_2O_3–Y_2O_3–CaO (AYC). A toughened strut microstructure developed as a result of enhanced grain growth due to the bimodal distribution of SiC, low viscosity of the liquid phase, and $\beta \rightarrow \alpha$ phase transformation of SiC. The toughened strut microstructure helped improve the flexural strength of porous SiC ceramics. The typical flexural strength of porous SiC ceramics sintered with 5 wt% AYC and 10 wt% AYC were 56 MPa at 47% porosity and 61 MPa at 44% porosity, respectively.

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