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Processing of Cellular SiC Ceramics Using Polymer Microbeads

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ABSTRACT

A simple pressing process using a SiC powder, Al_2O_3-Y_2O_3 sintering additive, and polymer microbeads for fabricating cellular SiC ceramics is demonstrated. The strategy for making the cellular ceramics involves: (i) forming certain shapes using a mixture of a SiC powder, Al_2O_3-Y_2O_3 sintering additive, and polymer microbeads by pressing; (ii) heat-treatment of the formed body to burn-out the microbeads; and (iii) sintering the body. By controlling the microsphere content and sintering temperature, it was possible to adjust the porosity in a range of 16% to 69%. The flexural and compressive strengths of cellular SiC ceramics with ~40% porosity were ~60 MPa and ~160 MPa, respectively.

Key words : Porous ceramics, Microbead, Porosity, Flexural strength, Compressive strength

1. Introduction

Cellular/microcellular ceramics are lightweight materials consisting of a cellular/microcellular structure. Due to the combination of properties resulting from the ceramic material and the cellular/microcellular structure, these ceramics have potential for wide applications in diverse areas such as filtration, thermal insulation, preforms for metal-ceramic composites, impact-absorbing structures, high specific strength materials, absorbents, and gas sensors.[1-6] Depending on the requirements of a given application, cellular/microcellular ceramics must exhibit specific cell sizes, cell size distributions, cell morphologies, and different mechanical properties. Accordingly, the processing techniques used to develop cellular/microcellular ceramics must result in well-controlled microstructures and yield mechanical properties that render the material serviceable for a specific application.[7,8]

One of the most popular processing methods used to fabricate cellular ceramics has been the infiltration of reticulated polyurethane foams with aqueous particulate ceramic slurries.[9,10] The infiltrated samples are dried and the polyurethane preform is subsequently burned out, yielding a ceramic structure that is then sintered to obtain a cellular ceramic. The structure of the cellular ceramic produced by this process is limited by the structure of the polyurethane perform. Notably, this process typically yields cellular ceramics with poor mechanical properties due to the formation of hollow struts during processing.[9]

Recently, four novel processing routes for fabricating microcellular ceramics with cell densities of $\geq 10^9$ cells/cm^3 and cells <30 μm have been developed. The first strategy for producing microcellular ceramics involves saturating preceramic polymers using gaseous or supercritical CO_2; nucleating and growing a large number of bubbles using thermodynamic instability by a rapid pressure drop or heating; and transforming the microcellular preceramics into microcellular ceramics by pyrolysis and optional subsequent sintering.[11,12] The second strategy involves forming certain shapes using a mixture of preceramic polymer and expandable microspheres; foaming and cross-linking the compact by heating; and transforming the foamed preceramics into microcellular ceramics by pyrolysis.[7,13] By controlling processing parameters and composition, it was possible to adjust the porosity in a range from 30% to 90%. The third strategy involves fabricating a formed body by combining a silicone resin, reactive filler(s), pore former, and optional sintering additive(s); cross-linking the silicone resin in the formed body; transforming the silicone resin by pyrolysis into SiO_2; and synthesizing microcellular ceramics by reacting SiO_2 and reactive filler(s). Microcellular SiC, mullite, and cordierite ceramics were successfully processed by this method.[8,14,15] The fourth strategy involves simple pressing of a silicone resin powder mixed with hollow polymer microspheres as sacrificial templates.[16]

The present study describes a simplified process for the fabrication of cellular SiC ceramics using a SiC powder, sintering additives, and polymer microbeads. The processing, microstructure, porosity, flexural strength, and compressive strength of the cellular ceramics are described.

2. Experimental Procedure

Commercially available β-SiC (Ultrafine grade, Betarundum, Ibiden., Ogaki, Japan), Al_2O_3 (AKP30, Sumitomo

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Chemical Co., Tokyo, Japan), Y_2O_3 (Grade F, H. C. Starck., Germany), and poly(methyl methacrylate-co-ethylene glycol dimethacrylate) microbeads (~20 μm, Sigma-Aldrich Inc, St. Louis, MO) were used as raw materials.

Five batches of powder were prepared and the content of polymer microbeads in those batches ranged from 0 to 40 wt% (Table 1). The following is an example of a sample notation: M20-1750 denotes a sample that contains 20 wt% polymer microbeads as a sacrificial template and is sintered at 1750°C for 1 h. All individual batches were mixed in ethanol for 24 h using SiC balls and a polyethylene jar. The milled slurry was dried and uniaxially pressed into rectanglar hexahedrons with dimensions of 25×30×10 mm at 50 MPa. The green compacts were heat-treated in nitrogen at 450°C for 1 h and subsequently at 800°C for 1 h with a heating rate of 2°C/min. The heat treatment enables the decomposition of polymer microbeads, resulting in cellular silicon carbide ceramics. The heat-treated compacts were further sintered at various temperatures ranging from 1750°C to 1850°C for 1 h with a heating rate of 20°C/min in argon.

The porosity of the cellular ceramics was calculated from the bulk density (D_b) of the cellular ceramics and the theoretical density (D_{th}, 3.31 g/cm^3) of the strut material according to

$$\text{Porosity } (\%) = (1 - D_b/D_{th}) \times 100 \quad (1)$$

Thus, the porosity includes both the porosity from the microbeads and the porosity from the strut. The cell morphology was observed by scanning electron microscopy (SEM). The cell density of the cellular ceramics was measured by counting the number of cells in 2-dimensional images of the microstructure and by converting the number of cells to 3-dimensions.[12] The flexural strength was measured by a four-point bending test with an inner and outer span of 10 and 20 mm, respectively, on samples with a size of 3×4×25 mm. The compressive strength was measured using samples with a size of 3×3×6 mm. The cross-head speed for measuring both strengths was 0.5 mm/min.

3. Results and Discussion

Initially, mixtures consisting of SiC, Al_2O_3, Y_2O_3, and poly-

Table 1. Batch Composition

Sample designation	Batch composition (wt%)
MC0	90% β-SiC + 7% Al_2O_3 + 3% Y_2O_3 + 2% polyethyleneglycol (PEG)
MC10	81% β-SiC + 6.3% Al_2O_3 + 2.7% Y_2O_3 + 10% microbead* + 2% PEG
MC20	72% β-SiC + 5.6% Al_2O_3 + 2.4% Y_2O_3 + 20% microbead + 2% PEG
MC30	63% β-SiC + 4.9% Al_2O_3 + 2.1% Y_2O_3 + 30% microbead + 2% PEG
MC40	54% β-SiC + 4.2% Al_2O_3 + 1.8% Y_2O_3 + 40% microbead + 2% PEG

*Poly(methyl methacrylate-co-ethylene glycol dimethacrylate) microbeads, ~20 μm, Sigma-Aldrich Inc, St. Louis, MO, USA.

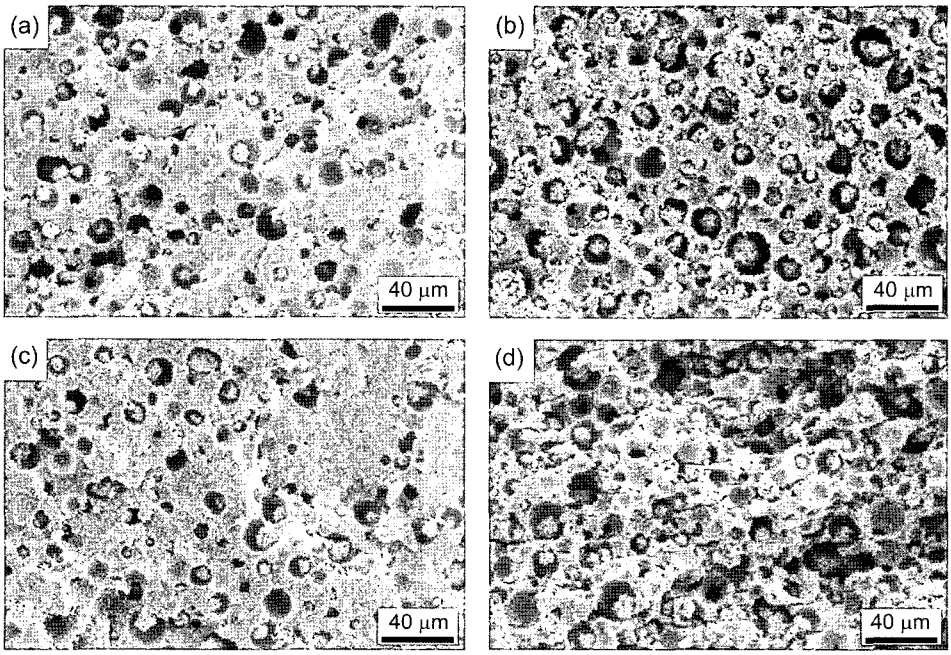

Fig. 1. Typical fracture surfaces of cellular SiC ceramics fabricated at 1750°C and 1850°C for 1 h in argon: (a) MC20-1750, (b) MC40-1750, (c) MC20-1850, and (d) MC40-1850 (refer to Table 1).

mer microbeads were used as feed material for shaping by uniaxial pressing. Al_2O_3 and Y_2O_3 were added as sintering additives. Cellular silicon carbide ceramics with high uniformity of cell size and shape were then fabricated by heat-treating the pressed body so as to decompose the polymer microbeads, followed by sintering.

Typical fracture surfaces of the cellular SiC ceramics are shown in Fig. 1. As shown, closed cells were formed for MC20 specimens, but partially-interconnected, open-cells were formed for MC40 specimens. This figure shows evidence that very fine and well-distributed cells were produced, as well as moderately dense struts in the cellular structure (see Fig. 2). The grain morphology was equiaxed for all the specimens observed and the grain size showed little difference with variation of sintering temperature. This is attributed to the role of pores as a grain growth inhibitor.[17] The morphology of the primary cells (cells replicated from polymer microbeads) is almost spherical. However, the holes in the cell walls are irregular in cellular SiC ceramics (Fig. 2), indicating that the shape of the polymer microbeads is retained in the SiC-Al_2O_3-Y_2O_3-polymer microbead compact up to its decomposition temperature. The cell size is below 20 μm, and there are no large voids in the bulk materials. This suggests that the proposed processing method prevents significant agglomeration of the polymer microbeads and, at the same time, allows for homogeneous distribution of the SiC and sintering additives between the sacrificial templates. The cell morphology changed from closed to open as the microbead content was increased in the cellular ceramics; this change was due to the greater opportunity for contact between the microbeads in the compacts.

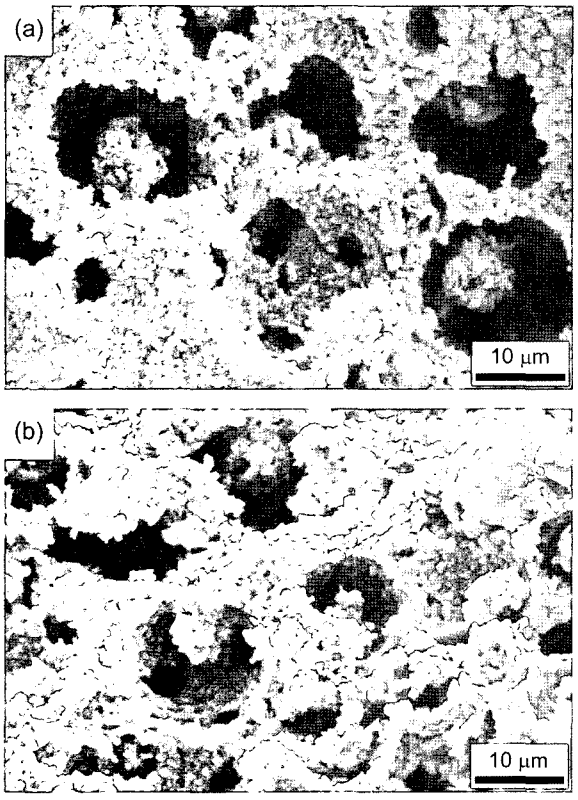

Fig. 2. Typical grain morphology of cellular SiC ceramics fabricated at 1750°C and 1850°C for 1 h in argon: (a) MC40-1750 and (b) MC40-1850 (refer to Table 1).

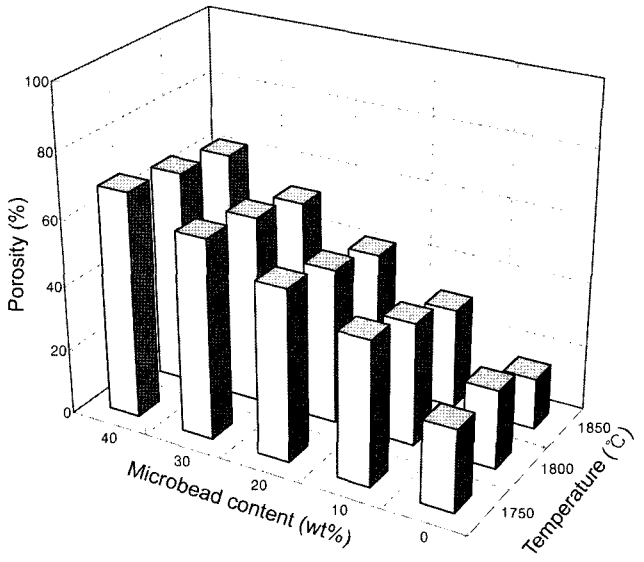

Fig. 3. Effect of microbead content and sintering temperature on porosity.

Fig. 3 shows the porosity of the cellular SiC ceramics as functions of microbead content and sintering temperature. The porosities obtained in this experiment spanned from 25% to 69% when the samples were sintered at 1750°C, from 24% to 66% when the samples were sintered at 1800°C, and from 16% to 62% when the samples were sintered at 1850°C; it is important to note that these ranges depended on both the microbead content and the sintering temperature. Porosity increased directly with an increase in the microbead content for all observed specimens. In contrast, higher sintering temperature led to lower porosity at the same microbead content, due to enhanced densification at higher temperatures.

Fig. 4 illustrates the flexural strength and the compressive strength as a function of relative density for the samples sintered at 1750°C, 1800°C, and 1850°C. As shown, both strengths increased as the relative density increased. The flexural strength and the compressive strength showed no dependence on sintering temperature. It appears that pores act as critical flaws in each specimen; the pore size was similar for all the specimens. Thus, the strength has no dependence on the sintering temperature. The flexural strength of the cellular SiC ceramics with ~20% and ~40% porosities was ~160 MPa and ~60 MPa, respectively. The compressive strength of the cellular SiC ceramics with ~20% and ~40% porosities were ~500 MPa and ~160 MPa, respectively. The flexural strength of a porous SiC ceramic with ~40% porosity that was fabricated by a partial sintering method was ~40 MPa.[18] The compressive strength of cellular mullite

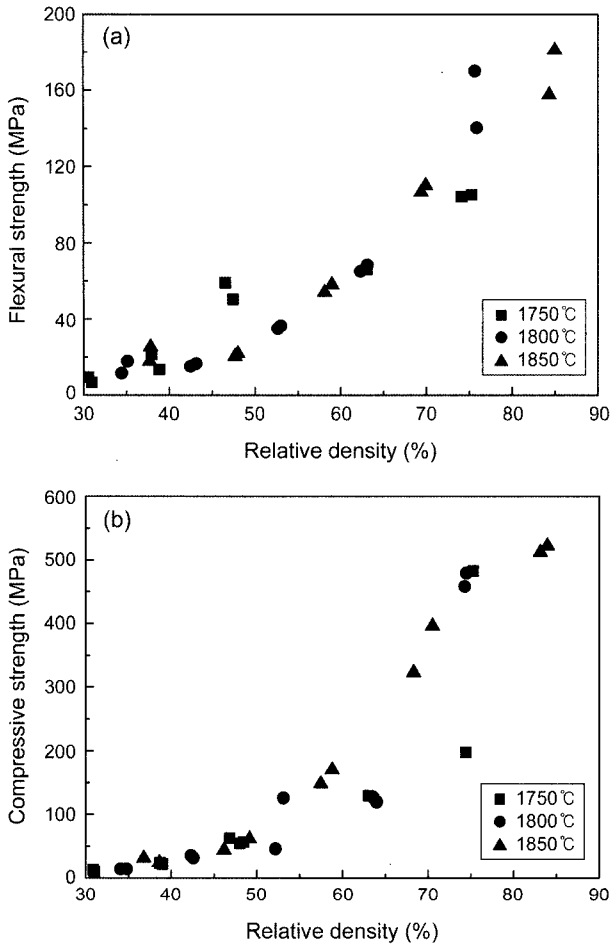

Fig. 4. Room-temperature flexural strength and compressive strength of cellular SiC ceramics: (a) flexural strength and (b) compressive strength.

with ~40% porosity was ~90 MPa.[4] The superior strength of the cellular SiC ceramics relative to that of the other materials is attributed to a lack of macroscopic defects and the small dimensions (≤20 μm) of the cells in the cellular ceramics.

Fig. 5 shows the variation of cell density as a function of the content of polymer microbeads. The cell density increased gradually from $1.3\sim1.9\times10^8$ cells/cm^3 for the specimens containing 10 wt%-microbeads to $4.1\sim5.5\times10^8$ cells/cm^3 for the specimens containing 40 wt%-microbeads as the microbead content was increased. All specimens had cell densities greater than 10^8 cells/cm^3 and cells smaller than 20 μm. The present results suggest that the content of microbeads and the sintering temperature are crucial variables in controlling the porosity of cellular SiC ceramics fabricated by the proposed method.

4. Conclusions

A simple pressing method utilizing a SiC powder, Al_2O_3-Y_2O_3 additive, and polymer microbeads yielded cellular silicon carbide ceramics with cell densities greater than 10^8 cells/cm^3 and cells smaller than 20 μm. Higher microbead content led to higher porosity in the cellular ceramics. By controlling the microbead content and the sintering temperature, it was possible to produce cellular SiC ceramics with porosities ranging from 16% to 69%. The flexural and compressive strengths of the cellular SiC ceramics with ~40% porosity were ~60 MPa and ~160 MPa, respectively. The present results, specifically the production of cellular ceramics with a lack of macroscopic defects and cells of small dimensions, suggest that the proposed simple processing method is suitable for the manufacture of porous ceramics with improved strength.

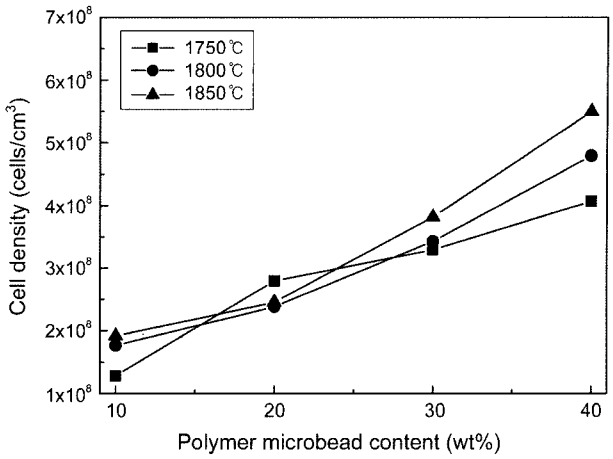

Fig. 5. Effect of microbead content on cell density.

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