Effect of starting particle size and barium addition on flexural strength of polysiloxane-derived SiOC ceramics

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The effects of starting particle size and Ba addition on the flexural strength of bulk SiOC ceramics were investigated in polymer-derived SiOC ceramics prepared by a conventional ceramic processing route. Crack-free, dense SiOC discs with 6–7 mm thickness and a 30 mm diameter were successfully fabricated from commercially-available polysiloxane without any fillers or 1 mol % barium isopropoxide-derived Ba as an additive. Agglomerates formed after pyrolysis of polysiloxane led to the formation of domain-like structures surrounded by pores after sintering. The flexural strength of bulk SiOC is strongly dependent on the domain size and Ba addition. Both minimization of the agglomerate size in the starting powders by milling after pyrolysis and judicious selection of additives which reinforce the SiOC structure are efficient ways to improve the flexural strength of bulk SiOC ceramics. The typical flexural strength of bulk Ba-doped SiOC ceramics fabricated from submicron-sized SiOC powders was 220 MPa.

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1. Introduction

Polymer-derived ceramics (PDCs) based on Si–O–C have attracted a variety of interests, especially for applications in functional and structural parts,1–6 processing of ceramic foams,7–9 and synthesis of cost-effective long fibers,10,11 due to their improved mechanical, thermal, and chemical properties compared to amorphous SiO2.12–17 However, because of the excessively large shrinkage and weight loss during pyrolysis of these ceramics, it is difficult to prepare dense, monolithic SiOC ceramics. In order to solve the shrinkage problem, inert or active fillers are usually added to the starting preceramic polymer powders.18 The filler-free SiOC ceramics developed and reported in the literature are mostly either porous or thin films.7,8,19,20 There is limited research on flexural strength of dense, monolithic SiOC ceramics. Renlund et al.19 reported an average flexural strength of 385 ± 227 MPa (by 3-point bending) in SiOC glass prepared by the pyrolysis of silicone resins (SR350 General Electric Silicon Products Div., Waterford, NY, USA). Soraru et al.12 reported an average flexural strength of 350 ± 230 MPa using rod-shape specimens prepared by the pyrolysis of sol–gel precursors. Walter et al.21 found that the flexural strength of sol-gel-derived SiOC ceramics increased with an increase in the C/Si ratio, which corresponds with the amount of SiC in the pyrolyzed ceramics. A maximum strength of 600 ± 90 MPa was obtained in rod-shape samples by 4-point bending. Estefanian et al.22 processed crack-free, dense SiOC samples (discs of 20 mm diameter and 2–3 mm thickness) using the conventional ceramic processing route, i.e., by hot-pressing a pyrolyzed silicone resin powder (PMS MK powder, Wacker, Burghausen, Germany). The flexural strength values of the bulk SiOC samples were 173–222 MPa when measured by the ball-on-three-balls testing methods. Recently, Mazo et al.23 successfully fabricated fully dense bulk SiOC ceramics by a conventional ceramic processing route consisting of (1) pyrolysis of tetraethyldisilicate/poly(dimethylsiloxane) (TEOS/PDMS) hybrids, (2) attrition milling of the pyrolyzed powders, (3) mixing of the SiOC powders with 6 wt % binders (isobutyl methacrylate or PDMS), (4) uniaxial pressing of the mixed powders, (5) cold isostatic pressing of the formed body, and finally (6) sintering at 1550°C for 4–12 h in nitrogen atmosphere. A maximum flexural strength of 153 ± 15 MPa was obtained by a 3-point bending test (a span of 20 mm) in the bulk SiOC ceramics.

The flexural strength data reported in bulk SiOC ceramics prepared by the pyrolysis of preceramic polymers are particularly scattered, because of widely distributed critical flaw sizes. In contrast, the flexural strength data obtained in bulk SiOC ceramics prepared by the conventional ceramic route are less scattered. However, the starting SiOC powders in the conventional ceramic processing route were as-pyrolyzed powders22 or micron-sized powders (4.51 μm after 2-h attrition-milling).23 There is no report on the effects of starting particle size on the flexural strength of bulk SiOC ceramics prepared by the conventional ceramic processing route. Furthermore, there is no report on the flexural strength of SiOC ceramics fabricated from submicron-size SiOC powders. In this paper, we first report the effect of starting SiOC particle size on the flexural strength of bulk SiOC ceramics prepared by the conventional ceramic processing route. In a previous study on alkaline earth-modified SiOC-bonded SiC ceramics,24 1 mol % Ba addition increased the flexural strength of SiOC-bonded SiC ceramics significantly because of the formation of both Si–O–Ba bonds and a compact silicon suboxide structure in the Ba-doped SiOC bonding materials. Thus, Ba-doped SiOC ceramics were also prepared by conventional hot-pressing, and the effects of Ba addition on the crystallization behavior and flexural strength of bulk SiOC ceramics were also investigated.
2. Experimental procedure

Commercially-available polysiloxane (YR3370, Momentive Performance Materials Japan Inc., Tokyo, Japan, chemical composition of pyrolysis residue SiO_{1.50}C_{0.68} and barium isopropoxide [Ba(OCH(CH_3)_2)]_2, Alfa Aesar, Johnson Matthey Co., Ltd., Ward Hill, MA, USA) were used as starting materials. To prepare a batch without Ba (hereafter, SiOC), as-received polysiloxane was ground using an agate mortar and pyrolyzed at 1000°C in flowing argon with a heating rate of 2°C/min and a dwell time of 2 h. To prepare a batch containing 1% Ba [Ba/(Ba+Si) mole ratio = 0.01] (hereafter, SiOC-Ba), 96.85% polysiloxane and 3.15% barium isopropoxide were mixed in polypropylene jars for 16 h using ethanol and SiC balls (Table 1). The milled slurry was dried and pyrolyzed under the same conditions as the batch without Ba. The pyrolyzed powders were separately milled for 0.5, 12, or 48 h using SiC balls and a planetary mill at 250 rpm. The milled powders were uniaxially pressed in a cylindrical mold (30 mm in diameter) and subsequently hot-pressed at 1550°C for 1 h under an applied pressure of 40 MPa in argon atmosphere. The heating and cooling rates over a temperature range of 1000–1550°C were 20 and 30°C/min, respectively. Discs of 30 mm in diameter and 6–7 mm in thickness were prepared by this method.

The specific surface area of the milled powders was evaluated employing the Brunauer, Emmet and Teller analysis. The particle morphology and size of the milled powders were observed using scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan) and transmission electron microscopy (TEM; JEM-2000 EX, JEOL Ltd., Tokyo, Japan) and transmission electron microscopy (TEM; JEM-2000 EX, JEOL Ltd., Tokyo, Japan). The bulk density of the resulting SiOC ceramics was calculated from the weight-to-volume ratio of the samples. The open porosity was measured using the Archimedes method. Crystalline phases were determined on ground powders via X-ray diffractometry (XRD, D8 Discover, Bruker AXS GmbH, Karlsruhe, Germany). The polished surfaces and the fracture surfaces were observed by SEM. Elemental distribution in the polished 0.5-h milled SiOC-Ba and 48-h milled SiOC-Ba specimens was analyzed by EPMA (JXA-8500F, Jeol, Tokyo, Japan) at 15 kV and 30 mA. For the flexural strength measurements, bar-shaped samples were cut to a size of 2 mm × 2.5 mm × 25 mm. Bend tests were performed at room temperature on 5–10 samples under each condition using a four-point method with inner and outer spans of 10 and 20 mm, respectively, and a crosshead speed of 0.5 mm/min.

3. Results and discussion

The specific surface areas of the 0.5-h milled, 12-h milled, and 48-h milled SiOC powders were 1.3, 3.4, and 7.5 m²/g, respectively. Figure 1 shows the morphology and particle size of the milled SiOC powders. The 0.5-h milled powders (hereafter, SiOC-0.5 h) consisted of mostly micron-sized powders and are agglomerated. In contrast, the 48-h milled powders (SiOC-48 h) consisted of submicron-sized powders and are extremely agglomerated. By assuming the morphology of milled particles to be spherical, the average particle sizes were calculated from the measured specific surface areas as 2.17 µm for 0.5-h milled powders, 0.85 µm for 12-h milled powders (SiOC-12 h), and 0.39 µm for 48-h milled powders.

Figure 2 shows the XRD patterns of the ground powders from SiOC and SiOC-Ba specimens (both were fabricated using 48-h milled powders). The SiOC specimen showed a broad hump at 2θ = 20–25 degrees which is a characteristic of the amorphous silicate structure. No crystalline peaks were observed in the SiOC specimen. In contrast, crystallization of β-cristobalite and β-SiC was observed in the 1 mol% Ba-doped SiOC specimen (SiOC-Ba). Saha and Raj(26) suggested that the crystallization resistance of amorphous SiOC varies with the carbon content. In SiOC materials with high-carbon content, crystallization is usually accompanied by weight loss resulting from the carbothermal reduction of SiO₂, whereas phase separation can lead to crystallization without significant weight loss in SiOC materials with low-carbon content. Rouxel et al.(27) observed the crystallization of β-cristobalite and β-SiC at 1200°C in amorphous SiOC with a composition of SiO_{1.35}C_{0.33}, which contains smaller amounts of carbon compared to the present SiOC specimen (SiO_{1.26}C_{0.68}). Esfahanian et al.(28) observed the crystallization of β-SiC after hot-pressing at 1400°C and the crystallization of β-SiC and turbostratic carbon after hot-pressing at 1600°C in amorphous SiOC with a composition of SiO_{1.46}C_{0.81}, which contains more carbon compared to the present SiOC specimen. Thus, the absence of crystallization peaks in the present SiOC ceramics is unusual because β-SiC crystallized in more carbon-rich SiOC.

| Sample designation | Composition (wt%) | Ba/(Ba+Si) mole ratio |
|---------------------|------------------|----------------------|
| SiOC                | 100% polysiloxane| 0                    |
| SiOC-Ba             | 96.9% polysiloxane + 3.1% bariumisopropoxide | 0.01                 |

Table 1. Batch composition and sample designation of bulk SiOC ceramics

Fig. 1. SEM and TEM micrographs of starting powders: (a) 0.5-h-milled SiOC, (b) 12-h-milled SiOC, and (c) 48-h-milled SiOC.

Fig. 2. XRD patterns of SiOC and SiOC-Ba specimens (refer to Table 1).
glass and both $\beta$-SiC and $\beta$-cristobalite crystallized in less carbon-rich SiOC glass, compared to the present SiOC, at much lower temperatures. The retardation of crystallization in the present SiOC is likely caused by (1) a rapid cooling rate from the hot-pressing temperature ($30^\circ\text{C/min}$) and (2) suppression of the evolution of CO, the byproduct of the carbothermal reduction of amorphous SiO$_2$, because of the applied pressure (40 MPa) in the closed graphite mold. In contrast, the addition of 1 mol% Ba accelerated the crystallization of $\beta$-cristobalite and $\beta$-SiC after hot-pressing at 1550°C. Saha and Raj suggested that crystallization of SiO$_2$ in SiOC is nucleation limited. Thus, the enhanced crystallization observed in the SiOC-Ba specimen can be due to the following two factors. First, the incorporation of Ba into the amorphous SiOC glass decreases the viscosity of SiOC glass, and the decreased viscosity increases the kinetics of nucleation of $\beta$-cristobalite and $\beta$-SiC in the bulk SiOC-Ba specimen. Second, the incorporation of Ba into the SiOC glass provides heterogeneous nucleation sites for crystallization of $\beta$-cristobalite and $\beta$-SiC and enhances the crystallization, compared to the SiOC specimen. Toma et al. observed segregation of SiC at extremely low temperatures (800°C) and crystallization of mullite at unusually low temperatures (about 1300°C) when nano-aluminum was added into SiOC ceramics. These results also support the above suggestion.

The sintered density and apparent porosity of bulk SiOC and SiOC-Ba specimens as a function of the starting particle size are shown in Fig. 3. The sintered density of both the SiOC and SiOC-Ba specimens increased as the starting particle size decreased: from 2.42 g/cm$^3$ for 2.17-$\mu$m particles to 2.45 g/cm$^3$ for 0.39-$\mu$m particles in the SiOC and from 2.29 g/cm$^3$ for 2.17-$\mu$m particles to 2.51 g/cm$^3$ for 0.39-$\mu$m particles in the SiOC-Ba. The difference in obtained density between the 0.85 and 0.39-$\mu$m particles was very small: 2.44 g/cm$^3$ for the 0.85-$\mu$m particles vs. 2.45 g/cm$^3$ for the 0.39-$\mu$m particles in the SiOC and 2.50 g/cm$^3$ for the 0.85-$\mu$m particles vs. 2.51 g/cm$^3$ for the 0.39-$\mu$m particles in the SiOC-Ba. The porosity of bulk SiOC ceramics decreased from 0.6 to 0.3% for the SiOC and from 2.6 to 0.4% for the SiOC-Ba as the starting particle size decreased from 2.17 to 0.39-$\mu$m particles.

From the above results, it is clear that submicron-sized SiOC powders are beneficial in achieving better densification, compared to micron-sized SiOC powders, when bulk SiOC is fabricated by a conventional ceramic processing route. It can be understood by considering the higher driving force of submicron-sized powders compared to micron-sized powders in the sintering process.

Figure 4 shows SEM images of the polished SiOC and SiOC-Ba specimens after hot-pressing. Domain-like structures were formed in all specimens and the size of domain decreased with decreasing starting particle size. The domains originated from agglomerates in starting powders, and sintering necks were formed between the agglomerates during sintering. Longer milling times decreased the agglomerate size, resulting in decreased domain size. The domains are surrounded by a series of pores, which might be formed by the followings: (1) densification of agglomerates during hot-pressing expels pores within the agglomerates and forms larger inter-agglomerate pores and/or (2) accumulation of CO gas as a result of carbothermal reduction inside the agglomerates. Since the pores observed were not spherical, the former is more plausible. If the gaseous phase is trapped inside the sintered body, the pore should be spherical because of the hydrostatic pressure build-up inside the pores. When the milling time is 0.5 h, the domain size of the SiOC-Ba is larger than that of the SiOC. This is attributed to the formation of bigger agglomerates in SiOC-Ba specimens. The higher porosity of the SiOC-Ba (2.6%) compared to SiOC (0.6%) was caused by the formation of bigger agglomerates, as shown in Fig. 4.

Figure 5 shows the flexural strength of bulk SiOC ceramics. The flexural strength of both the SiOC and SiOC-Ba specimens increased as the starting particle size decreased: from 91 MPa for 2.17-$\mu$m particles to 142 MPa for 0.39-$\mu$m particles in the SiOC and from 12 MPa for 2.17-$\mu$m particles to 220 MPa for 0.39-$\mu$m particles in the SiOC-Ba. The fracture surfaces of all specimens are shown in Fig. 6. It should be noted that the scale bar in Fig. 6(d) is 10 times larger (1/10 magnification) than the others in Fig. 6. As shown, transgranular fractures were observed in all specimens and the domain size clearly decreases with decreasing starting particle size in both the SiOC and SiOC-Ba. Thus, the increased strength of both SiOC and SiOC-Ba prepared from 48-h milled powders (0.39-$\mu$m powders) was caused by the decreased domain size, i.e., decreased agglomerate size in the starting composition. The 48-h-milled SiOC-Ba showed higher strength (220 MPa) than that of the SiOC (142 MPa), whereas 0.5-h-milled SiOC-Ba showed lower strength (12 MPa) than that
of the SiOC (91 MPa). These results also can be understood based on the domain size. The maximum domain sizes of 48-h-milled SiOC-Ba and 48-h-milled SiOC were $3 \times 10$ and $3 \times 15 \mu m$, respectively, whereas those of 0.5-h-milled SiOC-Ba and 0.5-h-milled SiOC were $350$ and $25 \mu m$, respectively. The present results suggest that the flexural strength of bulk SiOC ceramics are controlled by the domain size and the minimization of domain size is the way to produce stronger bulk SiOC ceramics.

Comparison of the fracture surfaces between the SiOC and SiOC-Ba showed that more tortuous fracture surfaces were obtained in the SiOC-Ba (Fig. 6). This was due to the formation of both Si–O–Ba bonds and a compact silicon suboxide structure in the SiOC-Ba specimen. Both were evidenced by FT-IR results in a previous paper. Thus, the higher strength (220 MPa) obtained in the 48-h-milled SiOC-Ba compared to the 48-h-milled SiOC was attributed to (1) a smaller domain size, (2) the formation of Si–O–Ba bonds, and (3) the formation of a compact silicon suboxide structure in the SiOC-Ba specimen. These results also suggest that judicious modification of the SiOC structure by adding some modifier(s) is a way to improve the mechanical properties of bulk SiOC ceramics.

Mazo et al. reported a maximal flexural strength of 153 MPa by 3-point bending in bulk SiOC ceramics processed by the conventional ceramic processing route. This is comparable to the value (142 MPa) obtained in the 48-h-milled SiOC and lower than the value (220 MPa) obtained in the 48-h-milled SiOC-Ba. Mazo et al. added 6 wt% polydimethylsiloxane as a binder after pyrolysis of polysiloxane. The other data from the literature are not adequate to compare with the present data directly because their processing routes (mostly sol–gel processes), measurement methods (ball-on-three-balls tests) and/or sample geometries (disc or rod) were different. Thus, the 1 mol% Ba addition is an efficient way to improve the flexural strength of bulk SiOC ceramics.

It is interesting that the 0.5-h-milled SiOC-Ba specimen showed very low flexural strength (12 MPa) compared to the other specimens. This was caused by the formation of large domains after hot-pressing, as shown in Figs. 4 and 6. To investigate the elemental distribution, especially of Ba in the SiOC-Ba specimen, both the 0.5-h-milled and 48-h-milled SiOC-Ba specimens were analyzed using EPMA, and the results are shown in Figs. 7 and 8. In the 0.5-h-milled specimen, strong segregation of Ba and O was observed in Fig. 7. In contrast, a more homogeneous distribution of those elements was observed in the
48-h-milled specimen (Fig. 8). Comparison of the 0.5-h milled and the 48-h milled specimens suggests that extension of the milling time leads to homogeneous distributions of Ba and O elements throughout the specimens. Thus, the segregation of Ba and O formed large agglomerates after pyrolysis and the large agglomerates were not disintegrated after 0.5-h milling, resulting in large domains after hot-pressing and poor flexural strength.

As shown in Fig. 2, XRD analysis showed the presence of cristobalite in Ba-doped SiOC ceramics. It is well known that cristobalite shows the phase transition at about 250°C with volume change, which causes cracks or residual stress around them. Usually such cracks or residual stress deteriorate mechanical properties of ceramic body. The 0.5-h-milled SiOC-Ba specimen showed very low strength (12 MPa) than the other specimens. In contrast, 48-h-milled SiOC-Ba specimen showed the highest strength (220 MPa) among the specimens investigated. These results suggest that the low strength of 0.5-h-milled SiOC-Ba specimen might be influenced by the formation of crystalline cristobalite in the specimen, but its influence might be negligible when the starting particle size is very small (0.39 μm). Further research is necessary to clarify the influence of cristobalite on flexural strength in 48-h-milled SiOC-Ba specimen.

4. Conclusions
Crack-free, dense SiOC discs with 6–7 mm thickness and 30 mm diameters were fabricated from commercially available polysiloxane without any additives or with a 1 mol% barium isopropoxide-derived Ba additive. Agglomerates formed after pyrolysis of polysiloxane led to the formation of domain-like structures surrounded by pores after sintering. The flexural strength of bulk SiOC is strongly dependent on the domain size formed after sintering. Minimization of the agglomerate size in the starting powders by milling after pyrolysis is an efficient way to increase the flexural strength of bulk SiOC ceramics.

The addition of 1 mol% barium isopropoxide-derived Ba enhanced the crystallization of β-cristobalite and β-SiC in the bulk SiOC-Ba specimen by decreasing the viscosity of SiOC glass and by providing heterogeneous nucleation sites for the crystallization of β-cristobalite and β-SiC. The incorporation of 1 mol% Ba into the SiOC glass also improved the flexural strength of bulk SiOC ceramics significantly by the formation of both Si-O–Ba bonds and a compact silicon suboxide structure in the bulk Ba-modified SiOC. The flexural strengths of the bulk SiOC ceramics without any additives and the bulk SiOC ceramics with the 1 mol% Ba additive (both were fabricated from submicron-sized SiOC powders) were 142 ± 24 and 220 ± 11 MPa, respectively.

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