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LETTER

Low temperature processing of highly porous silicon carbide ceramics with improved flexural strength

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Porous silicon carbide ceramics have many industrial applications, such as hot gas particulate filters, molten metal filters, preforms for a metal–matrix and polymer–matrix composites, gas burner media, and light weight structural parts on account of their low density, thermal stability, chemical stability, high specific strength, and high thermal shock resistance [1–6]. Different processing routes for highly porous SiC ceramics have been developed for specific applications to satisfy the associated requirements of porosity, pore size, and degree of interconnectivity. These manufacturing techniques are typically divided into three categories: replica techniques [4, 7], reaction techniques [8–10], and gel casting techniques [11]. Recently, the production of porous ceramics from preceramic polymers has attracted considerable attention due to the expected improvement in the properties of porous ceramics and the potential cost-effective polymer processing [12–15]. The synthesis of SiC ceramics via polymer precursor routes has attracted increasing interest in recent years [16, 17]. The most important advantage of this method is the ease of preparation at low processing temperatures. Polycarbosilane is a well-known polymeric precursor for SiC ceramics that is used for the processing of porous SiC ceramics.

This paper describes a simple pressing process for the fabrication of highly porous SiC ceramics using polycarbosilane (NIPUSI type-A, Nippon Carbon Co., Ltd, Tokyo, Japan) as a precursor for SiC, polymer microbeads (~8 μm, poly (methyl methacrylate-*co*-ethylene glycol dimethacrylate), Sigma–Aldrich Inc., St. Louis, USA) as a template, and a polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd, Tokyo, Japan) as a binder. Since the polysiloxane is dissolved in ethanol and makes a uniform coating on the polycarbosilane and polymer microbeads, it acts as a binder with respect to both materials. Six batches were mixed for 6 h in a polyethylene jar containing ethanol and SiC balls. The content of polymer microbeads in those batches ranged from 40 to 90 wt% (Table 1). The milled powder mixture was dried and pressed uniaxially under 50 MPa to produce the rectangular bars. The compacts formed were cross-linked by heating them to 200 °C in air. The cross-linked samples were pyrolyzed at 1100–1400 °C for 1 h at a heating rate of 1 °C/min in argon. The heat treatment allows for the decomposition of polymer microbeads and the polymer-to-ceramic conversion of the polycarbosilane in the compacts, resulting in a porous SiC ceramic.

The bulk density of the porous ceramics was calculated from the weight-to-volume ratio. The true density (i.e., skeleton density) of the silicon carbide material after pyrolysis was measured using a pycnometer for powdered samples. The cell morphology was observed by scanning electron microscopy (SEM). The porosity was determined by measuring the ratio of the bulk density to the true density. The cell density of the foams was measured by counting the number of cells in a two-dimensional image on the microstructure and converting it to three-dimensions [18]. The flexural strength of the samples, 3 mm × 4 mm × 30 mm in size, was measured using a three-point method with a span and crosshead speed of 20 mm and 0.5 mm/min, respectively.

Figure 1 shows the typical fracture surfaces of the porous SiC ceramics. A homogeneous microstructure with

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Table 1 Batch composition of porous SiC ceramics

Sample	Batch composition (wt%)		
	Polycarbosilane[a]	Microbead[b]	Polysiloxane[c]
CS1	60	40	3
CS2	50	50	3
CS3	40	60	3
CS4	30	70	3
CS5	20	80	3
CS6	10	90	3

[a] NIPUSI type-A, Nippon Carbon Co., Ltd, Tokyo, Japan

[b] Poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate) microbeads, Sigma–Aldrich Inc., St. Louis, USA

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

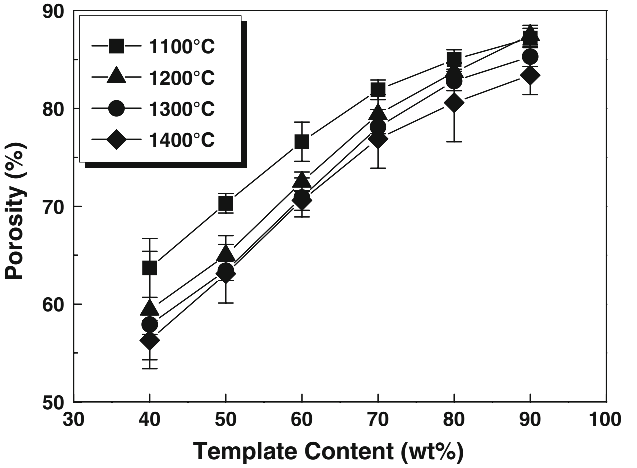

Fig. 2 Porosity of the porous SiC ceramics as a function of the template content

partially interconnect spherical cells was obtained for all specimens. The shape of the polymer microbeads was retained in those specimens up to its decomposition temperature. The coalescence of cells was also observed, which increased with increasing polymer microbead content. There was no difference in cell morphology or cell size in each specimen when pyrolyzed at the same temperature, but there were differences in porosity.

Figure 2 shows the porosity of the porous SiC ceramics as a function of the template content. The porosities of the porous ceramics ranged from 56 to 88%, depending on the template content and pyrolysis temperature. The bulk density of the porous ceramics ranged from 0.30 to 1.18 g/cm^3. The porosity increased with increasing template content. It was expected that a higher template content would lead to a larger number of cells, resulting in a lower bulk density and higher porosity. The porosity decreased with increasing pyrolysis temperature. Figure 3 shows the strut microstructure of the porous SiC specimens pyrolyzed at various temperatures. When the specimen was pyrolyzed at 1100 °C, the strut contained many small (<500 nm) pores. With increasing pyrolysis temperature, densification of the strut took place progressively (compare Fig. 3a–d), and the cell size decreased due to densification. The average cell sizes of the 1100 °C- and 1400 °C-pyrolyzed specimens were 8.0 ± 0.7 and 5.1 ± 0.5 μm, respectively. Therefore, the decrease in

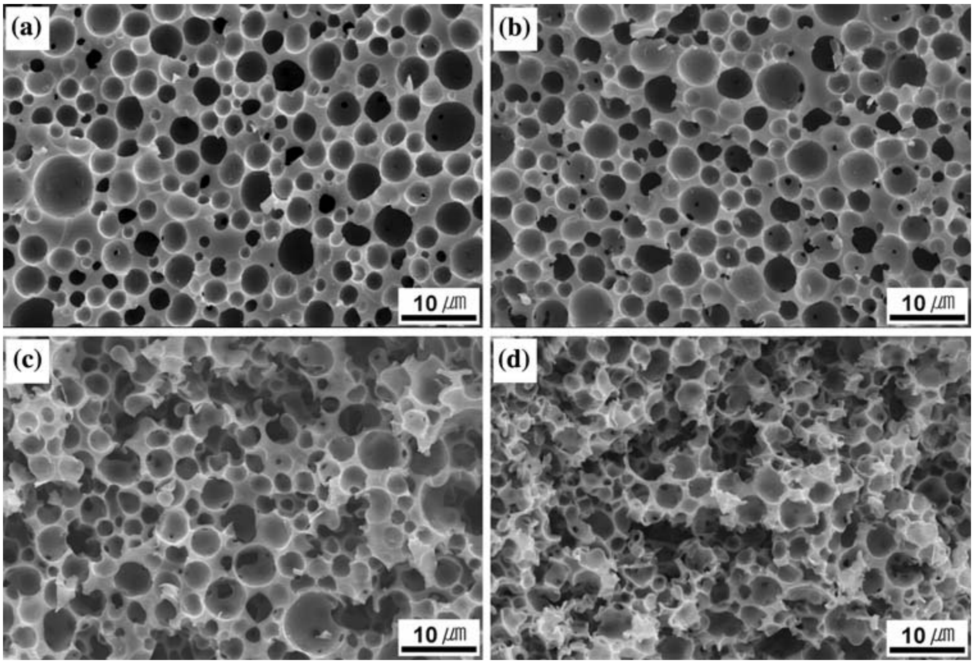

Fig. 1 Typical fracture surfaces of porous SiC ceramics pyrolyzed at 1300 °C for 1 h at a heating rate of 2 °C/min in argon: **a** CS3, **b** CS4, **c** CS5, and **d** CS6 (refer to Table 1)

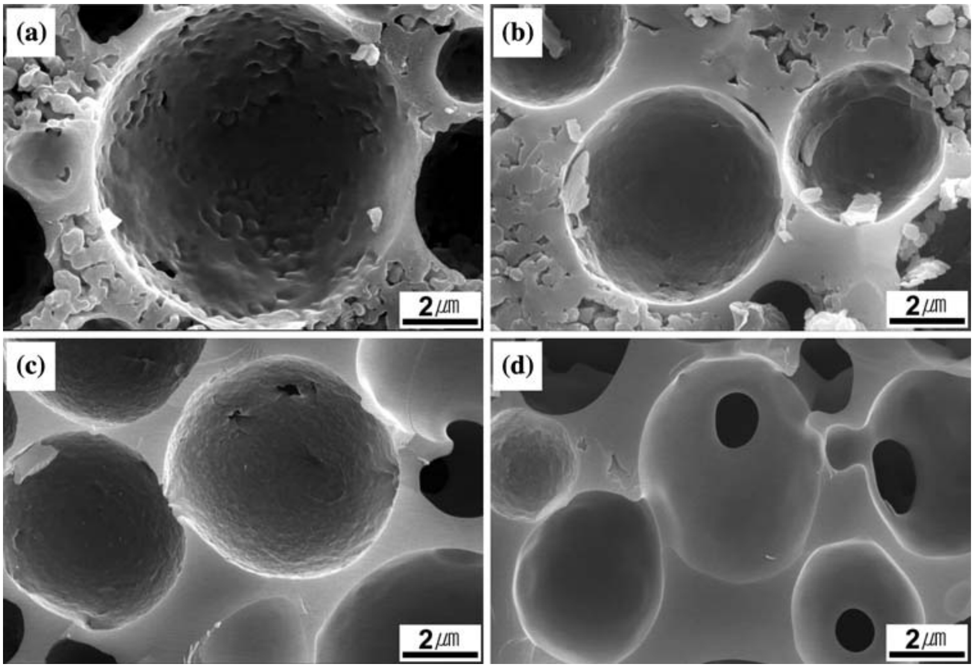

Fig. 3 Strut microstructure of the porous SiC ceramics pyrolyzed at various temperatures for 1 h in argon (CS3): **a** 1100 °C, **b** 1200 °C, **c** 1300 °C, and **d** 1400 °C

porosity with increasing pyrolysis temperature (Fig. 2) was attributed to the increased densification of the strut. The cell density increased gradually from 9.4 ± 0.3 × 10^9 cells/cm^3 for the 1100 °C-pyrolyzed specimen containing 40%-microbeads (CS1) to 1.6 ± 0.3 × 10^{10} cells/cm^3 for the 1400 °C-pyrolyzed specimen containing 90%-microspheres (CS6). All specimens had cell densities >9 × 10^9 cells/cm^3 and cells <10 μm in diameter.

Figure 4 shows the flexural strength as a function of porosity. The strength generally decreases with increasing porosity. However, the flexural strength of the porous SiC ceramics with 60–73% porosity showed a pyrolysis temperature dependency. The strength increased with increasing pyrolysis temperature. For example, the flexural strength of the 1400 °C-pyrolyzed specimen with ~71% porosity was ~32 MPa, whereas that of the 1100 °C-pyrolyzed specimen with ~70% porosity was ~10 MPa. The same trend was observed at ~63% porosity. The increase in flexural strength with increasing pyrolysis temperature at the same porosity was attributed to the enhanced densification of the strut after higher temperature pyrolysis, as shown in Fig. 3. Interestingly, a pyrolysis temperature dependency of strength was not observed at 75–88% porosity. Figure 1c, d clearly shows the occurrence of cell coalescence at a higher microbead loading, resulting in higher porosity (>75%). The increased cell size due to coalescence could act as a critical flaw in the fracture of those specimens. Therefore, the insensitivity of strength with pyrolysis temperature was observed at highly porous (>75%) SiC ceramics.

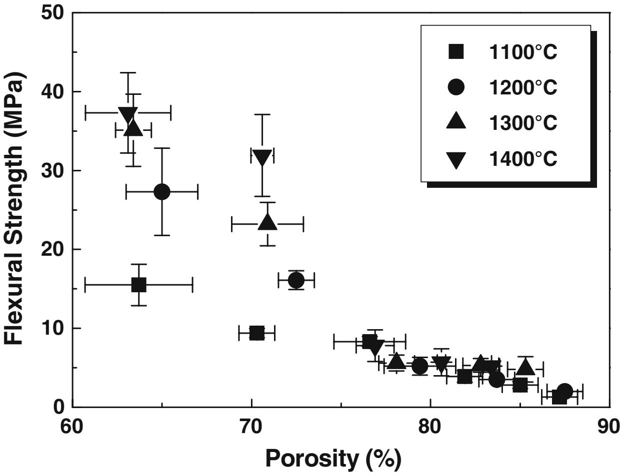

Fig. 4 Flexural strength of the porous SiC ceramics as a function of porosity

There are few reports showing the mechanical properties of highly porous SiC ceramics. The flexural strength of porous SiC ceramics made by a replica technique, reaction method and gel casting was 0.5–2.0 MPa at 80% porosity [7, 19], ~4 MPa at 73% porosity [20], and ~5 MPa at 80% porosity [7], respectively. The typical flexural strengths of the present porous SiC ceramics pyrolyzed at 1400 °C were ~30 MPa and ~6 MPa at 70 and 80% porosity, respectively. The superior strength of the polycarbosilane-derived porous SiC ceramics was attributed to the homogeneous microstructure, i.e., lack of macroscopic defects (see Fig. 1) and small cell size (5–8 μm, see Fig. 3). The cell sizes of the porous SiC ceramics made by the replica technique [4, 7], reaction technique [20], and gel casting [7] were 0.3–3 mm, 10–20 µm, and 100–400 µm, respectively. Colombo et al. [12] reported that the compressive strength of microcellular SiOC ceramics decreased with increasing cell size. Similarly, the smaller cell size of the present material decreased the critical flaw size and contributed to the improved strength compared to the materials prepared by other methods.

The ceramics produced from polycarbosilane are actually not SiC in composition but Si(O)C because oxygen is incorporated into SiC material from polysiloxane binder and from air during cross-linking. The incorporation of oxygen into SiC would considerably decrease its high temperature stability. Thus, further work on cross-linking in nonoxidizing atmosphere and the minimization or removal of polysiloxane binder is necessary for improving the high temperature stability of the porous Si(O)C ceramics.

In summary, highly porous Si(O)C ceramics with improved strength were fabricated successfully by pyrolyzing a cross-linked body consisting of polycarbosilane and polymer microbeads at 1400 °C in an argon atmosphere. The typical flexural strengths of the porous ceramics pyrolyzed at 1400 °C were ~30 MPa at 70% porosity and ~6 MPa at 80% porosity. These results suggest that a simple pressing route that employs polycarbosilane and polymer microbeads as starting materials is an efficient way of manufacturing highly porous SiC ceramics with improved flexural strength.

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