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LETTER

Effect of additive composition on microstructure and strength of porous silicon carbide ceramics

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Porous silicon carbide (SiC) ceramics have many potential applications due to their unique properties, which include high temperature stability, chemical stability, excellent abrasion resistance, high thermal shock resistance, high specific strength, and controlled permeability [1–9]. For example, SiC ceramics can be used as catalytic supports, molten metal filters, membrane supports, gas-burner media, and light-weight structural materials for high-temperature applications.

It has frequently been observed that the composition of the sintering additives affects the microstructural development of sintered SiC ceramics. Al_2O_3–Y_2O_3 [10], Al_2O_3–Y_2O_3–CaO [11], and AlN–Y_2O_3 [12] additives generally lead to the growth of SiC platelet grains when the SiC is sintered or annealed at a temperature above 1950 °C. In contrast, Y–Mg–Si–Al oxynitrides [13], B_4C–C [14], and AlN [15] additives lead to equiaxed microstructures, regardless of the sintering temperature. Thus, the mechanical properties of porous SiC ceramics may be affected by the sintering additives. Chi et al. [16] investigated the effect of incorporating various amounts of Al_2O_3 on the strength of porous SiC ceramics. They observed a maximum strength of ~17 MPa at a porosity of 61% when 5 wt% Al_2O_3 was added. Lee and Kim [17] fabricated porous SiC ceramics by powder processing using polymer microbeads as a template. The ceramics showed a strength of ~30 MPa at a porosity of 50% when 8 wt% Al_2O_3–Y_2O_3 was added in a 7:3 weight ratio. Ma et al. [18] fabricated porous SiC ceramics by adding silicone resin as a binder. The ceramics typically showed a strength of ~21 MPa at a porosity of 45%. However, there has been no systematic research on the effect of sintering additives in the processing of porous SiC ceramics.

In this study, porous SiC ceramics were fabricated by carbothermal reduction of a polysiloxane-derived SiOC with hollow microspheres, followed by sintering. The effects of the additive composition on the porosity, microstructure, and strength of the resulting porous SiC ceramics were investigated. The potential advantages of using polysiloxane for fabricating porous SiC ceramics are the utilization of low-cost polymer processing such as extrusion and the easiness of porosity control [19].

The following raw materials were used: a polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan), carbon black (Corax MAF, Korea Carbon Black Co., Ltd., Inchon, Korea), β-SiC (Ultrafine grade, Betarundum, Ibiden Co. Ltd., Ogaki, Japan), hollow microspheres (461DE20, Expancel, Sundsvall, Sweden), Al_2O_3 (AKP30, Sumitomo Chemical Co., Tokyo, Japan), Y_2O_3 (H·C. Starck GmbH & KG, Goslar, Germany), $Y_3Al_5O_{12}$ (YAG, High Purity Chemicals, Osaka, Japan), MgO (High Purity Chemicals, Osaka, Japan), SiO_2 (High Purity Chemicals, Osaka, Japan), CaO (High Purity Chemicals, Osaka, Japan), and AlN (grade F, Tokuyama Soda Co., Tokyo, Japan). The SiC was used as an inert filler, while the oxides and AlN were used as sintering additives. The inert filler was added to minimize shrinkage during sintering and to increase the strength of the resulting porous SiC ceramics [20]. The microspheres were hollow poly(methyl methacrylate) spheres with diameters ranging from 15 to 25 μm.

Eight batches of powder were prepared (Table 1). The microsphere content was fixed at 5 wt%. An example of the sample notation is as follows: 3A2Y denotes a specimen containing 3 wt% Al_2O_3 and 2 wt% Y_2O_3 as sintering

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Table 1 Batch composition of porous SiC ceramics

Sample	Batch composition (wt%)				
	Polysiloxane[a]	Carbon black[b]	SiC[c]	Hollow microsphere[d]	Sintering additive
3A2Y	51.87	8.13	30	5	3% Al_2O_3 + 2% Y_2O_3
5YAG	51.87	8.13	30	5	5% $Y_3Al_5O_{12}$
1A2Y2M	51.87	8.13	30	5	1% Al_2O_3 + 2% Y_2O_3 + 2% MgO
2A2Y1M	51.87	8.13	30	5	2% Al_2O_3 + 2% Y_2O_3 + 1% MgO
2Y2M1S	51.87	8.13	30	5	2% Y_2O_3 + 2% MgO + 1% SiO_2
3A1Y1C	51.87	8.13	30	5	3% Al_2O_3 + 1% Y_2O_3 + 1% CaO
3A1Y1M	51.87	8.13	30	5	3% Al_2O_3 + 1% Y_2O_3 + 1% MgO
2AN3Y	51.87	8.13	30	5	2% AlN + 3% Y_2O_3

[a] YR3370, GE Toshiba Silicones Co. Ltd., Tokyo, Japan

[b] Corax MAF, Korea Carbon Black Co., Ltd., Inchon, Korea

[c] Ultrafine, Betarundum, Ibiden Co. Ltd., Ogaki, Japan

[d] 461DE20, Expancel, Sundsvall, Sweden

additives. Each batch was mixed for 3 h in a polyethylene jar containing ethanol and SiC balls. The milled powder mixture was dried and uniaxially pressed 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 pyrolyzed at 1100 °C for 1 h with a heating rate of 1 °C/min in argon. The heat treatment resulted in the conversion of the polysiloxane to silicon oxycarbide [21]. Except for 2AN3Y, the pyrolyzed specimens were further heated to 1450 °C and held at the temperature for 1 h in argon. This step brought about the carbothermal reduction of the polysiloxane-derived SiOC. These samples were then sintered at 1750 °C in argon to cause the liquid-phase sintering of the SiC. The 2AN3Y specimens were heat treated and sintered in exactly the same way, except that nitrogen was used instead of argon. The heat treatment at 1450 °C and sintering at 1750 °C were all 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 investigated by scanning electron microscopy. X-ray diffractometry (XRD) was performed on the ground powders using a diffractometer and CuKα 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 $4 \times 5 \times 30$ mm^3. Bend tests were performed at room temperature using a four-point method with inner and outer spans of 10 and 20 mm, respectively. The compressive strengths of $4 \times 4 \times 8$ mm^3-sized samples were measured at a crosshead speed of 0.5 mm/min.

The general reaction for synthesizing SiC from a mixture of polysiloxane and carbon black is reported elsewhere [22, 23]. The reaction occurred in two steps: (i) the pyrolysis of polysiloxane at 1100 °C, which involves the loss of the organic material and also leads to the conversion of polysiloxane to an amorphous Si–O–C material (SiOC) and (ii) the carbothermal reduction of SiOC and C at 1450 °C, which converts the mixture to a SiC ceramic with the evolution of gaseous CO. Further heat-treatment of the specimens at 1750 °C with the aid of oxide additives led to the liquid-phase sintering of SiC that had been synthesized by carbothermal reduction and added as an inert filler. XRD analysis of the specimens showed that all the specimens sintered at 1750 °C consisted of β-SiC, indicating that the SiC synthesized by carbothermal reduction was β-SiC.

Figure 1 shows typical fracture surfaces of some selected, porous SiC ceramics sintered at 1750 °C for 1 h. These micrographs show evidence that fine and well-distributed open cells, and that porous struts in the cellular structure had been produced in 3A2Y, 5YAG, and 2AN3Y specimens. The microstructure of 3A1Y1C was similar to the specimens. The morphology of the primary cells (cells replicated from hollow microspheres) was almost spherical, indicating that the shape of hollow microspheres was retained in those specimens up to its decomposition temperature. In contrast, the cell morphology was irregular in 3A1Y1M (Fig. 1c), 1A2Y2M, 2A2Y1M, and 2Y2M1S specimens. It is interesting to note that all MgO containing specimens showed collapse of spherical pore structure after sintering at 1750 °C. Since the decomposition behavior of hollow microspheres is the same in both specimens without MgO (Fig. 1a and b) and specimens containing MgO (Fig. 1c), the shape of hollow microspheres are expected to be retained in the MgO-containing specimens up to its decomposition temperature. Thus, the change in cell morphology from spherical to irregular took place during liquid-phase sintering. Recently, Yao et al. [7] fabricated reticulated SiC ceramics at temperatures as low as

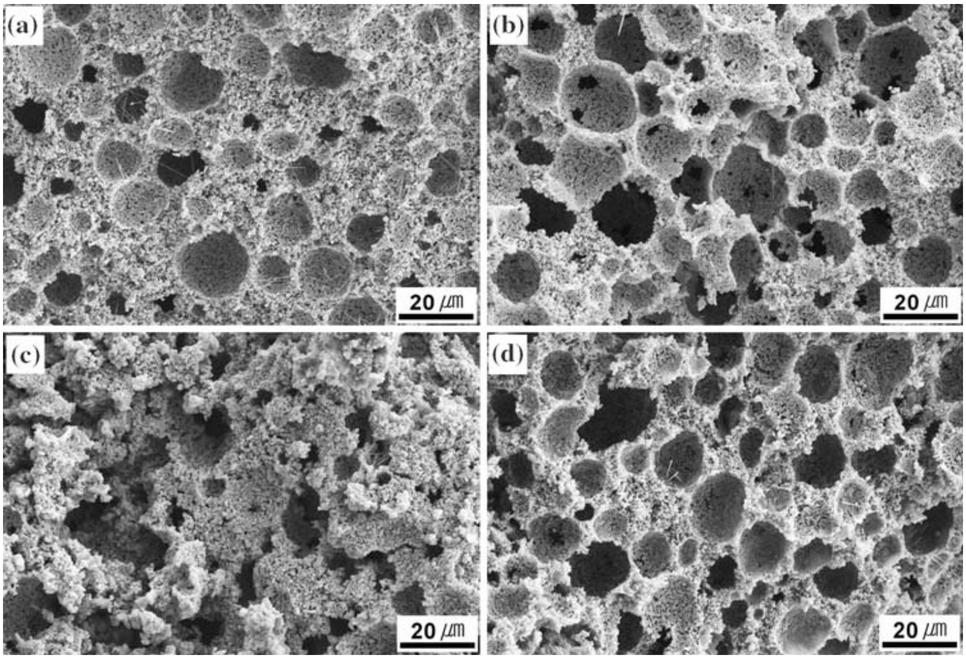

Fig. 1 Typical fracture surfaces of the various porous SiC ceramics sintered at 1750 °C for 1 h: **a** 3A2Y, **b** 5YAG, **c** 3A1Y1M, and **d** 2AN3Y (refer to Table 1)

1300–1450 °C by using $MgO–Al_2O_3–SiO_2$ additives. The results suggest that the viscosity of MgO-containing liquids in our specimens would be quite low at the sintering temperature (1750 °C). Locally, dense regions are also observed in 3A1Y1M specimen (Fig. 1c). It seems that low viscosity of MgO-containing liquid phase is formed during heating to the sintering temperature, resulting in local densification and collapse of the spherical pore structure in the specimens. The local agglomeration of liquid phase during sintering is driven by a driving force for reducing the surface tension of the liquid [24].

As shown in Fig. 1, nano fibers were observed inside the cell of some specimens (3A2Y, 5YAG, and 2AN3Y). The nano fibers are believed to be SiC and synthesized by a vapor phase reaction between SiO and CO [25]. Such kind of in situ grown nano fibers were also observed in a previous study [26] when polysiloxane and $Al_2O_3–Y_2O_3$ were used as a precursor for SiC and sintering additives, respectively. However, such kind of nano fiber was rarely observed in MgO-containing specimens, indicating that the formation of low-viscosity liquid phase suppresses the synthesis of the nano fibers inside the pores.

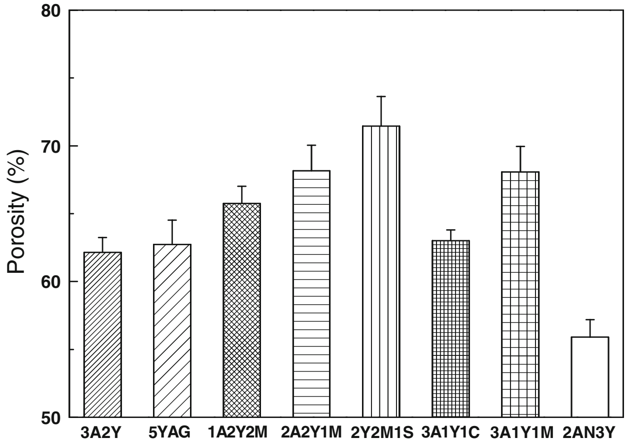

Fig. 2 Effect of the sintering additive composition on the porosity of the SiC ceramics sintered at 1750 °C for 1 h

Figure 2 shows the porosity of the porous SiC ceramics sintered with various additives. The porosities of the porous SiC ceramics ranged from 56% to 72% when sintered at 1750 °C. The 2AN3Y specimen showed the lowest porosity of 56%, whereas 2Y2M1S specimen showed the highest porosity of 72% among the compositions investigated herein. Those differences in porosity were attributed to the difference in sinterability of each composition at 1750 °C. In the specimens, the densification of strut was accomplished via liquid-phase sintering, and thus, sintering behavior should be affected by the liquid composition. In general, 2AN3Y, 3A2Y, 5YAG, and 3A1Y1C compositions showed good sinterability and resulted in lower porosity (<63%) than the others (>66%), such as MgO-containing specimens. Poor sinterability of the MgO-containing specimens may be due to the low viscosity of the liquid phase at 1750 °C, which leads to the local agglomeration and evaporation of the liquid phase during sintering. The weight losses of the MgO-containing specimens were 47–50% and larger than those (42–45%) of specimens without MgO.

Figure 3 shows the flexural strength data for the porous SiC ceramics as a function of porosity. The strength increased with decreasing porosity. This tendency has been

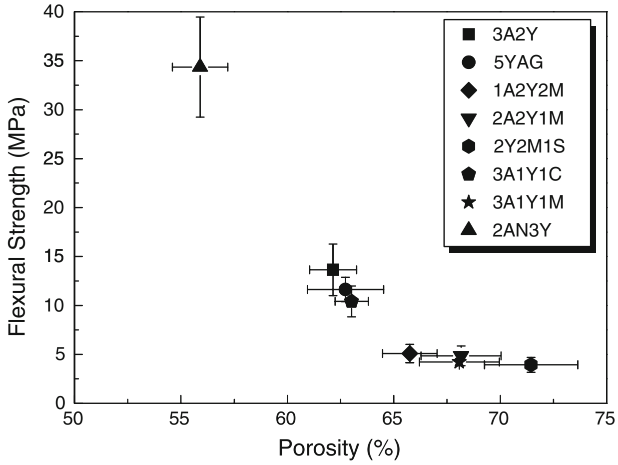

Fig. 3 Flexural strength of the porous SiC ceramics sintered at 1750 °C as a function of porosity

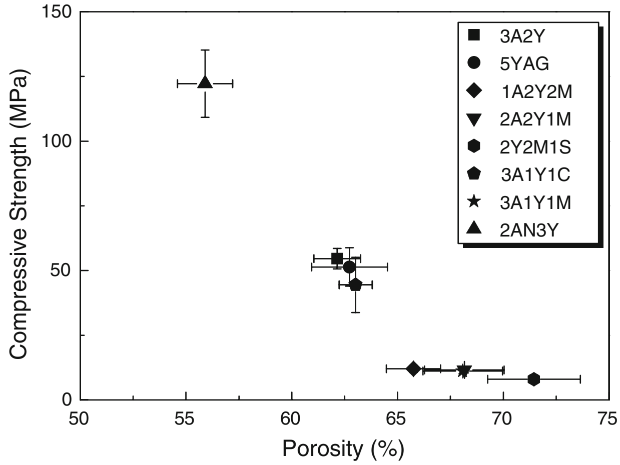

Fig. 4 Compressive strength of the porous SiC ceramics sintered at 1750 °C as a function of porosity

observed in many other porous ceramics [17, 19, 22] and was attributed to the higher probability of pore coalescence at the higher porosity under load. The pore coalescence leads to a larger defect size, resulting in lower strength.

However, 2AN3Y, 3A2Y, 5YAG, and 3A1Y1C specimens showed rapid increase in strengths at porosities in between 63% and 66%. 3A1Y1C specimen showed a strength value of 10.4 MPa at 63% porosity whereas 1A2Y2M specimen showed a strength value of 5.1 MPa at 66% porosity. The rapid increase in flexural strength from 5.1 to 10.4 MPa as the porosity decreases from 66% to 63% was due to the differences in pore morphology and degree of bonding formation between SiC grains in the strut region. Thus, relatively higher strength observed in 2AN3Y, 3A2Y, 5YAG, and 3A1Y1C specimens was attributed to more spherical morphology of pore structure (Fig. 1) and lower porosity than MgO-containing specimens. Among the compositions investigated herein, 2AN3Y led to the highest strength of 34 MPa at 56% porosity when sintered at 1750 °C.

The compressive strength data of the sintered porous ceramics are shown in Fig. 4. The compressive strength decreased with increasing porosity. However, 3A2Y, 5YAG, and 3A1Y1C specimens showed rapid increase at the porosity values between 63% and 66%. 3A1Y1C specimen showed 45 MPa at 63% porosity whereas 1A2Y2 M specimen showed 12 MPa at 66% porosity. Similarly, in the flexural strength, the rapid increase in compressive strength from 12 to 45 MPa as the porosity decreases from 66 to 63% can be explained based on the differences in pore morphology and degree of bonding formation between SiC grains in the strut region.

It has been frequently observed that the composition of sintering additives can significantly alter fracture behavior in self-reinforced bulk SiC ceramics [27]. Kim et al. [28] fabricated self-reinforced SiC ceramics with almost same microstructures but different additive compositions in the $Y_3Al_5O_{12}$–SiO_2 system and observed that one of the additive compositions showed a maximal strength. Comparable effects were also observed in many SiC and Si_3N_4 ceramics [29–31]. The results suggest that the chemistry of sintering additives affected densification of struts and pore structure. As a result of these phenomena, strength of the porous SiC ceramics was determined.

In summary, the porosities obtained ranged from 56% to 72% after sintering at 1750 °C, depending on the additive composition. The 2AN3Y specimens showed the highest strength (34 MPa, at a porosity of 56%) among the compositions investigated. The present results suggest that judicious selection of sintering additive composition is an efficient way to improve the mechanical strength of porous SiC ceramics.

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