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LETTER

Processing highly porous SiC ceramics using poly(ether-co-octene) and hollow microsphere templates

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Ceramic components with high porosity, high strength, and good permeability are especially required for hot-gas and molten metal filters, catalyst supports, preforms for making metal matrix composites, gas burner media, and lightweight structural parts [1–8]. Silicon carbide (SiC) has been considered a candidate material for hot-gas filters due to its unique combination of such properties as high thermal conductivity, superior mechanical features, high thermal shock capacity, and corrosion resistance [9–13]. Highly porous (porosity ≥ 80%) SiC ceramics are prepared using the following processing methods: (1) immersion of the polyurethane (PU) foams in a ceramic slurry, and drying, burning out the PU, and then sintering [1, 5, 14]; (2) freezing of gel containing SiC powders [4] or freezing the polycarbosilane/camphene solution [15]; (3) gel-casting of SiC powder mixtures using agar as the gelling agent [16]; and (4) pyrolysis of a cross-linked body consisting of a polycarbosilane precursor and polymer microbead templates [17], or pyrolysis and carbothermal reduction of a cross-linked body consisting of a polysiloxane precursor, polymer microbead templates, phenol resin, and optional sintering additives [18].

The recent research studies indicate that highly porous ceramic structures can be prepared by the compounding and pyrolysis of polysiloxane and low density polyethelene (LDPE) blends [19, 20]. The processing temperature using LDPE was 110–140 °C. Polysiloxane is likely to cross-link at such high temperatures [21], and the cross-linked polysiloxane structure will in turn suppress the LDPE phase dispersion in the polysiloxane phase. Moreover, under high shear conditions, the dispersed polymer phase will tend to agglomerate again due to the rapid relaxation of the polymer chain at high processing temperatures. Poly(ether-co-octene) (PEOc) is a type of thermoplastic elastomer with a low melting point (melting peak around 60 °C), high molecular weight, and low crystallinity [22]. Thus, the consequences of the high-temperature cross-linking of polysiloxane can be avoided during blending, and the degree of co-continuous structure and mechanical properties can be improved by using polysiloxane–PEOc polymer blends.

This study describes a new method of preparing highly porous SiC ceramics using polysiloxane, PEOc, and hollow microsphere templates. Commercially available polysiloxane (YR3370, softening point: 109 °C, melting point: ~155 °C GE Toshiba Silicones Co., Ltd, Tokyo, Japan), a carbon black (Corax MAF, Korea Carbon Black Co., Ltd., Inchon, Korea), α-SiC (FCP15C, Norton AS, Lillesand, Norway), hollow poly(methyl methacrylate) microspheres (461DU40, Expancel, Sundsvall, Sweden), PEOc (metallocene catalyzed copolymer of ethylene and 1-octene, Engage 8200, melting peak: 63.0 °C, Dow Chemical Co., Michigan, USA), AlN (Grade F, 1.3 μm, Tokuyama Soda., Tokyo, Japan), and Y_2O_3 (0.4 μm, 99.99% pure, Kojundo Chemical Laboratory Co., Sakado, Japan) were used as starting materials. Three batches of powders were prepared with 30 wt% PEOc, 14 wt% SiC, and 3.5 wt% sintering additives (1.4 wt% AlN + 2.1 wt% Y_2O_3). The content of hollow microspheres in those batches changed as follows: 7, 10.5, and 14 wt% (Table 1). Inorganic raw materials

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

Sample designation	Composition (wt%)						
	Polysiloxane[a]	PEOc[b]	Hollow microspheres[c]	Carbon black[d]	SiC[e]	AlN[f]	Y_2O_3[g]
7T	39.9	30	7	5.6	14	1.4	2.1
10T	36.82	30	10.5	5.18	14	1.4	2.1
14T	33.81	30	14	4.69	14	1.4	2.1

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

[b] Engage 8200 Dow Chemicals, USA

[c] 461DU40, Expancel, Sundsvall, Sweden

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

[e] FCP15C, Norton AS, Lillesand, Norway

[f] Grade F, Tokuyama Soda., Tokyo, Japan

[g] Kojundo Chemical Laboratory Co., Sakado, Japan

containing SiC, carbon black, AlN, and Y_2O_3 were first dry mixed in a container, and all individual batches were melt-blended using a counter-rotating Brabender mixer by maintaining a temperature of 80 °C with a rotator speed of 150 rpm for 15 min. Subsequently, cylindrical specimens with a thickness of 3 mm and a diameter of 50 mm were prepared by compression molding at 80 °C. The compacts were cross-linked by heating them to 200 °C in the air. The cross-linked samples were pyrolyzed at 1100 °C for 1 h at a heating rate of 1 °C/min in argon, allowing the polysiloxane to convert to silicon oxycarbide (SiOC) in the specimens [23]. The composition of SiOC after pyrolysis was $SiO_{1.50}C_{0.68}$ [24]. The pyrolyzed specimens were further heat-treated in argon to 1450 °C for 1 h at a heating rate of 10 °C/min for carbothermal reduction of SiOC and were subsequently annealed at 1750 °C for 2 h for the liquid-phase sintering of SiC using AlN and Y_2O_3. 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 the true density ratio. Flexural strength was measured at room temperature using the four-point bending method. The fracture surfaces were observed by scanning electron microscopy.

The uniform dispersion and mixing of the polysiloxane–sacrificial templates–inorganic materials blends is essential to improving the polysiloxane's processability and in controlling the cell morphology of the final ceramic structure [19]. A uniformly mixed blend of polysiloxane, PEOc-hollow microsphere templates, SiC and carbon black fillers, and AlN-Y_2O_3 additives could be achieved by dry mixing, melt-blending, and compression molding. As the blending and molding of the powder mixtures were done at 80 °C, the PEOc in the mixture completely melted and uniformly dispersed in the polysiloxane–hollow microspheres–inorganic powders mixture. During pyrolysis of the cross-linked compact at 1100 °C, the polysiloxane converted to an amorphous Si–O–C (SiOC) phase, while the PEOc and hollow microspheres decomposed and formed pores. The subsequent carbothermal reduction of SiOC with carbon black at 1450 °C converted SiOC to β-SiC with the evolution of gaseous CO [25, 26]. Further heat treatment with the aid of sintering additives led to liquid-phase sintering of the SiC fillers and synthesized SiC [27].

Typical fracture surfaces of the prepared SiC ceramics are shown in Fig. 1. Highly porous structures with duplex pore morphology and porous struts were obtained. Besides large, interconnected, tangled voids in a size range of 20–55 μm (indicated by arrows with solid lines in Fig. 1), small spherical open-cells in a size range of 3–14 μm (indicated by arrows with dashed lines in Fig. 1) were also present. The large interconnected voids were generated by decomposing PEOc, while small spherical open-cells were generated by the hollow microspheres. The polymer microspheres retained their shape until reaching their decomposition temperature. The homogeneous distribution of large interconnected pores indicates the uniform dispersion of the PEOc melt with the polysiloxane–hollow microspheres–inorganic powders blend during molding. The large quantity of spherical cells with a polysiloxane-derived SiC strut suggests that hollow microspheres were greatly inclined to mix with the polysiloxane prior to pyrolysis (see Fig. 1a). The reported reticulated porous ceramics and the highly porous SiC ceramics in this study are mainly differentiated by their unique microstructures. The continuous pore channels among the struts formed as result of the burning out of the PU foam in the reticulated SiC ceramics prepared by the replica method [7, 14]. However, microstructures in this study showed spherical cells. Such discontinuous pore channels may give the ceramic structure better strength than the ceramics fabricated by the replica method. By increasing the hollow

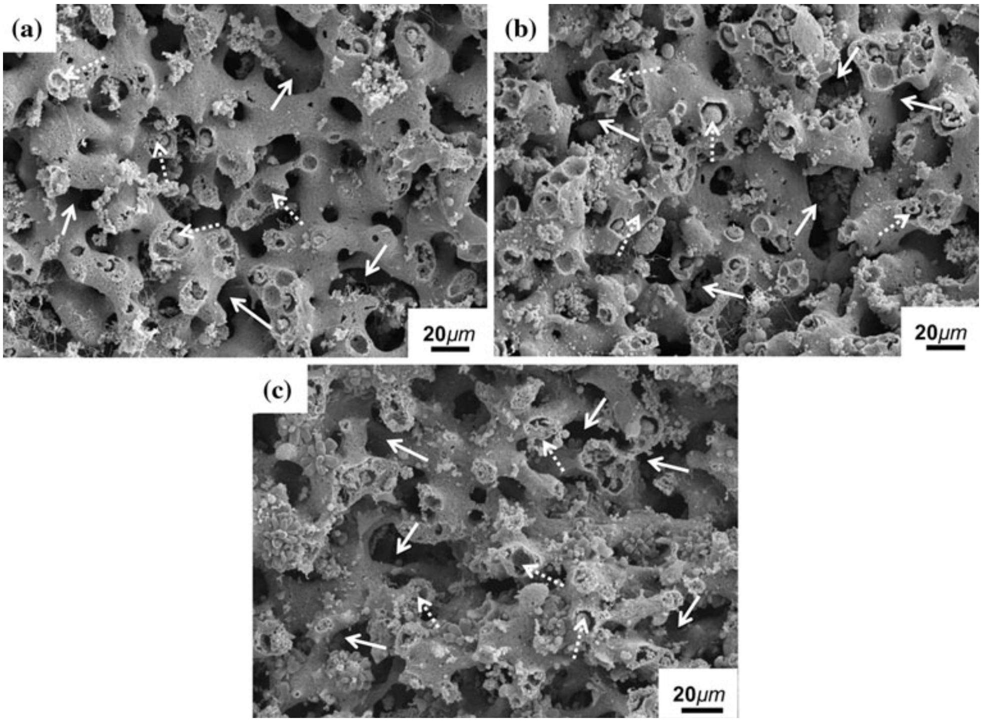

Fig. 1 Typical fracture surfaces of porous SiC ceramics prepared using 30 wt% PEOc and **a** 7 wt%, **b** 10 wt%, and **c** 14 wt% hollow microsphere templates. *Arrows* with *solid line* indicate the interconnected pore channels, and *arrows* with *dashed line* indicate the spherical cells

microsphere content from 7 to 10%, the microstructure showed increased spherical open-cells and their distribution. The coalescence of spherical cells was largely observed, while the PEOc-generated large irregular pore structure was hardly disturbed (see Fig. 1b). By further increasing the hollow microsphere content to 14%, the coalescence of the spherical cells increased and the large pore structure partly collapsed (see Fig. 1c). There was no difference in the size of the large pores or the spherical cells with varied hollow microsphere content, but there were differences in their porosity.

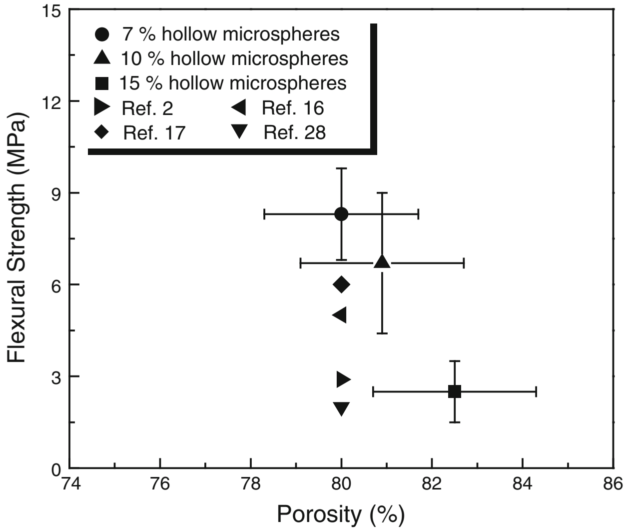

Fig. 2 Flexural strength as a function of the porosity and hollow microsphere content of the highly porous SiC ceramics. *Error bars* indicate standard deviation of values from at least six specimens of each composition. Literature data for the highly porous SiC ceramics is also shown

Porosity measurements of the prepared SiC ceramics exhibited high porosity, ranging from 80 to 83%, and the flexural strength varied from 2.5 to 8.3 MPa. Specimens prepared with 7, 10, and 14% hollow microsphere content showed 8.3 MPa strength and 80% porosity, 6.7 MPa strength and 81% porosity, and 2.5 MPa strength and 82.5% porosity, respectively (see Fig. 2). Few studies reported on the flexural strength of highly porous SiC ceramics. The flexural strength of highly porous SiC ceramics made by a replica technique, template method, foaming, and gel casting was 0.5–2.0 MPa at 80% porosity [7, 28], ~6 MPa at 80% porosity [17], ~2.9 MPa at 72-88% porosity [2], and ~5 MPa at 80% porosity [16, 28], respectively. The superior strength (8.3 MPa) of highly porous (80% porosity) SiC ceramics obtained with 7% hollow microsphere content in this study is due to both the homogenous microstructure and the discontinuous pore channel (see Fig. 3). The homogeneous microstructure is attributed to the efficient mixing of the polysiloxane, inorganic materials, and templates by blending and

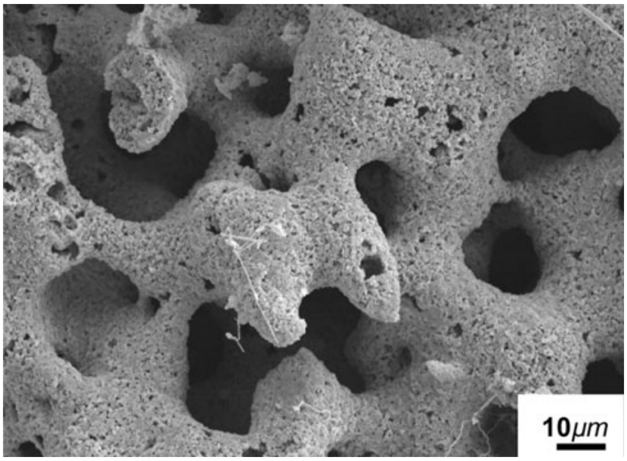

Fig. 3 Homogeneous microstructure and the lack of continuous pore channel inside the strut of the highly porous ceramics prepared using 30 wt% PEOc and 7 wt% hollow microsphere templates

compression molding. The decrease in strength with the increase in the porosity of the highly porous ceramics in this study can be attributed to spherical cell coalescence, and also to the partial collapse of the large interconnected pore structure (see Fig. 1c).

In summary, highly porous (porosity ≥ 80%) SiC ceramics were successfully prepared from the compression molded mixture of polysiloxane, PEOc and hollow microsphere templates, SiC and carbon black fillers, and AlN-Y_2O_3 additives by pyrolysis, carbothermal reduction, and subsequent sintering. The PEOc content was fixed at 30%, and the hollow microsphere content was varied from 7 to 14% to produce porous SiC ceramics with porosities ranging from 80 to 83%. The microstructure showed large interconnected pore channels, small spherical open-cells, and porous struts. When 7% hollow microspheres were used, a maximum flexural strength of ~8 MPa was obtained with SiC ceramics that had 80% porosity. This study suggests that the proposed technology can be implemented on an industrial production scale. The reported processing method using low-cost compression molding is particularly useful in fabricating large-sized components where the total amount of porosity and strength are key factors.

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