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Structure and mechanical properties of porous silicon oxycarbide ceramics derived from silicone resin with different filler content

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Abstract

Porous silicon oxycarbide ceramics were obtained through pyrolysis of a new silicone resin filled with its pyrolyzed SiOC powders via a simple self-blowing process. The effects of filler content on the porosity, compressive strength and microstructure of the porous ceramics were investigated. The porosity (total and open) increased firstly and then decreased with the filler content increasing. It was possible to control the total and open porosity of porous ceramics within a range of 66.1–88.2% and 42.7–72.5% respectively, by adjusting the filler content from 0 vol% to 30 vol% while keeping the heating rate fixed at 0.5 °C/min. The compressive strength decreased firstly and then increased with the increasing filler content, and the average compressive strength of the porous ceramics was in the range of 1.1–3.4 MPa. Micrographs indicated that the porous ceramics with the filler content less than 20 vol% had a well-defined open-cell and regular pore structure.

Keywords: B. Porosity; C. Strength; Filler content

1. Introduction

Porous SiOC ceramics possess a number of unique properties, such as good mechanical strength, creep resistance, resistance to oxidation and corrosion. With these excellent characteristics, they are considered as good candidates for structural and functional applications at elevated temperatures [1–3].

The preparation of porous SiOC ceramics through silicone resin self-blowing process has aroused wide attention in recent years, owing to its low fabrication temperature, simple and environmental friendly processing, low-cost and processing versatility, controllable structure and properties [4,5]. In this method, silicone resin containing amounts of ethoxy- and/or hydroxy-groups (according to the variety of silicone resin) can generate a certain amount of air bubbles in situ by condensation reactions during cross-linking, and the porous structure will be consolidated by the concurrent viscosity increase with proceeding cure of the polymer melt. Subsequently, the thermoset porous structure is pyrolyzed to convert the polymer into a porous ceramic [6–8].

As well known, preceramic polymers undergo a polymer-to-ceramic conversion when pyrolyzed, accompanied by high volume shrinkage or even a collapse [9]. In order to reduce the shrinkage and improve the strength of porous ceramics, adding fillers into preceramic polymer is necessary. In addition, the introduction of active fillers or inert fillers different from pyrolysates of preceramic polymer results in the formation of new phases which will surely influence the microstructure and properties of porous ceramics [10–12].

In our previous work [4,7,10], a new self-blowing precursor for the preparation of porous SiOC ceramics, i.e., silicone resin DC217, was adopted, and a kind of highly porous SiOC ceramics were fabricated. Meanwhile, the effects of heating rate, exterior gas pressure and diameter of SiC fillers on the structure and properties of highly porous SiOC ceramics were investigated.

The present work focuses on the relationship between filler content and microstructure, porosity and compressive

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strength of the porous SiOC ceramics. DC217 derived SiOC ceramic powders were used as fillers. The purpose of adopting pyrolyzed SiOC powders as fillers is to keep the components of the final porous ceramics consistent, and eliminate the heat-stress brought by the difference of thermal expansion coefficients between SiOC ceramics and fillers.

2. Experimental procedures

Commercially available silicone resin (Dow Corning 217, Flake Resin) was chosen as precursor. Its derived SiOC ceramics (1200 °C, 1 h, argon) were ground to powders with a mean size of 9.1 μm and these powders were used as fillers. The mixtures of DC217 and SiOC powders with different volume ratios were ball-milled for 5 h with alcohol as solvent for DC217. Then the alcohol was evaporated to obtain DC217-coated SiOC powders. The above powders were ground and passed through a 100 mesh sieve and then uniaxially pressed into wafers under 200 MPa. The wafers were cross-linked by heating them up to 250 °C at a heating rate of 0.5 °C/min, with a holding time of 4 h in an oven in air, and then heated at 1200 °C for 1 h with a heating rate of 5 °C/min in Ar atmosphere.

The apparent density of the porous ceramics was computed from the weight-to-volume ratio, and the true density (i.e., skeleton density) of the SiOC fillers was 1.95 g/cm^3, measured using a pycnometer. The total porosity was calculated from the bulk density to true density ratio. The open porosity of the porous ceramics was determined by the Archimedes principle, using kerosene as buoyant medium. The cell size was measured using an image analyzer (Image-Pro Plus, Media Cybernetics). The cell morphology and microstructure were characterized using scanning electron microscopy (SEM, Hitachi S4800). The porous ceramics were cut in rectangular pieces (20 mm × 20 mm × 20 mm) for compression test with a cross-head speed of 2 mm/min. Each time five pieces were tested to obtain the average compressive strength.

3. Results and discussion

Fig. 1 shows the macro-photographs (left, made by optical microscope) and typical fracture surfaces (right, made by SEM) of the porous SiOC ceramics with the filler content changed. It reveals that the filler content had a great influence on the cell morphology and connectivity of the porous ceramics. The cell morphology of porous ceramics with the filler content more than 20 vol% was comparatively irregular, and the connectivity was extraordinary bad (Fig. 1d). However, the ones with the filler content less than 20 vol% had a well-defined open-cell and regular pore structure with spherical cells (Fig. 1a–c). In addition, with the filler contents increasing from 0 to 30 vol%, the mean cell size of the porous ceramics increased and then decreased, and the maximum cell size of 1.8 mm was obtained at the filler content of 10 vol%.

Fig. 2 shows the porosity (total and open) and compressive strength of the porous SiOC ceramics as a function of the filler contents. As shown, in the range of 0–30 vol%, the porosity increased firstly and then gradually decreased. The maximum total and open porosity of 88.2% and 72.5%, respectively, were obtained at the filler content of 10 vol%. In addition, the compressive strength of the porous SiOC ceramics decreased firstly with the filler content increasing up to 20 vol% and showed a minimum at 20 vol%, followed by an increase in strength when the filler content reached 30 vol%. The average compressive strength of the porous ceramics was in the range of 1.1–3.4 MPa.

According to interrelated Refs. [5,6,8,9] and our previous research [4,7,10], the formation of the porous ceramics included the following stages: firstly, the filler-based green compacts became nearly fully densified polymer melt at a lower temperature; secondly, water and ethanol were released from condensation reactions of the hydroxy and ethoxy groups, and bubbles nucleated in the polymer melt at a higher temperature; thirdly, the bubbles grew up along with a suppression of the surface tension of the polymer melt. At last, the grown bubbles were stabilized in the cross-linked body by viscosity increase.

Obviously, the condition of the surface tension (value and uniformity) around the bubbles is critical to the porosity and final pore structure. It is influenced by many parameters, such as variety of precursors, kind, content and the dispersing of fillers. When the precursor and filler are fixed, the content and the dispersing of the fillers turn to the key to the final structure.

Under this condition, on the one hand, the content of the fillers will alternate the rheological properties of the polymer melt, as the presence of solid filler particles will influence the viscosity of the liquid that contains them and, in turn, alternate the value of the surface tension around the bubbles and the foaming behaviors of the blends [13,14]. Generally, the increase of the filler content would lead to the enhancement of the viscosity of the polymer melt and, in turn, the increase of the surface tension around the bubbles. Hence, the bubbles would form with more difficultly, leading to a smaller pore size and a smaller porosity (Fig. 1). Moreover, if the filler content is too high, the bubbles in the polymer melt could not even initiate blowing and subsequently resist the surface tension to form, even though condensation reaction has occurred [7]. In contrast, the decrease of the filler content would lead to the reduction of the surface tension around the bubbles. Accordingly, the bubbles could grow up more easily, resulting in a bigger pore size and a higher porosity. Subsequently, more adjoining bubbles would be united. As a result, the connectivity (open porosity) of the porous ceramics improved with the decreasing of the filler content (Fig. 1). However, if the filler content was zero, the porous structure would have a high volume shrinkage when pyrolyzed, showing obvious decrease in total and open porosity (Fig. 2). On the other hand, the content of the

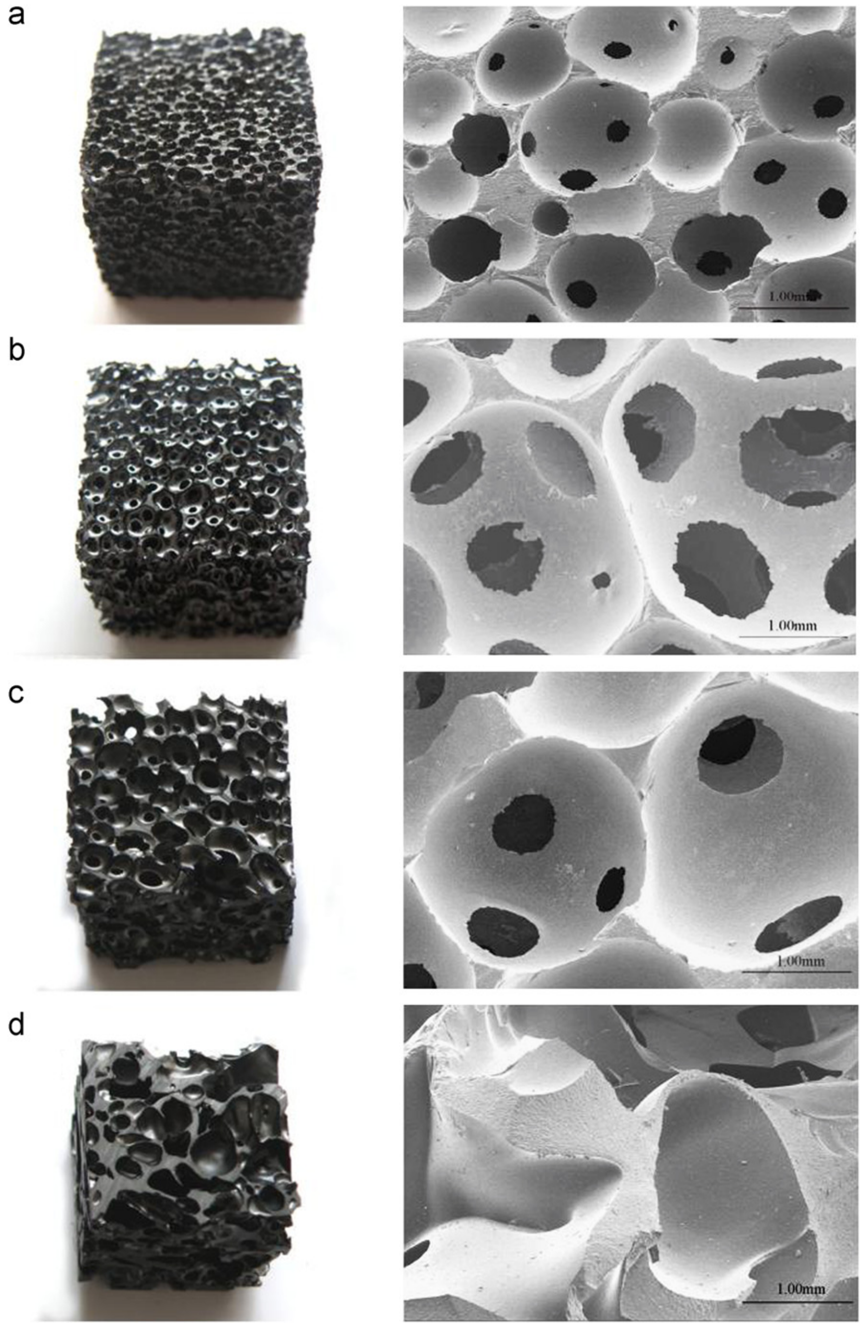

Fig. 1. Effect of filler content on the macro-photographs (left) and typical fracture surfaces (right) of porous SiOC ceramics. (a) 0 vol%, (b) 10 vol%, (c) 20 vol%, and (d) 30 vol%.

fillers will affect the dispersing of the fillers. As well known, the more filler contents adopted, the more easily fillers assembled. Thus, it was difficult to disperse the fillers well-proportionally in the polymer melt. As a result, the bubbles in the region of little fillers in the polymer melt were much easier to nucleate and form compared with the ones in the region of numerous fillers. So it is easy to understand why the cell morphology of porous ceramics with the filler content more than 20 vol% became extraordinary irregular(Fig. 1d).The compressive strength decreased firstly and then increased with the rising of the filler contents (Fig. 2). For the most part, this tendency was in contrast to the change in porosity with filler content, i.e., the bigger porosity is, the lower compressive strength will be, vice versa. This may be attributed to that the compressive strength of the porous SiOC ceramics is controlled not only by the porosity, but also by the cell morphology. As discussed afront, when the filler content was more than 10 vol%, the cell morphology became irregular, leading to stress concentration in porous

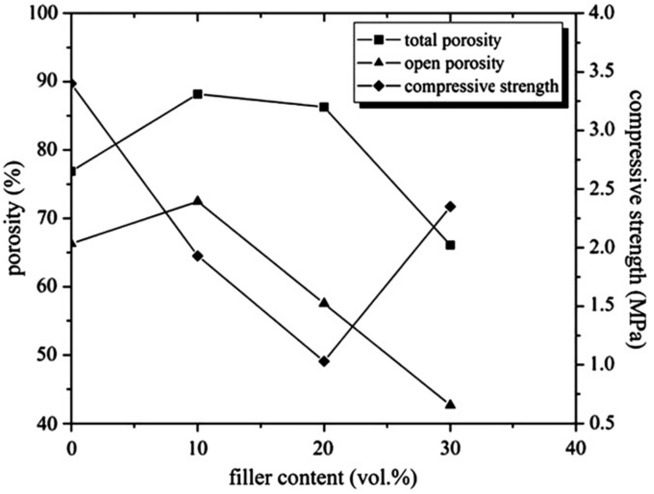

Fig. 2. Porosity and compressive strength of the porous SiOC ceramics against the filler content.

ceramics. Consequently, the porous ceramics with filler contents of 20 vol% and 30 vol% showed lower compressive strength even though they had a lower porosity.

4. Conclusions

Porous SiOC ceramics were obtained from a new self-blowing precursor silicone resin DC217, by pyrolysis at 1200 °C in argon. Its pyrolyzed SiOC powders were incorporated into the silicone resin as inert fillers. The porosity, pore structure, and the compressive strength were tailored by variation of the filler content in the starting mixture. With the filler content increased from 0 to 30 vol%, the total and open porosity of porous ceramics increased firstly and then decreased. The maximum total and open porosity of 88.2% and 72.5%, respectively, was obtained at the filler content of 10 vol%. The compressive strength decreased firstly and then increased with the increasing of the filler contents. The porous ceramics with the filler content less than 20 vol% had a three-dimensional web and regular pore structures.

Acknowledgment

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