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Processing of closed-cell silicon oxycarbide foams from a preceramic polymer

YOUNG-WOOK KIM*, SHIN-HAN KIM
Department of Materials Science and Engineering, The University of Seoul,
90 Jeonnong-dong, Dongdaemoon-ku, Seoul 130-743, Korea
E-mail: ywkim@uos.ac.kr

HAI-DOO KIM
Ceramic Materials Group, Korea Institute of Machinery and Materials, Chang-Won,
Kyung-Nam 641-010, Korea

CHUL B. PARK
Microcellular Plastics Manufacturing Laboratory, Department of Mechanical and Industrial
Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G8

A novel processing route for fabricating closed-cell ceramic foams has been developed. The strategy for making the ceramic foams involves: (i) forming some shapes using a mixture of preceramic polymer and expandable microspheres by a conventional ceramic forming method, (ii) foaming the compact by heating, (iii) cross-linking the foamed body, and (iv) transforming the foamed body into ceramic foams by pyrolysis. By controlling the microsphere content and the pyrolysis temperature, it was possible to adjust the porosity ranging from 56 to 85%.

1. Introduction

Ceramic foams are often divided into two categories based on whether their cells are open or closed. Depending on their compositions and structures, typical or potential applications for ceramic foams are absorbents, insulation materials, various filters, biomedical devices, kiln furniture, reinforcement for metal matrix composites, components in solid oxide fuel cells, light-weight shock absorbents, etc. [1–7]. Since the distribution of size and shape of the pore space in porous ceramics directly relates to their ability to perform a desired function in a particular application, the need to establish uniformity of the cell size and shape in order to achieve superior part properties has been strongly emphasized [8–10].

Ceramic foams can be fabricated by a variety of methods including replication methods [1, 11, 12], space holder methods [13, 14], and direct foaming methods [8, 9, 15–20]. Recently, our feasibility study demonstrated that an extremely fine and uniformly distributed microcellular structure could be developed in various preceramic polymers with CO_2 by implementing the thermodynamic instability principle [21–23]. The suggested strategy for making microcellular ceramics involves: (i) saturating preceramic polymers using gaseous, liquid, or supercritical CO_2, (ii) nucleating and growing a large number of bubbles using a thermodynamic instability via a rapid pressure drop or heating, and (iii) transforming the microcellular preceramics into microcellular ceramics by pyrolysis and optional, subsequent sintering. More recently, Colombo and Bernardo [24] reported a novel way of fabricating microcellular ceramics from a preceramic polymer using poly(methyl methacrylate) microbeads as sacrificial templates.

In the present work, a concept of generating closed-cell ceramic foams based on using expandable microspheres as a blowing agent was developed for a preceramic polymer (polyalkylsiloxane). The microsphere content and the pyrolysis temperature were varied to tailor the porosity.

2. Experimental procedure

A commercially available polyalkylsiloxane (YR3370, GE Toshiba Silicones Co., Ltd., Tokyo, Japan) and an expandable microsphere (461DU40, Expancel, Sundsvall, Sweden) were used as raw materials. Pyrolysis of the polyalkylsiloxane in an inert atmosphere yields SiO_xC_y, with a weight loss of about 19% [21]. The expandable microspheres consist of a thermoplastic (poly(methyl methacrylate)) shell encapsulating a hydrocarbon gas. When heated the gas inside the shell increases its pressure and the thermoplastic shell softens, resulting in an increase of the volume of the microspheres. The diameters of these spheres ranged from 9 to 15 μm.

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*Author to whom all correspondence should be addressed.

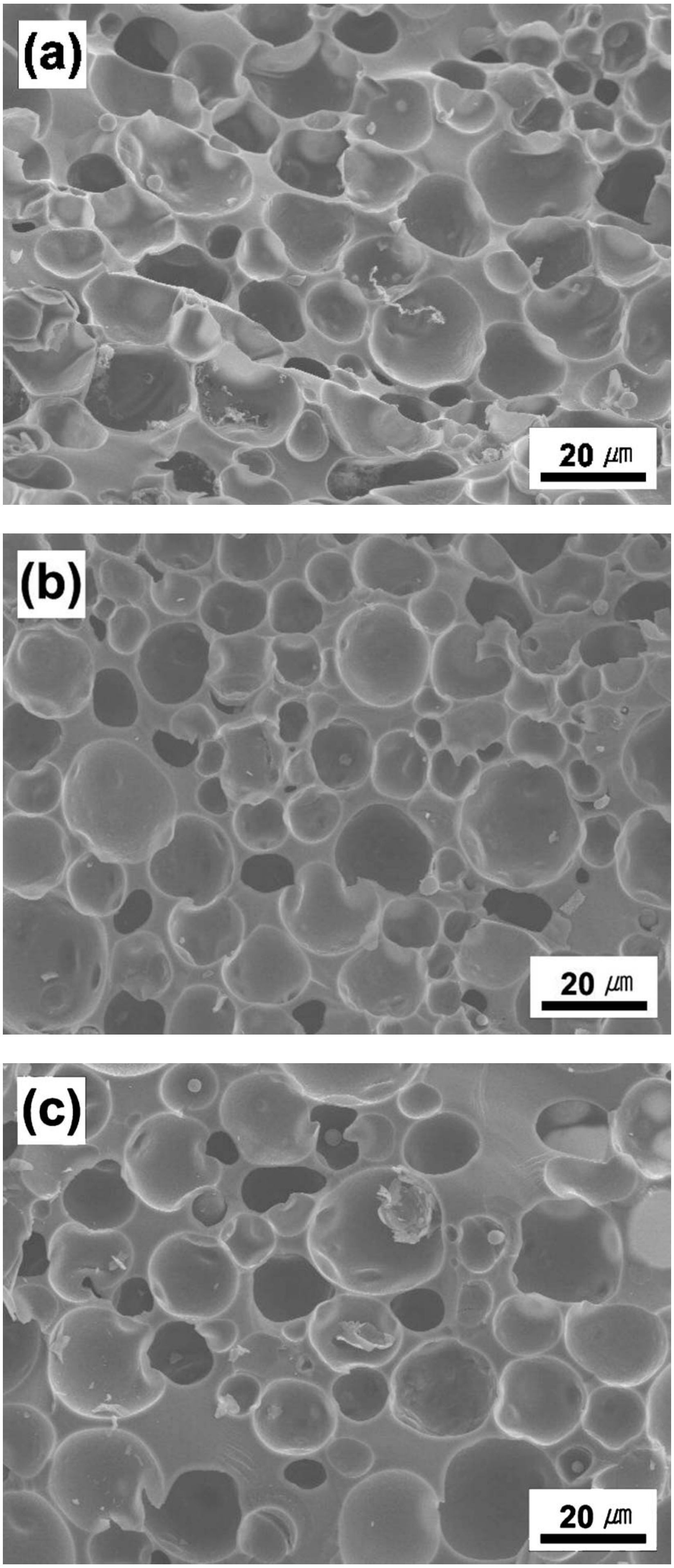

Figure 1 Typical fracture surfaces of closed-cell silicon oxycarbide foams pyrolyzed at 1200°C for 1 h with a heating rate of 2°C/min in nitrogen: (a) SOC1, (b) SOC2, and (c) SOC4 (refer to Table I). Note closed-cells in the foams.

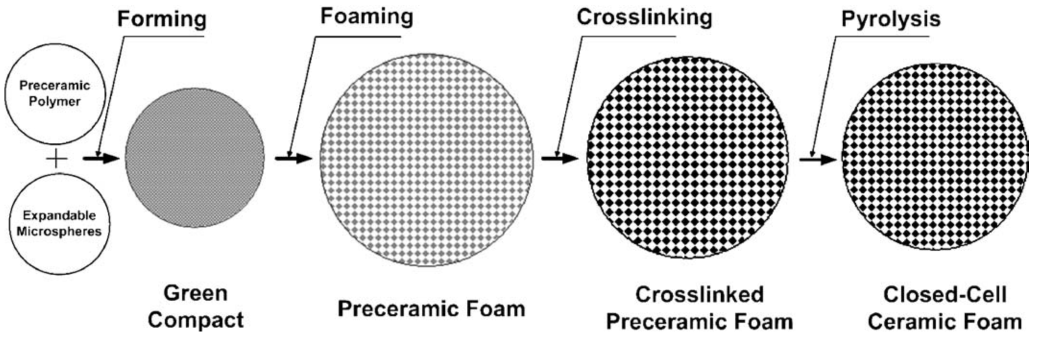

Figure 2 Morphology change of the preceramic polymer-expandable microsphere system during processing of closed-cell ceramic foams.

Five batches of powder were mixed and the content of microspheres in those batches was ranged from 30 to 70 wt% (Table I). All individual batches were mixed for 6 h using Teflon balls and a polyethylene jar. The milled powder was uniaxially pressed into disks at 20 MPa. The green compacts were expanded in an oven where the sample was heated up to 140°C in air with a heating rate of 2°C/min. When heated the microspheres expanded and the preceramic polymer softened, resulting in a dramatic increase of the volume of the compacts. The expanded compacts (preceramic foams) were cross-linked by doping a condensation catalyst (aminoalkylalkoxysilane) and subsequently heating them up to 180°C in air. The cross-linked foams were pyrolyzed at temperatures ranging from 1000 to 1300°C for 1 h with a heating rate of 2°C/min in nitrogen. The heat treatment allows for the polymer-to-ceramic conversion of the preceramic foams, resulting in silicon oxycarbide foams.

The bulk density of the foams was computed from the weight-to-volume ratio. The true density (i.e., skeleton density) of the silicon oxycarbide material after pyrolysis was measured using a pycnometer for powdered samples. The cell morphology was observed by scanning electron microscopy (SEM). The cell size and porosity were measured on a polished surface using an image analyzer (Image-Pro Plus, Media Cybernetics, Silver Spring, MD, USA). The cell density of the foams was measured by counting the number of cells in a two-dimensional image on the microstructure and by converting it to 3-dimension [22].

3. Results and discussion

Typical fracture surfaces of ceramic (silicon oxycarbide) foams are shown in Fig. 1. As shown, closed cells are foamed for all specimens. A uniform cellular structure could be achieved when foaming was carried out at 140°C and pyrolysis was carried out at temperatures ranging from 1000 to 1300°C. To produce foams by expanding the microspheres, the foaming temperature should be higher than the softening temperature of the preceramic polymer in order to allow foaming. On the other hand, the foaming temperature should be lower than its melting temperature, because otherwise the cells could easily collapse. In this work, 140°C as a foaming temperature was good enough for the preceramic polymer used. The softening and melting temperatures of the polyalkylsiloxane were 109°C and ~155°C, respectively.

TABLE I Batch composition and sample designation

	Batch composition (wt%)	
Sample	Polyalkylsiloxane[a]	Expandable microsphere[b]
SOC1	30	70
SOC2	40	60
SOC3	50	50
SOC4	60	40
SOC5	70	30

[a] YR3370, GE Toshiba Silicones Co., Ltd., Tokyo, Japan.
[b] 461DU40, Expancel, Sundsvall, Sweden.

It is very difficult for a foamed preceramic to maintain the cellular structure during pyrolysis without crosslinking the specimens. Thus, the crosslinking of the foamed body before pyrolysis is required. The doping of crosslinking-catalyst and the thermal pre-treatments of the foamed specimens at 88°C for 6 h, 110°C for 6 h, and 180°C for 2 h in air before pyrolysis made the preceramic specimens maintain the foamed structures during pyrolysis, and as a consequence, cellular ceramics were finally fabricated. During the thermal pre-treatments of the foamed specimens condensation of —OH groups takes place by eliminating water and form a Si—O—Si bond, resulting in the cross-linking [25].

The morphology change of the preceramic polymer during process can be summarized in Fig. 2. Initially

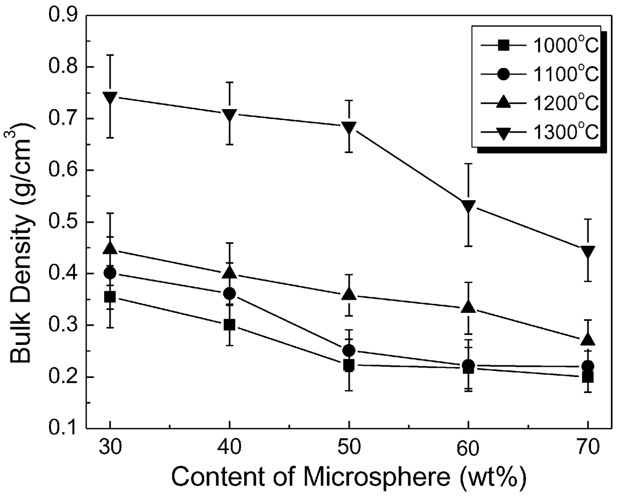

Figure 3 Bulk density of the silicon oxycarbide foams as a function of expandable microsphere content.

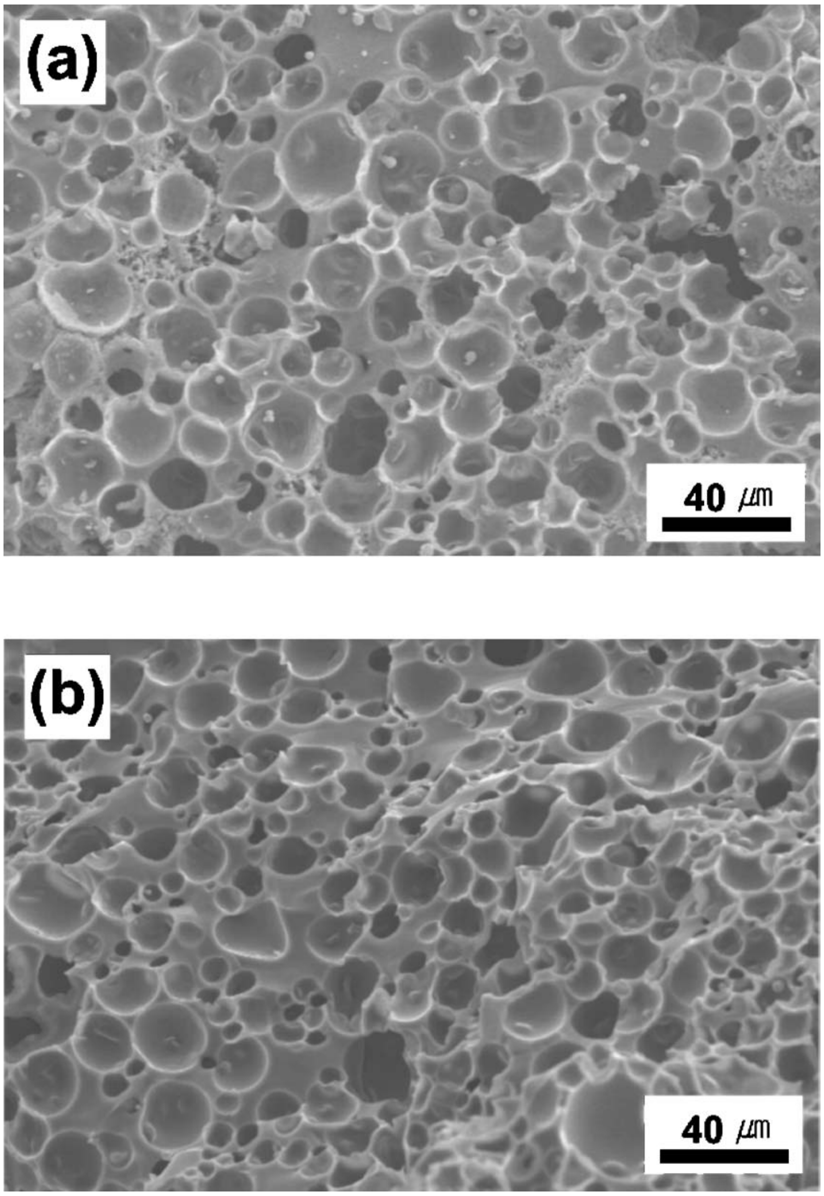

Figure 4 Typical fracture surfaces of closed-cell silicon oxycarbide foams (SOC3) pyrolyzed at various temperatures for 1 h with a heating rate of 2°C/min in nitrogen: (a) 1000°C and (b) 1300°C.

a mixture consisting of a preceramic polymer and the expandable microspheres is used as a feed material for shaping by one of the conventional ceramic forming methods, e.g., a uniaxial pressing. Then, a large number of cells are formed by heating the compacts up to the temperature above the softening temperature of the preceramic polymer and by ensuring the maximum expansion. When heated the gas inside the shell of the microspheres increases its pressure and the thermoplastic shell softens, resulting in a dramatic increase of the volume of the microspheres. The volume expansion was 8-fold for SOC5 and 16-fold for SOC1. By cross-linking the foamed body followed by transforming the foamed body into ceramic foams via pyrolysis, closed-cell ceramic foams with high uniformity of the cell size and the shape were fabricated.

Fig. 3 shows the bulk density of the SiOC foams as a function of the content of the expandable microspheres. The bulk densities of the foams were ranged from 0.20 ± 0.03 g/cm^3 to 0.74 ± 0.08 g/cm^3, depending on both the content of the expandable microspheres and the pyrolysis temperature. The higher content of microspheres, the lower bulk density was obtained for all specimens. It is expected that a higher content of microspheres leads to larger number of cells, resulting in a lower bulk density.

The heat-treatment temperature was also an important variable in pyrolysis process because the heat-treatment temperature affected both the bulk density and cell size. Some typical microstructures of closed-cell silicon oxycarbide foams (SOC3) pyrolyzed at 1000 and 1300°C for 1 h in a nitrogen atmosphere are shown in Fig. 4. The morphology of cells in the specimens showed closed cells. The porosities ranged from 56% for SOC5 pyrolyzed at 1300°C to 85% for SOC1 pyrolyzed at 1000°C. The average cell sizes were 15.9 ± 5.4, 15.2 ± 4.8, 13.9 ± 4.6, and 12.1 ± 4.5 μm for the specimens pyrolyzed at 1000, 1100, 1200, and 1300°C, respectively. The average cell sizes decreased with increasing the pyrolysis temperature, indicating the occurrence of the densification process during heat-treatment. The maximum cell sizes in all specimens

TABLE II True density of the silicon oxycarbide material derived from SOC5 after pyrolysis (refer to Table I)

Pyrolysis temperature (°C)	True density (g/cm^3)
1000	2.08 ± 0.09
1100	2.14 ± 0.07
1200	2.23 ± 0.06
1300	2.28 ± 0.05

were ranged from 25 to 30 μm, suggesting that the cells were blown from the microspheres added. The higher pyrolysis temperature, the higher bulk density was obtained. Both the enhanced densification of pyrolysis residue (see Fig. 3) and the increased true density (see Table II) at a higher pyrolysis temperature must have contributed to the increase of the bulk density. Pyrolysis of the preceramic may be almost completed during heating-up to 1100–1300°C (e.g., it takes 450 min during heating from 400 to 1300°C at a rate of 2°C/min) and densification may take place during the heat-treatment. Fig. 3 shows the abrupt increase in the bulk density of silicon oxycarbide foams pyrolyzed at 1300°C, compared to those pyrolyzed at 1000–1200°C. For example, the bulk density (0.223 g/cm^3) for the 1000°C-pyrolyzed SOC3 increased to 0.685 g/cm^3 for the 1300°C-pyrolyzed SOC3. The glass transition temperatures of the SiOC-glasses were known to be in the range 1300–1350°C [26, 27]. Thus, a viscous sintering process above the glass transition temperature of the SiOC-glass is responsible to the densification process of the 1300°C-pyrolyzed specimens [28]. The densification observed at 1100–1200°C was due to the solid-state sintering mechanism by atomic diffusion.

Fig. 5 shows the variation of cell density as a function of the content of microspheres. SOC1 showed the highest cell density at all heat-treatment temperatures and SOC5 the lowest cell density because of the least number of microspheres added. The cell density increased gradually from 1.8 ± 0.4 × 10^9 cells/cm^3 for the specimen containing 30%-microspheres (SOC5) to 5.9 ± 0.5 × 10^9 cells/cm^3 for the specimen containing 70%-microspheres (SOC1) with increasing the content of microspheres. All specimens had cell densities greater than 10^9 cells/cm^3 and cells smaller than 30 μm. The present results suggest that the content of microsphere and the pyrolysis temperature are the crucial variables in controlling the porosity of the ceramic foams fabricated by the presented method.

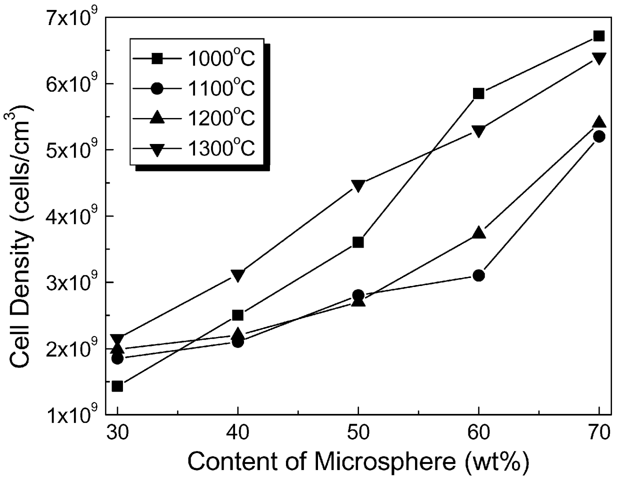

Figure 5 Cell density of the silicon oxycarbide foams as a function of expandable microsphere content.

4. Summary

Closed-cell silicon oxycarbide foams with cell densities greater than 10^9 cells/cm^3 and cells smaller than 30 μm were obtained from a preceramic polymer using expandable microspheres. A higher microsphere content and a lower pyrolysis temperature led to a higher porosity in the closed-cell ceramic foams. By controlling both the expandable microsphere content and the pyrolysis temperature, it was possible to produce closed-cell silicon oxycarbide foams possessing a wide range of porosities, ranging from 56 to 85%. The present results suggest that the proposed novel processing method is suitable for the manufacture of highly porous ceramics with high uniformity of the cell size and shape.

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