

Flexural Strength of Polysiloxane-Derived Strontium-Doped SiOC Ceramics

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ABSTRACT

The effect of Sr addition on the flexural strength of bulk SiOC ceramics was investigated in polymer-derived SiOC ceramics prepared by conventional hot pressing. Crack-free, dense SiOC discs with a 30 mm diameter were successfully fabricated from commercially available polysiloxane with 1 mol% strontium isopropoxide derived Sr as an additive. Agglomerates formed after the pyrolysis of polysiloxane led to the formation of domain-like structures. The flexural strength of bulk SiOC was strongly dependent on the domain size formed and Sr addition. Both the minimization of the agglomerate size in the starting powders by milling after pyrolysis and the addition of Sr, which reinforces the SiOC structure, are efficient ways to improve the flexural strength of bulk SiOC ceramics. The typical flexural strength of bulk Sr-doped SiOC ceramics fabricated from submicron-sized SiOC powders was ~209 MPa.

Key words : Silicon oxycarbide, Flexural strength, Polysiloxane

1. Introduction

Silicon oxycarbide ceramics, in which silicon, oxygen, and carbon are incorporated into an amorphous network structure, have attracted increasing attention, especially for processing ceramic foams,¹⁻⁸⁾ coatings, and thin films for functional parts,⁹⁻¹¹⁾ and synthesizing nano-sized SiC particles¹²⁾ and cost-effective long fibers,^{13,14)} due to their improved mechanical and chemical properties compared to amorphous SiO₂.^{15,16)} However, because of the excessively large shrinkage and weight loss during the pyrolysis and densification 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.¹⁷⁾ The filler-free SiOC ceramics developed and reported in the literature are mostly either porous or thin films.^{4,8,10)}

There are limited studies on the flexural strength of dense, monolithic SiOC ceramics. Renlund and Prochazka¹⁸⁾ reported an average flexural strength of 385 ± 227 MPa in SiOC ceramics prepared by the pyrolysis of commercially available polysiloxane. Soraru *et al.*¹⁵⁾ reported an average flexural strength of 350 ± 230 MPa using rod-shape specimens prepared by the pyrolysis of sol-gel precursors. Esfahanian *et al.*¹⁹⁾ first 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

field-assisted sintering a pyrolyzed SiOC 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.

The flexural strength data reported in bulk SiOC ceramics prepared by the pyrolysis of preceramic polymers are particularly scattered. This is due to 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. There is no report on the effect of Sr addition on the flexural strength of bulk SiOC ceramics. In a previous study on alkaline earth-modified SiOC-bonded SiC ceramics,²⁰⁾ 1 mol% Sr addition increased the flexural strength of SiOC-bonded SiC ceramics significantly. Thus, in this study, Sr-doped SiOC ceramics were prepared by conventional ceramic processing routes, and the effects of Sr addition on the crystallization behavior and flexural strength of bulk SiOC ceramics were investigated.

2. Experimental Procedure

Commercially available polysiloxane (YR3370, GE Toshiba Silicones Co. Ltd., Tokyo, Japan) and strontium isopropoxide (Sr(OCH(CH₃)₂)₂, Alfa Aesar, Johnson Matthey Co., Ltd., Ward Hill, MA, USA) were used as starting materials. To prepare a batch without Sr (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. The pyrolyzed powders were milled for 48 h using SiC balls and a planetary mill at 250

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rpm. To prepare a batch containing 1% Sr (Sr/(Sr+Si) mole ratio = 0.01) (hereafter, SiOC-Sr), 97.5% polysiloxane and 2.5% strontium isopropoxide were mixed in polypropylene jars for 16 h using ethanol and SiC balls. The milled slurry was dried and pyrolyzed under the same conditions as the batch without Sr. The pyrolyzed powders were milled for 0.5 h, 12 h, or 48 h using SiC balls and a planetary mill at 250 rpm. The milled powders were hot-pressed at 1550°C for 1 h under an applied pressure of 40 MPa in argon atmosphere. Crack-free discs of 30 mm in diameter and 8 mm in thickness were prepared by this method.

The bulk density of the resulting SiOC ceramics was calculated from the weight-to-volume ratio of the polished 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 using scanning electron microscopy (SEM, S4300, Hitachi Ltd., Hitachi, Japan). 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 4 samples under each condition by 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

By assuming the morphology of milled particles to be spherical, the average particle sizes were calculated from the measured specific surface areas. These sizes were 2.2 μm for 0.5-h milled powders, 0.9 μm for 12-h milled powders, and 0.4 μm for 48-h milled powders. Fig. 1 shows the XRD patterns of the ground powders from SiOC and SiOC-Sr specimens (both were fabricated using 48-h milled powders). The SiOC specimen showed broad humps at $2\theta = 22 - 24$ and ~ 35 degrees, which are characteristics of the amorphous silicate structure and SiC, respectively.²¹⁾ There were no sharp diffraction lines characteristic of crystals. This means the SiOC structure is

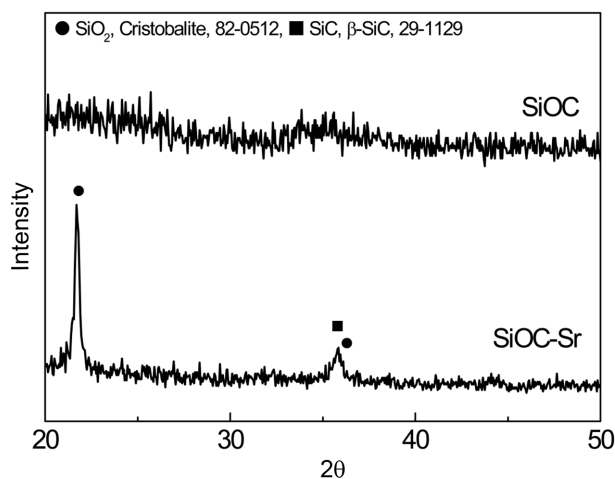


Fig. 1. X-ray diffraction patterns of SiOC-Sr and SiOC specimens.

therefore amorphous or very fine (2 nm or less in dimension) crystalline in the SiOC specimen.¹⁸⁾ In contrast, the crystallization of β -cristobalite and β -SiC was observed in the 1 mol% Sr-doped SiOC specimen (SiOC-Sr). The crystallization of amorphous SiOC can be achieved by two mechanisms: the carbothermal reduction of SiO₂ and phase separation.²²⁾ The carbothermal reduction accompanies weight loss whereas the phase separation can lead to crystallization without significant weight loss.²²⁾ Rouxel *et al.*²³⁾ observed the crystallization of β -cristobalite and β -SiC at 1200°C in amorphous SiOC with a composition of SiO_{1.33}C_{0.33}. Esfahanian *et al.*¹⁹⁾ observed both the crystallization of β -SiC after field-assisted sintering at 1400°C and the crystallization of β -SiC and turbostratic carbon after field-assisted sintering at 1600°C in amorphous SiOC with a composition of SiO_{1.46}C_{0.80}. Non-detectable crystallization in the present SiOC without Sr is likely caused by suppressing the evolution of CO, the byproduct of the carbothermal reduction of amorphous SiO₂, because of the applied pressure (40 MPa) in a closed graphite mold. In contrast, the addition of 1 mol% Sr accelerated the crystallization of β -cristobalite and β -SiC after hot-pressing at 1550°C. Saha and Raj²²⁾ suggested that the crystallization of SiO₂ in SiOC is nucleation controlled. Thus, the enhanced crystallization observed in the SiOC-Sr specimen can be due to the following two factors. First, the incorporation of Sr into the amorphous SiOC glass decreases the viscosity of SiOC glass,²⁴⁾ and the decreased viscosity increases the kinetics of nucleation of β -cristobalite and β -SiC in the bulk SiOC-Sr specimen. Second, the incorporation of Sr into the SiOC glass provides heterogeneous nucleation sites for the crystallization of β -cristobalite and β -SiC and speeds up the crystallization, compared to the SiOC specimen without Sr addition.

The sintered density and apparent porosity of SiOC-Sr specimens as a function of the starting particle size are shown in Fig. 2. The sintered density of the SiOC-Sr specimens increased as the starting particle size decreased: 2.39 g/cm³ for 2.2-μm particles, 2.44 g/cm³ for 0.9-μm particles, and 2.46 g/cm³ for 0.4-μm particles, respectively. In contrast, the sintered density of the SiOC specimen without Sr addition was 2.47 g/cm³ for 0.4-μm particles. The porosity of bulk SiOC-Sr ceramics decreased from 0.6% to 0.3% as the starting particle size decreased from 2.2-μm to 0.4-μm particles. From the above results, it is clear that submicron-sized

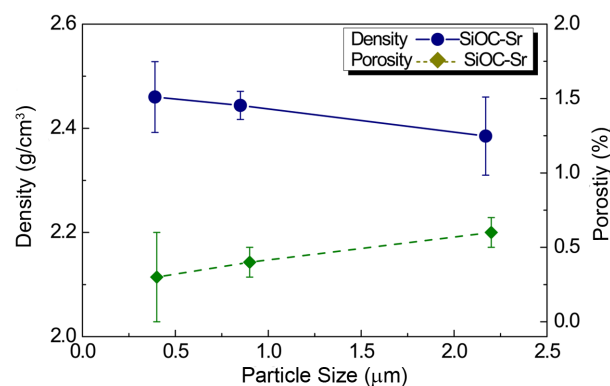


Fig. 2. Density and porosity of 1 mol% Sr-doped SiOC ceramics.

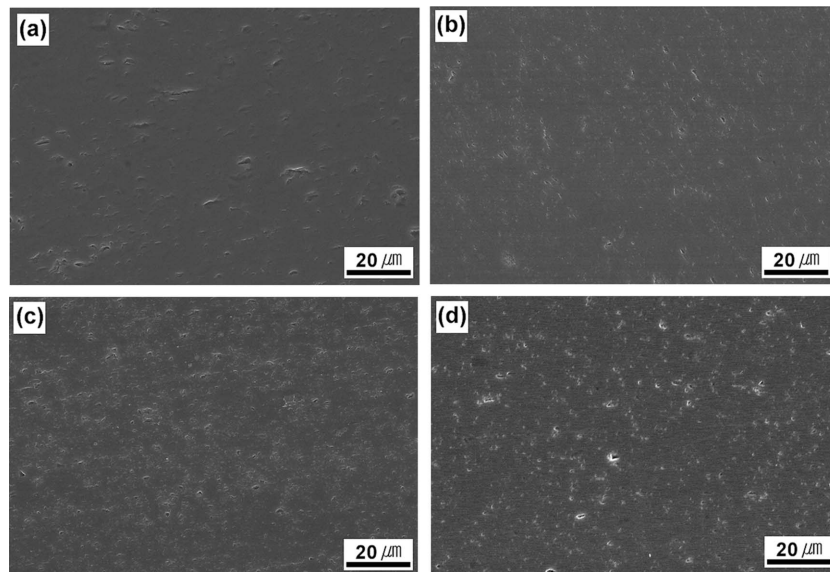


Fig. 3. Typical microstructures of polysiloxane-derived SiOC ceramics: (a) 0.5-h-milled SiOC-Sr, (b) 12-h-milled SiOC-Sr, (c) 48-h-milled SiOC-Sr, and (d) 48-h-milled SiOC without Sr.

SiOC-Sr powders are beneficial in achieving better densification, compared to micron-sized SiOC-Sr powders, when bulk SiOC is fabricated by conventional hot-pressing. This can be understood by considering the higher driving force of submicron-sized powders compared to micron-sized powders in the sintering process.

Figure 3 shows SEM images of the polished SiOC-Sr and SiOC specimens after hot-pressing. Relatively large pores (5–13 μm) were observed in the SiOC-Sr specimen prepared from 2.2- μm starting powders. In contrast, smaller pores (1–4 μm) were observed in the SiOC-Sr specimen prepared from 0.4- μm starting powders. The coarser the starting particle size, the larger the pore size obtained, as shown in Fig. 3.

Figure 4 shows the flexural strength of bulk SiOC-Sr and SiOC ceramics. The flexural strength of the SiOC-Sr specimens increased as the starting particle size decreased (from 58 MPa for 2.2- μm particles to 209 MPa for 0.4- μm particles in the SiOC-Sr). Fig. 5 shows the fracture surfaces of SiOC-Sr and SiOC specimens. As shown, transgranular fractures were observed in all specimens and dense domain-like structures were formed in all specimens. The size of domain decreased with a decreasing starting particle size. The domains originated from agglomerates in starting powders, and necks were formed between the agglomerates during sintering.¹⁹⁾ Thus, the increased strength of the SiOC-Sr prepared from 0.4- μm powders was caused by the decreased domain size, i.e., decreased agglomerate size in the starting powders. The 48-h milled SiOC-Sr showed higher strength (209 MPa) than that of the 48-h milled SiOC (153 MPa). This result also can be understood based on the domain size. The maximum domain sizes of 48-h milled SiOC-Sr and 48-h milled SiOC were $\sim 10 \mu\text{m}$ and $\sim 17 \mu\text{m}$, respectively. The present results suggest that the flexural strength of bulk SiOC ceramics are controlled by the domain size and minimizing the domain size is the best way to produce stronger bulk SiOC ceramics. Comparison of the fracture surfaces between the SiOC and SiOC-Sr showed that more

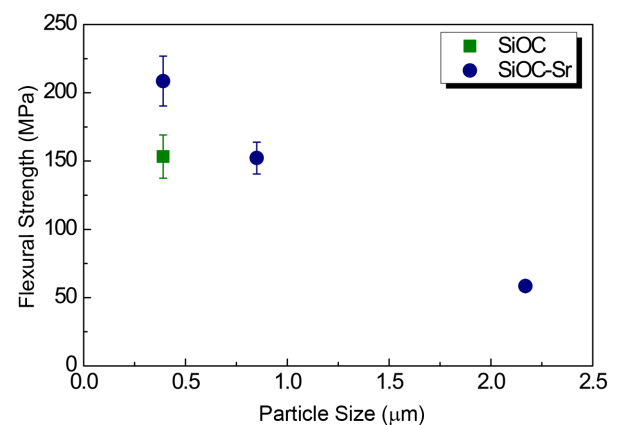


Fig. 4. Flexural strength of polysiloxane-derived SiOC-Sr and SiOC ceramics.

tortuous fracture surfaces were obtained in the SiOC-Sr (Fig. 5 (c) and (d)). The SiOC was amorphous whereas the SiOC-Sr was composed of crystalline β -cristobalite, β -SiC, and amorphous silica, as identified in Fig. 1. The higher strength (209 MPa) obtained in the SiOC-Sr compared to the SiOC (153 MPa) was attributed to (1) a smaller domain size, (2) the crystallization of β -cristobalite and β -SiC in the amorphous silica matrix, and (3) the formation of stronger bonding between domains in the SiOC-Sr specimen. The possibility of Si-O-Sr bonds forming, and their contribution to the strengthening of SiOC-Sr specimens, cannot be ruled out, as in the case of Ba-doped SiOC-bonded SiC ceramics.²⁰⁾ These results also suggest that judicious selection of some additives, which reinforce the SiOC structure, is the best way to improve the mechanical properties of bulk SiOC ceramics.

Mazo *et al.*²⁵⁾ reported a maximal flexural strength of 153 MPa by 3-point bending in bulk SiOC ceramics processed by

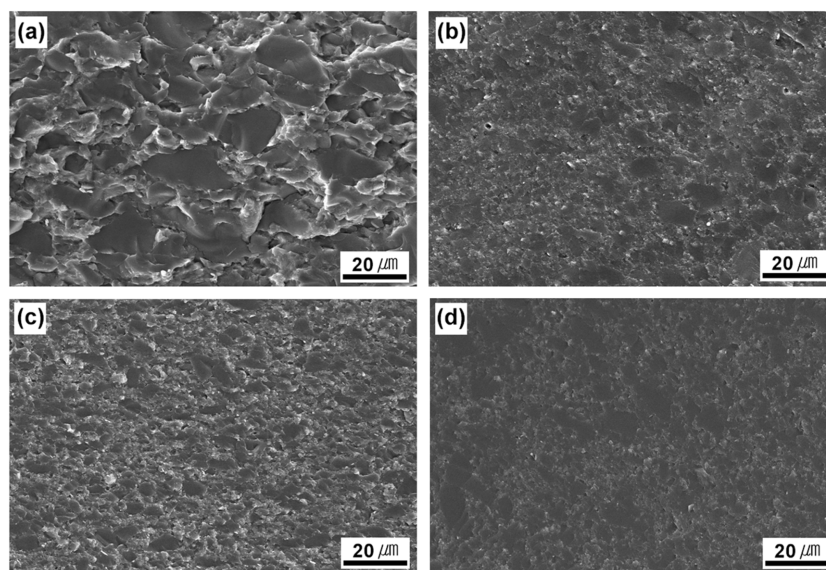


Fig. 5. SEM micrographs of the fracture surfaces of the polysiloxane-derived SiOC ceramics: (a) 0.5-h-milled SiOC-Sr, (b) 12-h-milled SiOC-Sr, (c) 48-h-milled SiOC-Sr, and (d) 48-h-milled SiOC without Sr.

the conventional ceramic processing route. This is the same value (153 ± 16 MPa) obtained in the 48-h milled SiOC by 4-point bending and lower than the value (209 MPa) obtained in the 48-h milled SiOC-Sr. Thus, the 1 mol% Sr addition is an efficient way to improve the flexural strength of bulk SiOC ceramics.

4. Conclusions

Crack-free, dense bulk SiOC ceramics were fabricated from commercially available polysiloxane with a strontium isopropoxide-derived Sr additive. The addition of 1 mol% Sr enhanced the crystallization of β -cristobalite and β -SiC in the bulk SiOC-Sr 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% Sr into the SiOC glass also improved the flexural strength of bulk SiOC ceramics significantly. Typical flexural strengths of the bulk 1% Sr-doped SiOC ceramics fabricated from $0.4 \mu\text{m}$ powders were 209 ± 18 MPa.

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