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Effect of inert filler addition on pore size and porosity of closed-cell silicon oxycarbide foams

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Ceramic foams are a specific class of porous materials composed of pores (usually referred to as cells), with a size ranging from a few micrometers to a few millimeters, and ceramic walls (closed-cell foams) or struts (open-cell foams). Fabrication of ceramic foams from preceramic polymers has recently attained increasing interest because of low fabrication temperatures and the unique properties of the foams, such as low density, low thermal conductivity, high permeability, high surface area, high thermal shock resistance, and high specific strength [1–4]. These characteristics make them good candidates for both structural and functional applications, such as filters, insulators, absorbents, catalyst supports, and biomedical devices [2–8].

Various processing routes have been proposed for the production of porous ceramics, including replication methods [6, 9], space holder methods [10, 11], direct foaming methods [1, 8, 12, 13], and microcellular foaming with CO_2 by implementing the thermodynamic instability principle [14–16].

More recently, the generation of closed-cell ceramic foams based on the following strategy has been developed: (i) forming a compact using a mixture of preceramic polymer and expandable microspheres, (ii) forming the compact by heating, (iii) cross-linking the foamed body, and (iv) transforming the foamed body into a ceramic foam by pyrolysis [17]. In the present letter, the effect of inert filler addition on the pore (cell) size and porosity of closed-cell silicon oxycarbide foams was investigated using expandable microspheres as a blowing agent and SiO_2 powder as an inert filler.

A commercially available polysiloxane (YR3370, GE Toshiba Silicones Co., Ltd., Tokyo, Japan), an expandable microsphere (461DU40, Expancel, Sundsvall, Sweden), and SiO_2 (0.8 μm, High Purity Chemicals, Saitama, Japan) were used as raw materials. Two batches of powder were mixed, each containing polysiloxane:microsphere in a weight ratio of 6:4, with one containing no silica and the other containing 10 wt% SiO_2. The batch compositions are shown in Table I. The two batches were mixed individually for 6 hr 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 in which the sample was heated up to 138 °C with a heating rate of 2 °C/min. When heated, the microspheres expanded and the preceramic polymer softened, resulting in a dramatic increase in the volume of the compacts. The expanded compacts (preceramic foams) were cross-linked by doping with a condensation catalyst (aminoalkylalkoxysilane) and subsequently heating them up to 180 °C in air. The cross-linked foams were pyrolyzed at different temperatures from 1000 to 1200 °C for 1 hr 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 doping with the crosslinking-catalyst and the thermal pre-treatments of the foamed specimens at 88 °C for 12 hr, at 110 °C for 6 hr, and 180 °C for 2 hr before pyrolysis allowed the preceramic specimens to maintain the foamed structures during pyrolysis, and as a consequence, cellular ceramics were finally fabricated.

The cell (pore) morphology was observed by scanning electron microscopy (SEM). The cell size and porosity were measured using an image analyzer (Image-Pro Plus, Media Cybernetics, Silver Spring, MD, USA). A total of 700 to 1100 pores were used for statistical analysis of each specimen. The cell density of the foams was measured by counting the number of cells in a two-dimensional image of the microstructure and by converting it to three dimensions [15].

Typical fracture surfaces of silicon oxycarbide foams are shown in Fig. 1. Closed cells were foamed for all specimens. Initially a large number of cells were formed by heating the compacts up to 138 °C (the temperature between the softening temperature and the melting temperature of the polysiloxane). When heated, the gas inside the shell of the microspheres increased its pressure and the thermoplastic shell softened, resulting in

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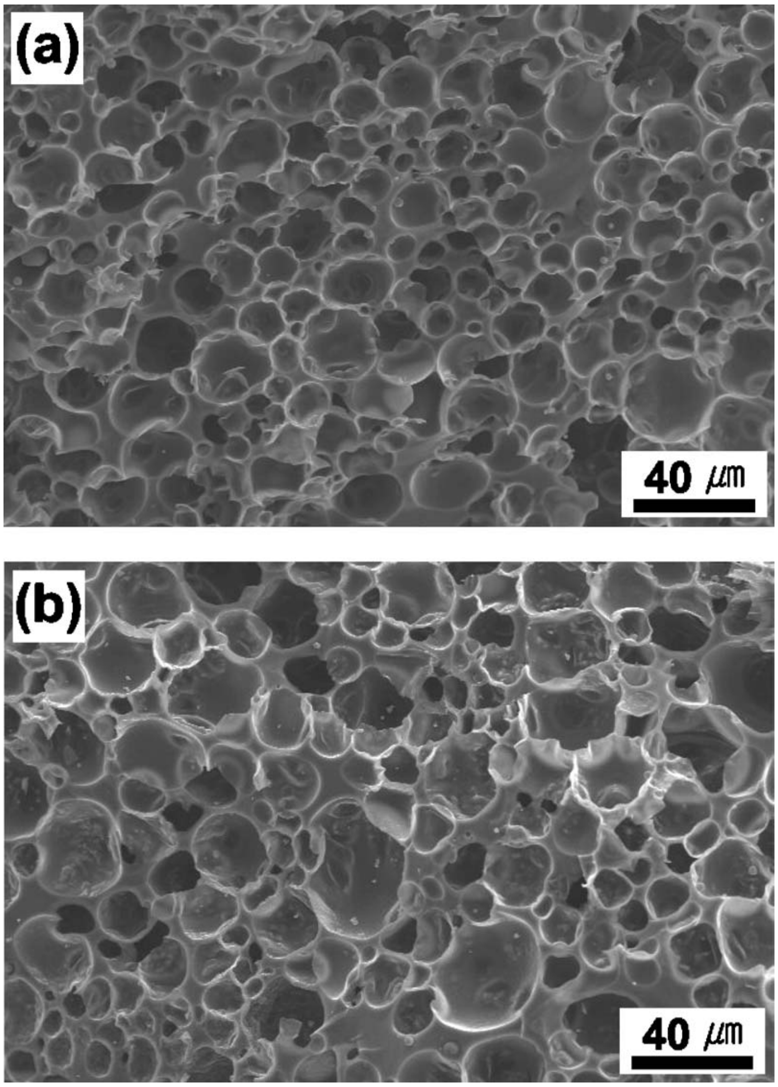

Figure 1 Typical fracture surfaces of silicon oxycarbide foams pyrolyzed at 1100 °C for 1 hr with a heating rate of 2 °C/min in nitrogen: (a) no filler and (b) with silica. Note the closed cells in the foams.

a dramatic increase in the volume of the microspheres. In this work, 138 °C as a foaming temperature was adequate for the preceramic polymer used. A uniform cellular structure could be achieved in both specimens when pyrolysis was carried out at temperatures ranging from 1000 to 1200 °C. The addition of fillers did not affect openness of the cells.

Fig. 2 shows the porosities of the silicon oxycarbide foams as a function of the pyrolysis temperature. The porosities of the foams without fillers ranged from 67 to 73%, depending on the pyrolysis temperature. In contrast, the porosities of the foams containing fillers ranged from 73 to 80%. The higher the pyrolysis temperature, the lower the porosity that was obtained for both specimens. It is expected that the higher pyrolysis temperature leads to lower porosity because of the enhanced densification of pyrolysis residue at higher temperatures. The porosities of silicon oxycarbide foams with fillers were 5–7% higher than those of silicon

TABLE I Batch composition

	Batch composition (wt%)		
Sample	Polysiloxane[a]	Expandable microsphere[b]	SiO_2^c
No filler	60	40	0
With filler	54	36	10

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

[b] 461DU40, Expancel, Sundsvall, Sweden.

[c] SiO_2, 0.8 µm, High Purity Chemicals, Saitama, Japan.

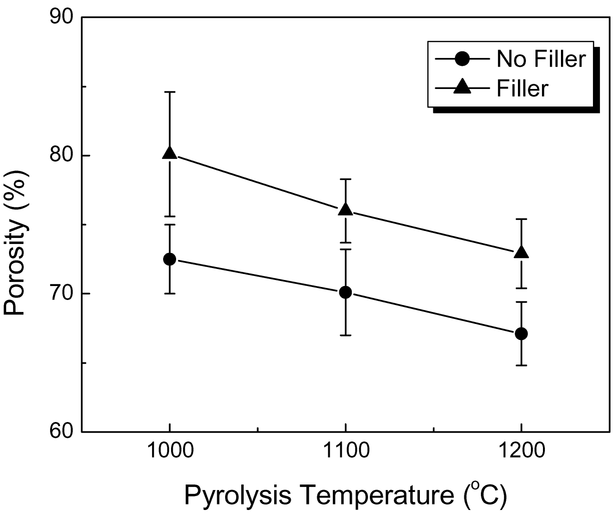

Figure 2 Porosity of silicon oxycarbide foams as a function of pyrolysis temperature.

TABLE II Cell density (cells/cm^3) of silicon oxycarbide foams

	Pyrolysis temperature (°C)		
Sample	1000	1100	1200
No filler	3.6×10^9	4.8×10^9	3.9×10^9
With filler	2.4×10^9	2.9×10^9	4.8×10^9

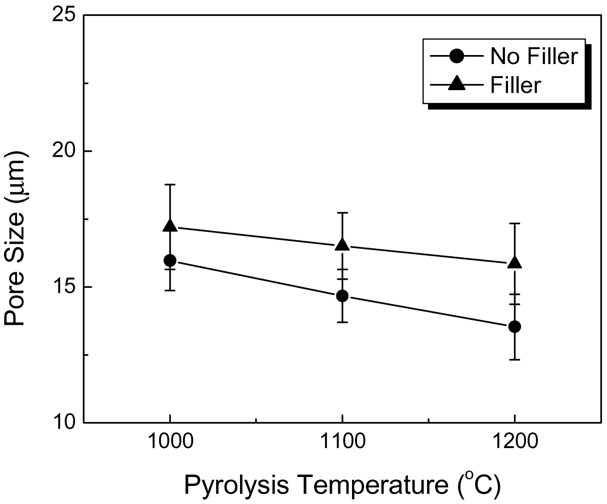

Figure 3 Pore (cell) size of silicon oxycarbide foams as a function of pyrolysis temperature.

oxycarbide foams without fillers at equivalent pyrolysis temperatures (Fig. 2). This is due to the higher volume expansion of powder compacts with fillers than the compacts without fillers. The volume expansion during heating at 138 °C was 8-fold for the compacts without fillers and 10-fold for the compacts with fillers. Thus, the addition of filler is beneficial in obtaining higher expansion.

Because of the higher expansion of microspheres in polysiloxane foams with SiO_2 fillers, the average cell (pore) sizes of silicon oxycarbide foams with fillers were 8–17% larger than those of silicon oxycarbide foams without fillers (Fig. 3). For example, the average cell sizes of 1000 °C pyrolyzed foams with and without fillers were ~17.2 and ~16.0 μm, respectively. The maximum cell sizes of silicon oxycarbide foams with and without fillers were 35 and 25 μm, respectively. The cell densities of silicon oxycarbide foams are shown in Table II. There was no trend in cell density with respect to the pyrolysis temperature because the cell density was calculated with respect to the unfoamed volume.

It can be summarized that the addition of inert fillers leads to higher porosity and larger cell size due to the beneficial effect of fillers in expansion. All specimens containing fillers had cell densities greater than 10^9 cells/cm^3 and cells smaller than 35 μm.

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