

Microstructural development of macroporous silicon carbide ceramics during annealing

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Macroporous silicon carbide ceramics with porosities ranging from 67% to 84% were fabricated by a carbothermal reduction process from a carbon-filled polysiloxane and subsequent annealing. Microstructural development during annealing was investigated using scanning electron microscopy (SEM). The grain size increased with an increase in the annealing time and the morphology changed from equiaxed to cube or hexagonal platelets depending on the annealing temperature. By controlling the annealing time and annealing temperature, it was possible to adjust the size and morphology of SiC grains in macroporous SiC ceramics.

Key words: porous ceramics, silicon carbide, microstructure, porosity, carbothermal reduction.

Introduction

Interest in porous SiC ceramics has grown continuously, because such materials have superior chemical stability, mechanical strength, and high-temperature stability. The application of porous SiC ceramics has been broadened to include the filtration of molten metals, filtration of particles from diesel engine exhaust gases, filtration of hot corrosive gases in various industrial applications, gas burner media, membrane supports for hydrogen separation, preforms for metal matrix composites, and light-weight structural parts [1-4].

Several processing routes for porous SiC ceramics have been developed including a replica techniques [1], sacrificial template techniques [5, 6], and reaction techniques [7-11]. Recently, a new processing method for producing macroporous SiC ceramics was developed from extruded blends of carbon-filled polysiloxane using expandable microspheres as sacrificial templates [12]. The fabrication process involves the following steps: (i) extrusion and *in situ* foaming of a mixture of polysiloxane, carbon black (used as a carbon source), Al₂O₃-Y₂O₃ (used as a sintering additive), expandable microspheres (used as sacrificial templates), and SiC (an optional inert filler); (ii) cross-linking the polysiloxane in the extruded blends; (iii) transforming the polysiloxane by pyrolysis into silicon oxycarbide; and (iv) fabricating porous SiC ceramics by carbothermal reduction and subsequent sintering.

In this study, macroporous SiC ceramics were fabricated by the above method. The macroporous ceramics were annealed at 1750°C or 1950°C for 1-6 h after carbothermal

reduction. Microstructural development during annealing was investigated using scanning electron microscopy. The effect of inert filler addition on the microstructure and porosity of macroporous SiC ceramics was also investigated.

Experimental Procedure

The raw materials used in this experiment were commercially available polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan), carbon black (Corax MAF, Korea Carbon Black Co., Ltd., Incheon, Korea), SiC (Ultrafine grade, Betarundum, Ividen Co., Ltd., Ogaki, Japan), expandable microspheres (091DU40, Expancel, Sundsvall, Sweden), Al₂O₃ (AKP30, Sumitomo Chemical Co., Tokyo, Japan), and Y₂O₃ (Shin-Etsu Chemical Co., Tokyo, Japan). The SiC was added as an optional inert filler and the Al₂O₃ and Y₂O₃ were added as sintering additives. The expandable microspheres consisted of a thermoplastic polymeric shell encapsulating a hydrocarbon liquid droplet at room temperature.

Two batches of raw materials (Table 1) were compounded directly using a counter-rotating twin-screw extruder with a filament die 2.286 mm in diameter and 11.938 mm in length. The die temperature was 130°C and the extruder speed was 40 rpm. The expandable microspheres were *in situ* foamed during the extrusion process because the processing temperature was high enough to foam the microspheres. For the pyrolysis process, the extruded specimens were thermally cross-linked by heating the specimens up to 180°C in air. The cross-linked blends were then pyrolyzed at 1200°C for 1 h in argon at a heating rate of 1 Kminute⁻¹. The heat treatment allows for the polymer-to-ceramic conversion of the polysiloxane and for the decomposition of the expanded

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Table 1. Sample designation and batch composition of porous SiC ceramics.

| Sample | Batch composition (wt%) | | | | |
|--------|---------------------------|---------------------------|------------------|---------------------------------|---|
| | Polysiloxane [†] | Carbon black [‡] | SiC [*] | Hollow microsphere [§] | Sintering additive |
| SC1 | 74.8 | 10.5 | 0 | 10 | 1.9% Al ₂ O ₃ + 2.8% Y ₂ O ₃ |
| SC2 | 66.0 | 9.3 | 10 | 10 | 1.9% Al ₂ O ₃ + 2.8% Y ₂ O ₃ |

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

[‡]Corax MAF, Korea Carbon Black Co., Ltd., Incheon, Korea.

^{*}Ultrafine, Betarundum, Ividen co. Ltd., Ogaki, Japan.

[§]091DU40, Expancel, Sundsvall, Sweden.

microspheres, resulting in porous silicon oxycarbide (SiOC) containing free carbon and sintering additives [13]. The pyrolyzed compacts were then heated at 1450°C for 1 h for the carbothermal reduction of polysiloxane-derived SiOC by carbon black, and subsequently annealed at 1750 or 1950°C for 1-6 h in argon.

The bulk density of the porous ceramics was calculated from the weight-to-volume ratio of the samples. The porosity was determined from the bulk density to true density ratio. The microstructures were observed by SEM. Using CuK α radiation, X-ray diffractometry (XRD) was performed on ground powders.

Results and Discussion

The general reaction for synthesizing SiC from a mixture of polysiloxane and carbon black occurred in two steps as suggested previously [11]: (i) the pyrolysis of polysiloxane at 1200°C, which 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 higher temperatures (1750 and 1950°C) led to the grain growth of the SiC grains. In this process, the amorphous SiOC phase formed after pyrolysis at 1200°C played a role of transient binder for carbon and SiC fillers. After the carbothermal reduction, Al₂O₃-Y₂O₃ played a role of binder for synthesized SiC crystals and fillers.

XRD analysis of the specimens showed that the 1750°C-annealed specimens consisted of β -SiC and a trace of α -SiC. In contrast, the 1950°C-annealed specimens showed the presence of α -SiC and β -SiC, indicating

the occurrence of the $\beta \rightarrow \alpha$ phase transformation of SiC during annealing.

Fig. 1 shows typical fracture surfaces of the porous SiC ceramics annealed at 1750°C. The figure shows well-distributed open cells, and that porous struts in the cellular structure had also been produced. Both cell and grain growth were observed in the specimens as the annealing time was increased from 1 h to 6 h. As shown in Fig. 1, an increase in the annealing time also led to a change in the pore morphology from spherical to irregular because of the enhanced mass transport and grain growth during prolonged annealing. The cell size increased from 15-25 μm to 25-40 μm as the annealing time increased from 1 h to 6 h at 1750°C. The grain size increased and the grain morphology changed from small, equiaxed grains to faceted grains as the annealing time was increased from 1 h to 6 h. As shown in Fig. 1(b) and (c), the grain size increased from 2-7 μm to 5-11 μm as the annealing time was increased from 3 h to 6 h at 1750°C. The grain size of the 1-h-annealed specimen was difficult to measure from the micrographs because of well-sintered structure of struts.

Fig. 2 shows typical fracture surfaces of the porous SiC ceramics annealed at 1950°C. The 1-h-annealed specimen consisted of large faceted grains and small (1-3 μm) equiaxed grains. The size range of faceted grains in the 1-h-annealed specimen (Fig. 2(a)) at 1950°C was 10-20 μm . In contrast, that of the faceted grains in the 6-h-annealed specimen (Fig. 1(c)) at 1750°C was 4-10 μm . Annealing at 1950°C led to the faster formation of faceted grains than that at 1750°C, because of the enhanced grain growth at the higher temperature. The 3-h- and 6-h-annealed specimens consisted of faceted grains only. The size ranges of

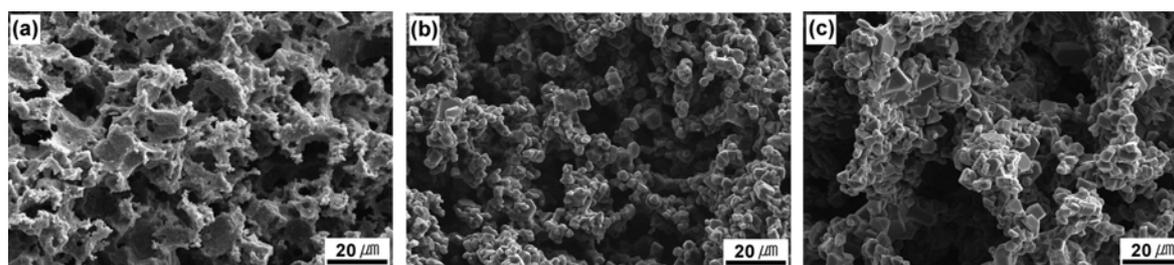


Fig. 1. Typical fracture surfaces of macroporous SiC ceramics (SC1) annealed at 1750°C for various times: (a) 1 h, (b) 3 h, and (c) 6 h.

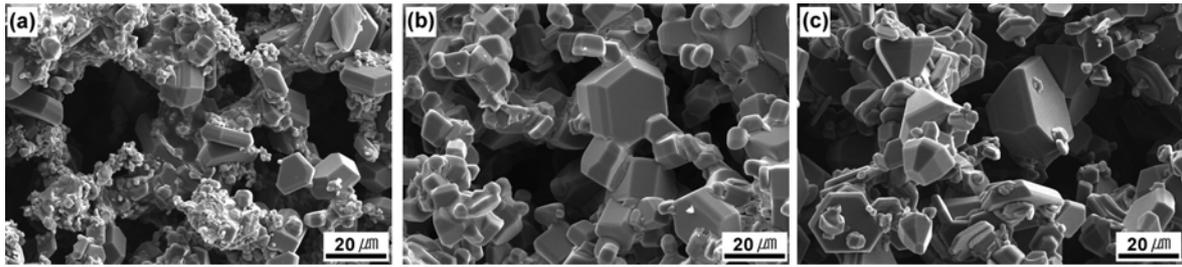


Fig. 2. Typical fracture surfaces of macroporous SiC ceramics (SC1) annealed at 1950°C for various times: (a) 1 h, (b) 3 h, and (c) 6 h.

faceted grains in the 3-h- and 6-h-annealed specimens were 8–22 μm and 8–30 μm , respectively. Prolonged annealing at 1950°C led to the continued growth of faceted grains at the expense of smaller, equiaxed grains.

Fig. 3 shows typical fracture surfaces of 6-h-annealed specimens containing fillers (SC2). The grain size and grain morphology of the specimens with fillers were equivalent with those of 6-h-annealed specimens without fillers (SC1). However, cells that are closer to spheres in shape and smaller in size were observed in the specimens with fillers (compare Fig. 3 with Fig. 1(c) and Fig. 2(c)). The addition of fillers leads to less polysiloxane in the starting composition, i.e., less volatiles (see Table 1), resulting in more dense struts and spherical cells. These results are consistent with the previous results on porous SiC ceramics fabricated by a batch process (uniaxial pressing and carbothermal reduction) [13].

Fig. 4 shows the typical grain morphology of porous SiC ceramics. The typical grain morphology of α -SiC is known to be hexagonal platelets whereas the grain

morphology of β -SiC is observed as equiaxed grains [14–16]. However, 6-h annealing at 1750°C led to the growth of cubic-shaped grains (indicated by arrows in Fig 4(a)) and grains that have a transient morphology between cube and hexagonal platelets. Both grains were well-faceted. In contrast, 6-h annealing at 1950°C led to the growth of hexagonal platelets and thick grains that look like stacked hexagonal platelets. The hexagonal-platelet shaped grains seem to be formed from the grains with the stacked hexagonal-platelet morphology. The major phases of 1750°C-annealed and 1950°C-annealed specimens were β -SiC and α -SiC, respectively. The present results suggest that the equilibrium shapes of β -SiC and α -SiC grains are cube and hexagonal platelets, respectively.

Fig. 5 shows the porosity of the macroporous SiC ceramics as a function of the annealing time. The porosity of macroporous SiC ceramics without fillers ranged from 67 to 79%, whereas that of macroporous SiC ceramics with fillers ranged from 74% to 84%. The

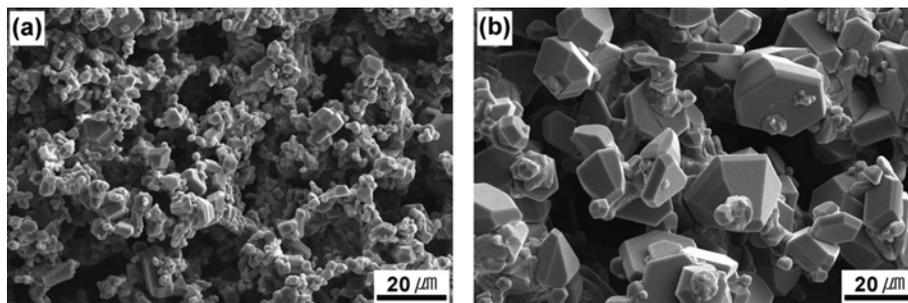


Fig. 3. Typical fracture surfaces of macroporous SiC ceramics with 10 wt% SiC fillers (SC2) annealed at (a) 1750°C and (b) 1950°C for 6 h.

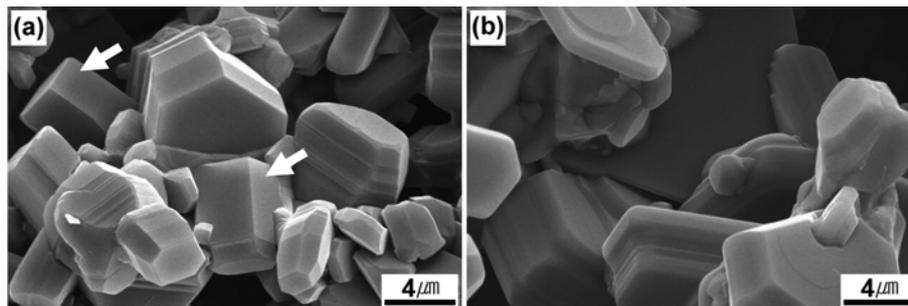


Fig. 4. Typical grain morphology of macroporous SiC ceramics (SC1) annealed at (a) 1750°C and (b) 1950°C for 6 h. The arrows denote cubic β -SiC grains.

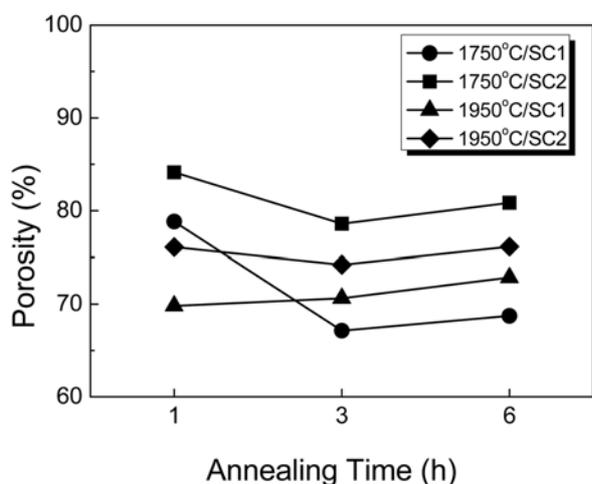


Fig. 5. Porosity of macroporous SiC ceramics as a function of annealing time.

addition of fillers led to the higher porosity for both materials (SC1 and SC2). The addition of fillers leads to less polysiloxane in the starting composition (see Table 1), i.e., less binder. Thus, microspheres expanded more easily when fillers were added. Similar results were also observed in a batch-processing of macroporous SiC ceramics [13].

The annealing at 1750°C decreased the porosity slightly because of the further densification during annealing. The porosities of 1-h- and 6-h-annealed SC1 specimens were 79% and 69%, respectively. The porosities of 1-h- and 6-h-annealed SC2 specimens were 84% and 81%, respectively. In contrast, the annealing at 1950°C increased the porosity slightly; the porosities of 1-h- and 6-h-annealed SC1 specimens were 70% and 73%, respectively. The weight loss of the specimens during carbothermal reduction and annealing processes increased from 67.2 to 70.5% with an increase of the annealing time from 1 h to 6 h at 1950°C. Thus, the increased porosity of the specimens was attributed to the increased weight loss during annealing. The conversion of the polysiloxane into a silicon oxycarbide, and the reactions between SiC and a polysiloxane-derived SiO₂ and between SiC and additives added were thought to be responsible for the severe weight loss [11, 13, 17].

Conclusions

Microstructural development of macroporous silicon carbide ceramics during annealing was investigated. The grain size increased with an increase of the annealing time and the morphology of SiC grains changed from equiaxed to cube at 1750°C and to hexagonal platelets at 1950°C. The equilibrium shapes of β-SiC and α-SiC grains are believed to be cube and hexagonal platelets, respectively. The introduction of an inert filler increased

the porosity, but had no other influence on the microstructural development. The annealing at 1750°C decreased the porosity because of the further densification during annealing. In contrast, the annealing at 1950°C increased the porosity slightly because of the increased weight loss during annealing. By controlling the annealing time and annealing temperature, it was possible to adjust the grain size and morphology of SiC grains in macroporous SiC ceramics.

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