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Ceramics International 38 (2012) 2101–2104

CERAMICS INTERNATIONAL

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Effects of heating rate on the structure and properties of SiOC ceramic foams derived from silicone resin

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Received 8 October 2011; received in revised form 16 October 2011; accepted 17 October 2011
Available online 23 October 2011

Abstract

Silicon oxycarbide ceramic foams were fabricated in a single step manufacturing process using in situ foaming of SiOC powders loaded silicone resin. The effects of heating rate on the porosity, compressive strength and microstructure of the ceramic foams were investigated. The porosity (total and open) increased firstly and then decreased with increasing heating rate. It was possible to control the total and open porosity of ceramic foams within a range of 81.9–88.2% and 62.4–72.5% respectively, by adjusting the heating rate from 0.25 °C/min to 3 °C/min while keeping the silicone resin content at 90 vol%. However, the compressive strength decreased with increasing the heating rate progressively, and the average compressive strength of the foams was in the range of 1.0–2.3 MPa. Micrographs indicated that the ceramic foams which cross-linked at a heating rate less than 1 °C/min had a well-defined open-cell and regular pore structure.

Keywords: B. Porosity; Strength; Heating rate

1. Introduction

Ceramic foams possess a number of unique properties, such as low density, low thermal conductivity, high specific strength, high resistance to chemical corrosion, and high thermal shock resistance. With these excellent characteristics, ceramic foams are currently applied in various fields including metal melt filters, catalyst supports, heat exchangers, electrodes, and biomaterials [1–3].

The preceramic polymer pyrolysis appearing in late 20th century is a new route to fabricate ceramic foams. It offers many potential advantages such as low processing temperature, controllable ceramic composition and structure, processing versatility. According to the different pore-forming principles, the preceramic polymer pyrolysis can be classified into replica technique, sacrificial template method and direct foaming methods [4–6]. In direct foaming methods, ceramic foams are produced by forming a certain amount of air bubbles directly in the precursor or precursor solution, which is subsequently consolidated in order to keep the structure created by air bubbles. There are a wide variety of strategies (physical or chemical) to form air bubbles, including adding evaporable solvents [7], incorporating physical blowing agents (CO_2) [8], and in situ generating volatile products by condensation reactions during cross-linking, i.e. self-blowing [9].

By far, self-blowing method has aroused wide attention, owing to its simple and environmental friendly processing, controllable structure and properties [10]. In order to produce a ceramic foam structure with controlled porosity, cell morphology and connectivity by this strategy, various processing parameters which can affect the final structure have been investigated, such as the overall functionalities of the precursors [10], variety of the fillers [11], thermal pre-curing procedure [12], exterior gas pressure [13], and the precursor:filler ratio in the starting composition [14]. However, the effect of heating rate on the final structure of the porous ceramics was rarely reported. In the present work, the relationship between the heating rate and the microstructure, porosity and compressive strength of the ceramic foams was researched.

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.10.048

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. The powders were used as fillers in order to restrain the shrinkage during pyrolysis and keep the components of the final ceramic foams consistent.

The mixtures of DC217 and SiOC powders with a volume ratio of 90:10 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 were uniaxially pressed into wafers under 200 MPa. The wafers were cross-linked by heating them up to 250 °C at different heating rates, with a holding time of 4 h in air, and then fired at 1200 °C for 1 h with a heating rate of 5 °C/min in Ar atmosphere.

The viscosity (η) of the DC217 and the DC217 filled with SiOC powders (DC217:SiOC = 90:10 vol) were characterized in air, using a strain-controlled rheometer (AR 2000,TA Instruments), with increasing temperature, from the melting temperature of the DC217 to 300 °C. A heating rate of 0.25 °C/min was applied. The bulk density of the ceramic foams 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 computed from the bulk density to true density ratio. Open porosity of the ceramic foams 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). SEM (JSM-5600LV, JEOL) observations were conducted to examine the microstructures.

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. Five pieces were tested to obtain the average compressive strength.

3. Results and discussion

Fig. 1 shows the viscosity of (a) DC217 and (b) DC217 filled with SiOC powders. With the increase of temperature, the viscosity of the DC217 decreases firstly and then increases. For the tendency of the curve, there are two factors affect it. On the one hand, the viscosity of a given polymer melt generally follows the Arrhenius type relation [9]:

$$\eta(T) = \eta_0 \exp\left(\frac{E_\eta}{RT}\right)$$

where η_0 is an empirical constant and E_η is the activation energy for viscous flow. R is the gas constant and T is the absolute temperature. So at the first stage the viscosity of the polymer decreases with rising temperature. On the other hand, with the increase of temperature, the curing of the polymer melt will take place and then the number of ≡Si–O–Si≡ intermolecular cross-links increases, which results in an increase of the viscosity. This turned to be dominant at the second stage above 190 °C, as shown in Fig. 1. DC217 filled with SiOC powders showed a very similar curing behavior as compared to the unfilled DC217 (Fig. 1b).

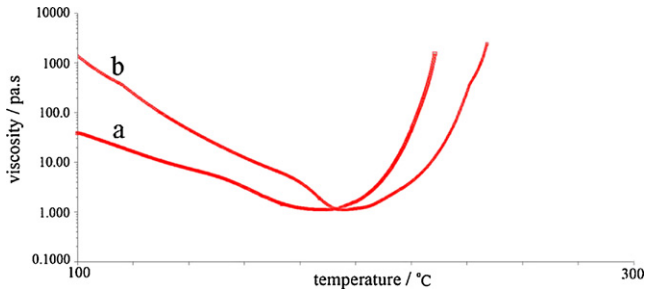

Fig. 1. Absolute value of the viscosity of (a) DC217 and (b) DC217 filled with SiOC powders during heating at 0.25 °C/min from the melting point to 300 °C.

Fig. 2 shows the macro-photographs (left, made by optical microscope) and typical fracture surfaces (right, made by SEM) of the SiOC ceramic foams cross-linked under various heating rates. It reveals that the heating rate had a great influence on the cell morphology and connectivity of ceramic foams. The cell morphology of ceramic foams cross-linked under the heating rate more than 1 °C/min was comparatively irregular, and the connectivity was extraordinary bad (Fig. 2d and e). However, the ones under the heating rate less than 1 °C/min have a well-defined open-cell and regular pore structure with spherical cells (Fig. 2a–c). In addition, with the heating rate increasing from 0.25 °C/min to 3 °C/min, the mean cell size of the ceramic foams increased and then decreased. The maximum cell size of 1.8 mm was obtained at the heating rate of 0.5 °C/min.

Fig. 3 shows the porosity (total and open) and compressive strength of the SiOC ceramic foams as a function of the heating rate. As shown, in the range of 0.25–3 °C/min, the porosity increased firstly and then gradually decreased. The maximum total and open porosity of 88.2% and 72.5%, respectively, was obtained at the heating rate of 0.5 °C/min. The minimum of 81.9% and 62.4%, respectively, was achieved at the heating rate of 3 °C/min. However, the compressive strength decreased progressively with increasing heating rate.

As well known, the formation of the ceramic foams can be considered including following stages [6,9,10,12]: firstly, the filler-based green compacts became nearly fully densified polymer melt at a lower temperature; secondly, water and ethanol were released upon condensation reactions of the hydroxy and ethoxy groups, and bubbles nucleated in the polymer melt at a higher temperature; thirdly, the bubbles grew up 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, bubble formation (nucleation, growth) requires being under a certain viscosity of the polymer melt. If the polymer melt viscosity is too high during the blowing stage, the insufficient gas pressure cannot initiate blowing and subsequently resist the surface tension to growing up, even though condensation reaction has occurred [9,15,16]. According to this, as the viscosity curve of the DC217 decreases firstly and then increases with the temperature elevating (Fig. 1), we can

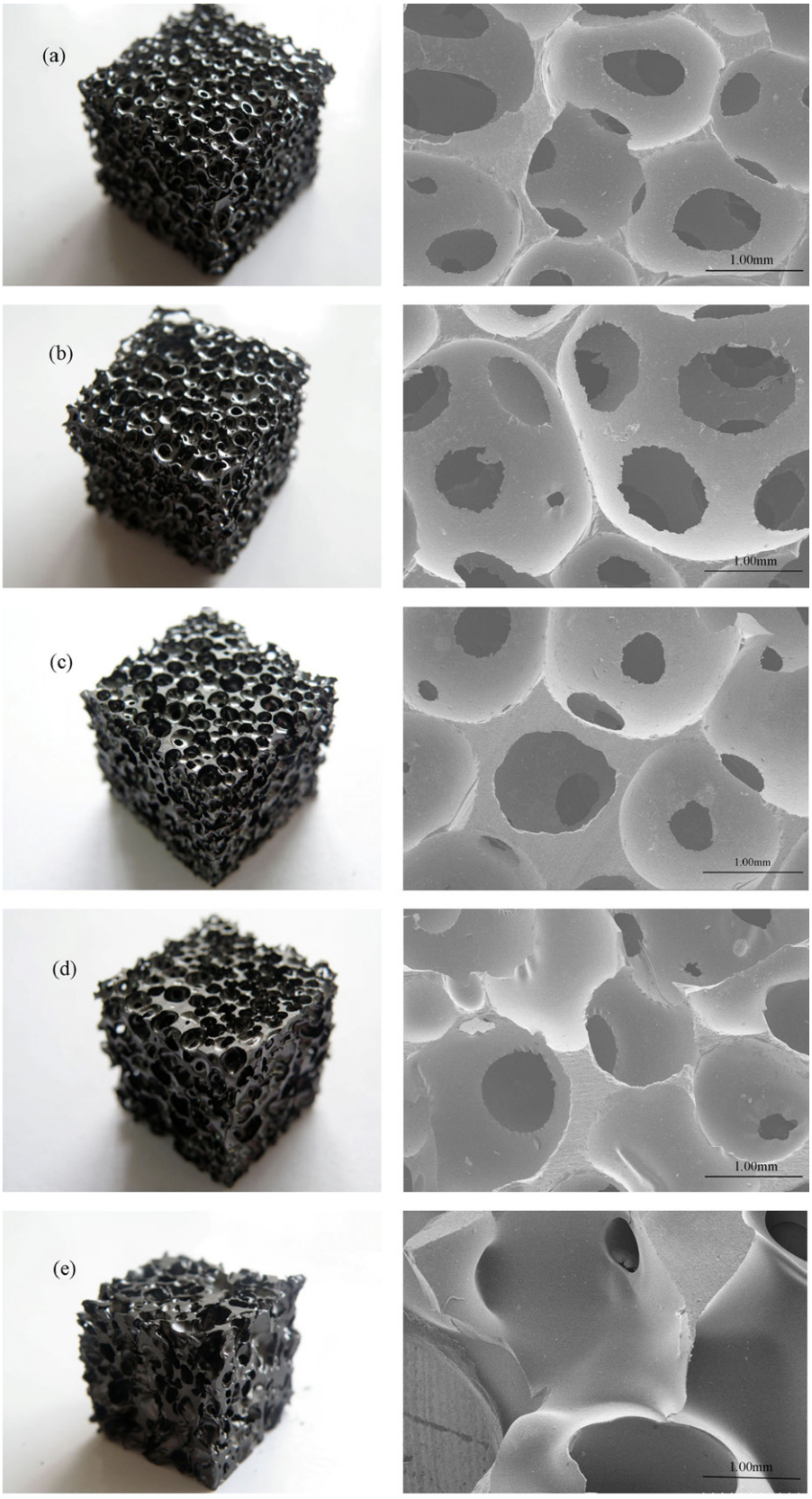

Fig. 2. Effect of heating rates on the macro-photographs (left) and typical fracture surfaces (right) of SiOC ceramic foams: (a) 0.25 °C/min, (b) 0.5 °C/min, (c) 1 °C/min, (d) 2 °C/min and (e) 3 °C/min.

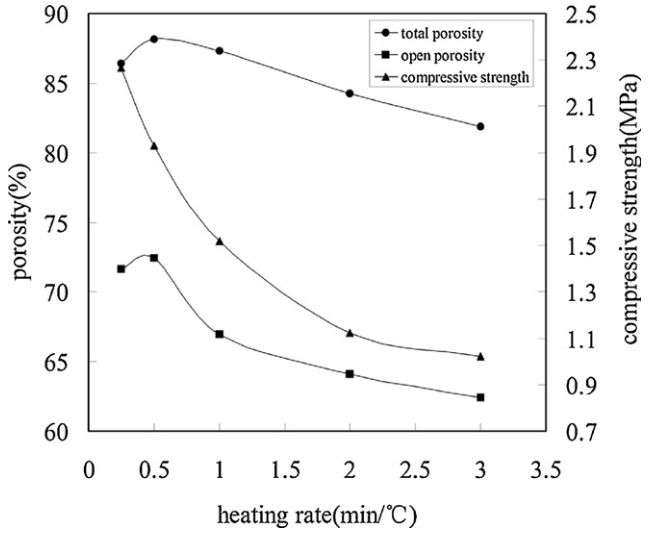

Fig. 3. Porosity and compressive strength of ceramic foams against the heating rate.

make a conclusion that the foaming only occur in a specific range of temperature for a given siloxane resin.

Adjusting the heating rates will influence the holding time in the specific range of temperature which can foaming. The slower heating rates was adopted, the time of bubble growth would be longer. Accordingly, the bubbles have a longer time to grow up, resulting in a bigger pore size and a higher porosity. What is more, with the bubbles growing continually, more adjoining bubbles would be united. As a result, the connectivity (open porosity) of foams improved with decreasing heating rate (Fig. 3). However, if the heating rates were too slow, interconnected pores would occur shrinkage, resulting that porosity (total and open) degraded to a certain degree (Fig. 3).

The compressive strength decreased progressively with increasing heating rates. This may result from the aberrance of the final pore structure. With the heating rate increasing, owing to the thermal conduction effect, the thermal field in the polymer melt would be asymmetrical. Under this condition, the bubbles in the high temperature region of the polymer melt were much easier to nucleate and grow up compared with the ones in the low temperature region, and then finally leading to the un-equirotal growth of cell size, and the disordered cell distribution. In addition, the surface tension around the bubbles which in the polymer melt would be asymmetrical too, resulting in an anomalistic pore morphology (Fig. 2d and e). Thus, the faster heating rate would lead to the irregular pore structure, resulting in decrease in compressive strength.

4. Conclusions

SiOC ceramic foams were obtained through pyrolysis of a silicone resin filled with SiOC powders via a simple self-blowing process. The porosity, pore structure, and the compressive strength were tailored by variation of the heating rate during the cross-linking stage. With the heating rate increased from 0.25 °C/min to 3 °C/min, the total and open porosity of porous ceramics increased firstly and then degraded. The maximum total and open porosity of 88.2% and 72.5%, respectively, was obtained at the heating rate of 0.5 °C/min. However, the compressive strength decreased progressively from 2.3 to 1.0 MPa. The ceramic foams which cross-linked at the heating rate less than 1 °C/min had a three-dimensional web and regular pore structures.

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