Processing of Polymer-derived Microcellular Ceramics Containing Reactive Fillers

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Abstract

Processing techniques for producing microcellular silicon carbide, mullite, and cordierite ceramics have been developed by a reaction method that incorporates a polysiloxane and reactive fillers. The techniques developed in this study offer substantial flexibility for producing microcellular ceramics whereby cell size, cell density, degree of interconnectivity, composition, and porosity can all be effectively controlled. It is demonstrated that the adjustment of filler composition enables the possibility of tailoring the composition and properties of the microcellular ceramics. The present results suggest that the proposed novel processing techniques are suitable for the manufacture of microcellular ceramics with high morphological uniformity.

Keywords : porous ceramics, processing, porosity

1. Introduction

Polymer-derived microcellular ceramics are lightweight materials consisting of a microcellular structure. Due to the combination of properties resulting from the polymer-derived ceramic material and the microcellular structure, these ceramics have a high potential for a number of industrial applications such as filters, insulators, gas sensors, catalytic carriers, absorbents, and lightweight structural materials [1-3]. Several processing routes for microcellular ceramics have been designed with an eye to specific applications and their associated demands regarding porosity, cell morphology, and degree of interconnectivity [1,3,4]. Since the distribution of the size and shape of the cell space in ceramic foams is directly related to their ability to perform a desired function in a particular application, the need to establish uniform cell sizes and shapes in order to achieve superior part properties has come under much investigation [2,5,6].

Recently, three different manufacturing techniques - a gas-bubble formation method [7], a replication method [6], and a reaction method [8] - for producing microcellular ceramics have been developed. The present study describes the reaction method for producing polymer-derived microcellular ceramics containing reactive fillers. Depending on the composition of reactive fillers (carbon, talc, and Al_2O_3), it was possible to tailor the composition of microcellular ceramics.

2. Experimental and Results

The following raw materials were used in the experiment: a commercially available polysiloxane (YR3370, GE Toshiba Silicones Co., Tokyo, Japan); expandable microspheres (461DU40, Expancel, Sundsvall, Sweden); polymer microbeads (~20 μm, Sigma-Aldrich Inc, St. Louis, MO); carbon (carbon black, Corax MAF, Korea Carbon Black Co., Ltd., Incheon, Korea); talc (Samchun Pure Chemical Co. Ltd., Pyongtack, Kyungki-do, Korea); Al_2O_3 (AKP30, Sumitomo Chemical Co., Tokyo, Japan); and Y_2O_3 (Shin-Etsu Chemical Co., Tokyo, Japan). The carbon, talc, and Al_2O_3 were employed as reactive fillers.

The batch compositions and sample designations are shown in Table 1.The batches were mixed, dried and uniaxially pressed into disks at 28 MPa. The green compacts containing microspheres were expanded, and cross-linked by heating them up to 180^oC in air.

Table 1. Batch composition of microcellular ceramics

Sample	Batch Composition (wt%)
SiC1	75.8% PS[a] + 9.2% C[b] + 10% MS[c] + 3Y2A[d]
SiC2	72.6% PS + 7.4% C + 15% MS + 3Y2A
C	23.5%PS+32.7%talc+26.3%A+15%MS+2.5%K[e]
M	18.4% PS + 47.5% A + 33.8% MB[f] + 0.3% Y

[a] Polysiloxane./ [b] Carbon./ [c] Expandable microspheres./ [d] 3% Y_2O_3 + 2% Al_2O_3/ [e] Kaolin / [f] Microbead

The cross-linked foams were heat-treated at various conditions: 1200°C for 1 h in argon and subsequently sintered at 1650°C for 2 h in argon for the SiC samples; 1350°C for 4 h in air for the cordierite sample (C in Table 1); and 1550°C for 2 h in air for the mullite sample (M).

Pyrolysis of the polysiloxane in an inert atmosphere yielded SiOC whereas pyrolysis of the polysiloxane in air yielded SiO$_2$ [9]. The general reaction for synthesizing SiC, cordierite and mullite are summarized in Table 2. XRD on each specimen showed β-SiC for SiC1 and 2 samples, cordierite for sample C, and mullite for sample M, indicating the completion of each reaction. Typical microstructures of microcellular ceramics fabricated by the present method are shown in Fig. 1. As can be seen, homogeneous microcellular structures were achieved in SiC and mullite ceramics and dense struts in the microcellular structure were also produced. The cell morphology was almost spherical in microcellular SiC and mullite and the holes in the cell walls were circular in the samples, indicating that both the shape of microspheres in SiC samples and that of microbeads in the mullite sample were retained in their compacts up to their decomposition temperatures. However, relatively irregular cell morphology was obtained in the cordierite sample. It seems that too much filler (59%) in sample C led to partial collapse of the microcellular structure during processing. In SiC samples, closed-cells were obtained when the microsphere content was 10% whereas open-cells were obtained when the microsphere content was 15% (see Fig. 1 (a) and (b)). These results suggest that control of the degree of interconnectivity is possible by controlling the microsphere content. The mullite sample contained both open and closed cells and the cordierite sample contained mostly open cells.

The porosity (85%) of SiC2 was higher than that (73%) of SiC1. The more microsphere content led to the higher porosity. The porosities (73~85%) of SiC and cordierite samples were relatively higher than that (~57%) of the mullite sample, indicating that the microspheres were more effective than microbeads as a pore former for producing highly porous, microcellular ceramics. For the SiC and mullite samples, cell sizes were smaller than 30 μm and cell densities were greater than 10^9 cells/cm^3.

Table 2. General Reactions for Synthesizing SiC, Cordierite and Mullite

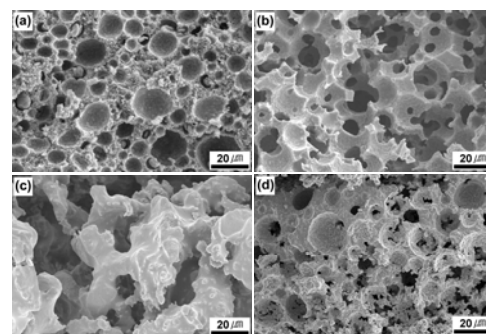| Material	General Reaction
SiC	Polysiloxane(PS) + C $\rightarrow$ SiOC + C SiOC + C $\rightarrow$ SiC + CO↑
Cordierite	PS + O$_2$ $\rightarrow$ SiO$_2$ + CO$_2$↑ 7SiO$_2$ + 6Al$_2$O$_3$ + 2(3MgO·4SiO$_2$·H$_2$O) $\rightarrow$ 3(2MgO·2Al$_2$O$_3$·5SiO$_2$) + 2H$_2$O↑
Mullite	PS + Al$_2$O$_3$ $\rightarrow$ SiOC + Al$_2$O$_3$ 2SiOC + 2O$_2$ + 3Al$_2$O$_3$ $\rightarrow$ mullite + 2CO↑

Fig. 1. Typical microstructures of polymer-derived microcellular ceramics: (a) SiC1, (b) SiC2, (c) cordierite, and (d) mullite.

In contrast, some larger cells and lower cell density (~10^8 cells/cm^3) were observed in the cordierite sample. It may be due to the coalescence of cells during processing in the sample. Such kind of coalescence was also observed in various microcellular ceramics when large amount of fillers (>35%) were added [10,11]

3. Summary

By judiciously selecting the composition of reactive fillers, it was possible to control the composition of polymer-derived microcellular ceramics.

4. References

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