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Ceramics International 38 (2012) 5039–5043

CERAMICS
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Effects of inert filler addition on the structure and properties of porous SiOC ceramics derived from silicone resin

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Received 20 February 2012; accepted 1 March 2012
Available online 8 March 2012

Abstract

Porous SiOC ceramics were obtained from a new self-blowing precursor silicone resin DC217, by pyrolysis at 1200 °C in argon. Silicon carbide powders were incorporated into the silicone resin as inert fillers. The effects of the mean particle size of SiC fillers on the porosity, compressive strength and microstructure of the porous ceramics were investigated. With the mean particle size of SiC powders increasing from 5 μm to 10 μm, the porosity (total and open) of the porous ceramic increased and the compressive strength decreased. However, the porosity, compressive strength and cell morphology of the porous ceramics showed no evident changes when the mean particle size of fillers increased from 10 μm to 15 μm. Micrographs indicated that, when the mean particle size of fillers exceeded 5 μm, the porous ceramics could have a well-defined and regular pore structure. Furthermore, comparing with the porous ceramics which fabricated under the same condition with the SiOC powders as fillers, the cell morphology was similar. But the compressive strength and the oxidation resistance of the porous ceramics with SiC powders as fillers were much better.

Keywords: B. Porosity; C. Strength; Inert filler addition

1. Introduction

Porous SiOC ceramics, which exhibit good mechanical strength, creep resistance, high temperature stability, resistance to oxidation and corrosion, are good candidates for structural and functional applications at elevated temperatures [1,2]. The preparation of porous SiOC ceramics through silicone resin self-blowing process has attracted increasing interest in recent years for its advantages such as low fabrication temperature, simple and environmental friendly processing, low-cost and processing versatility, controllable structure and properties [3–5].

Recently, we have improved the self-blowing method for the preparation of porous SiOC ceramics, i.e., introducing an exterior gas pressure during the cross-linking stage (foaming stage) in a pressure kettle [6]. The porosity, pore structure, and compressive strength were tailored by variation of the exterior gas pressure. However, as it is well known, preceramic polymers undergo a polymer-to-ceramic conversion when pyrolyzed, with a high volume shrinkage or even a collapse [1]. In order to restrain the shrinkage and enhance the strength of porous ceramics, we chose the SiOC powders derived from silicone resin pyrolysis as fillers in our pioneering research [6].

According to Refs. [7–12], the structure and properties of the porous ceramics can furthermore be varied by changing the preceramic polymer used (yielding oxide, carbide or nitride ceramics) or by adding different variety of fillers (active or inert) to the precursor solution. In the present work, the porous ceramics were fabricated by the same method, but the fillers were altered to SiC powders. The effects of the mean particle size of SiC fillers on the porosity, microstructure and compressive strength were investigated. Besides, the structure and properties of the porous ceramics were compared with the ones which prepared under the same condition with SiOC powders as fillers [6].

2. Experimental procedures

2.1. Sample preparation

Commercially available silicone resin (Dow Corning 217, Flake Resin) and SiC powders (mean sizes of 5 μm, 10 μm and

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doi:10.1016/j.ceramint.2012.03.005

Table 1
Comparison of the properties of porous ceramics with different particle size of SiC fillers in the starting mixture.

Mean particle size of SiC fillers (μm)	Total porosity (%)	Open porosity (%)	Compressive strength (MPa)
5	52.3 ± 0.3	36.3 ± 1.9	27.3 ± 1.1
10	63.7 ± 1.2	56.8 ± 0.4	19.8 ± 0.7
15	62.5 ± 0.7	55.1 ± 0.9	20.0 ± 0.7

15 μm, respectively) were used as raw materials. The mixtures of DC217 precursor and SiC fillers with a volume ratio of 70:30 were ball-milled for 5 h with alcohol as solvent for DC217. Then the alcohol was evaporated to obtain DC217-coated SiC 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 at 250 °C for 4 h under 4 MPa exterior gas pressure in a pressure kettle. The cross-linked body subsequently was pyrolyzed at 1200 °C for 1 h with a heating rate of 5 °C/min under Ar atmosphere. The porous ceramics with SiOC powders as fillers were prepared by the same method and the detailed process can be seen in Ref. [6].

2.2. Analytical methods

The bulk (apparent) density of the porous ceramics was computed from the weight-to-volume ratio, and the true density was measured on powdered samples using a pycnometer. The total porosity was computed from the bulk density to the 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 with SiC powders as fillers and the ones with SiOC powders as fillers [6] were heated at 800, 1000 and 1200 °C in air for 1 h to compare their oxidation resistance property. 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

3.1. The influence of the mean particle size of SiC fillers

Table 1 shows the porosity (total and open) and compressive strength of the SiOC porous ceramics as a function of the mean particle size of SiC fillers. With the mean particle size of SiC fillers increasing from 5 μm to 10 μm, the porosity and the compressive strength underwent remarkable changes. Indeed, the total porosity of the porous ceramics increased from 52.3% to 63.7%, and the open porosity increased from 36.3% to 56.8%, respectively. Accordingly, the compressive strength decreased from 27.3 MPa to 19.8 MPa. However, the porosity, compressive strength and cell morphology of the porous ceramics showed no evident difference when the mean particle size of fillers within the range between 10 μm and 15 μm.

Fig. 1 shows the macro-photographs (left, made by optical microscope) and typical fracture surfaces (right, made by SEM) of the porous ceramics changing with the mean particle size of SiC fillers. From these images, when the filler size of 5 μm was adopted, the cell morphology of porous ceramics was comparatively disordered. However, when filler size was 10 μm and 15 μm, the pore structure of porous ceramics was more regular and well-defined. In addition, the cell morphology and the mean pore size of these two kind of porous ceramics showed no evident difference, and the mean cell size of the porous ceramics was about 0.8 mm.

According to interrelated Refs. [4,5,7,8] and our previous researches [3,6], the formation of the porous ceramics can be divided into four stages: firstly, the filler-based green compacts became nearly fully densified polymer melt at a lower temperature; secondly, water and/or ethanol were released upon condensation reactions of the hydroxy and/or 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 and the isostatic pressure which was introduced by the exterior gas pressure. At last, the grown bubbles were stabilized in the cross-linked body via viscosity increase.

Obviously, the final pore structure of porous ceramics strongly depends on the condition of the suppression forces (value and uniformity) around the bubbles. For the bubbles in the polymer melt, the factors affecting the forces include variety of precursors, content of fillers and the dispersing of fillers. When the precursor (silicone resin DC217) and the filler's content (30 vol.%) are fixed, the dispersing of the fillers is critical to the final structure.

Under this condition, the smaller the mean particle size of fillers adopted, the easier fillers assembled when keeping the same volume ratio. Thus, it is difficult to disperse the fillers well-proportionally in the polymer melt. As a result, the bubbles in the less fillers region of the polymer melt were much easier to nucleate and grow up compared with the ones in the numerous fillers region, and then finally leading to a disordered cell distribution (Fig. 2a). However, when the filler size was 10 μm and 15 μm, the dispersing condition might be almost similar, leading to the same porosity and the similar cell morphology (Fig. 2b and c).

3.2. The influence of the variety of fillers

Table 2 shows the porosity (total and open) and compressive strength of the porous ceramics as a function of the variety of

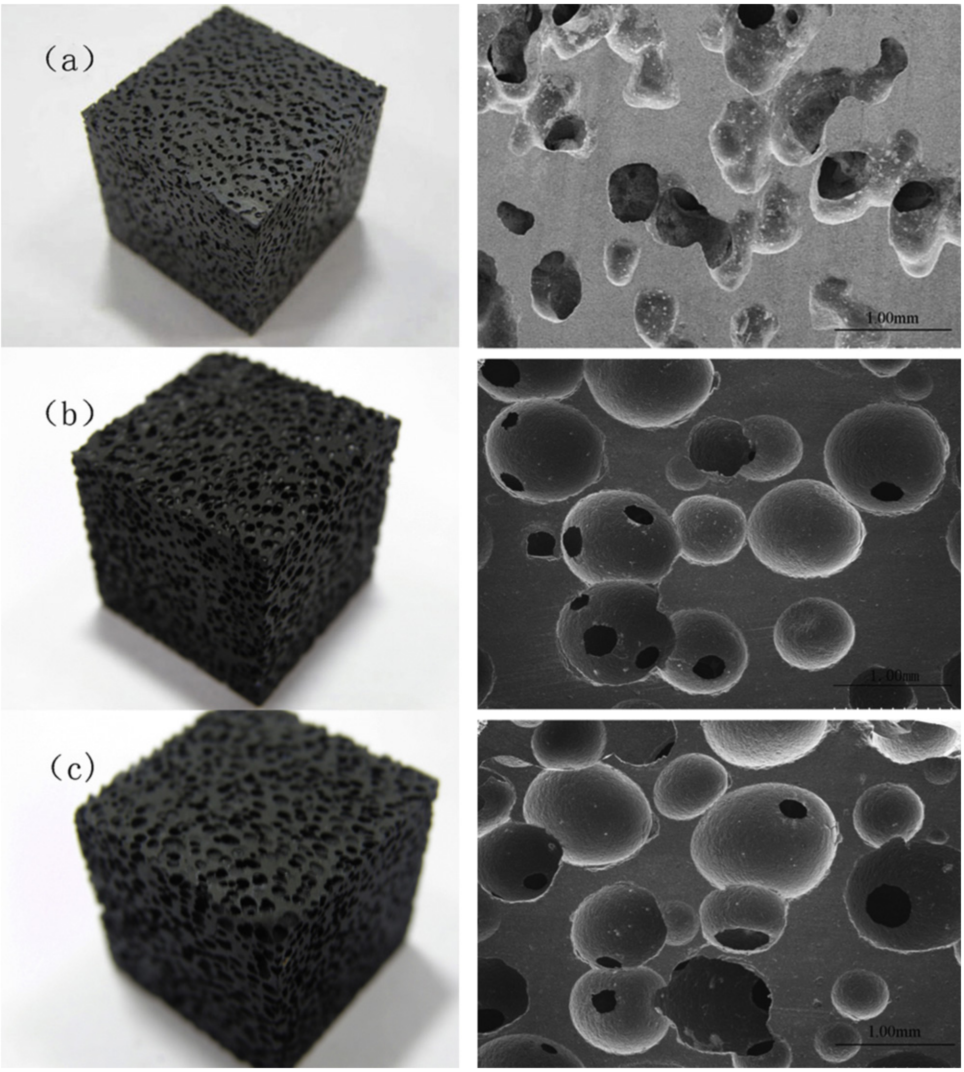

Fig. 1. Macro-photographs (left) and typical fracture surfaces (right) of the porous ceramics with different mean particle size of SiC filler. (a) 5 μm, (b) 10 μm, and (c) 15 μm.

fillers. It shows clearly that those porous ceramics with different variety of fillers exhibit various porosities and strengths. As shown, both the porosity and the compressive strength of the porous ceramics with SiC powders as fillers were higher than the ones with SiOC powders as fillers [6].

Fig. 2 shows the macro-photographs (left, made by optical microscope) and typical fracture surfaces (right, made by SEM) of the porous ceramics with different fillers. From these images, the cell morphology of porous ceramics with different fillers cross-linked under a certain pressure (4 MPa) was similar, and they both have a well-defined and regular pore structure with spherical cells. However, the mean cell size of the porous ceramics showed a remarkable difference. It was smaller with SiOC powders as fillers than the ones with SiC powders as fillers.

The porosity of the porous ceramics with SiC powders as fillers was higher than the ones with SiOC powders as fillers. This may be because the average viscosity of the polymer melt with SiC powders as fillers was lower than the polymer melt with SiOC powders as fillers during the foaming step. As a result, the bubbles of the former were easier to grow up than the latter, leading to a bigger pore size. However, the compressive

Table 2
Comparison of the properties of porous ceramics with different variety of fillers in the starting mixture.

Variety of fillers	Total porosity (%)	Open porosity (%)	Compressive strength (MPa)
SiOC[a]	58.4 ± 2.8[a]	44.0 ± 2.1[a]	14.9 ± 1.4[a]
SiC	63.7 ± 1.2	56.8 ± 0.4	19.8 ± 0.7

[a] From Ref. [6] which we studied previously.

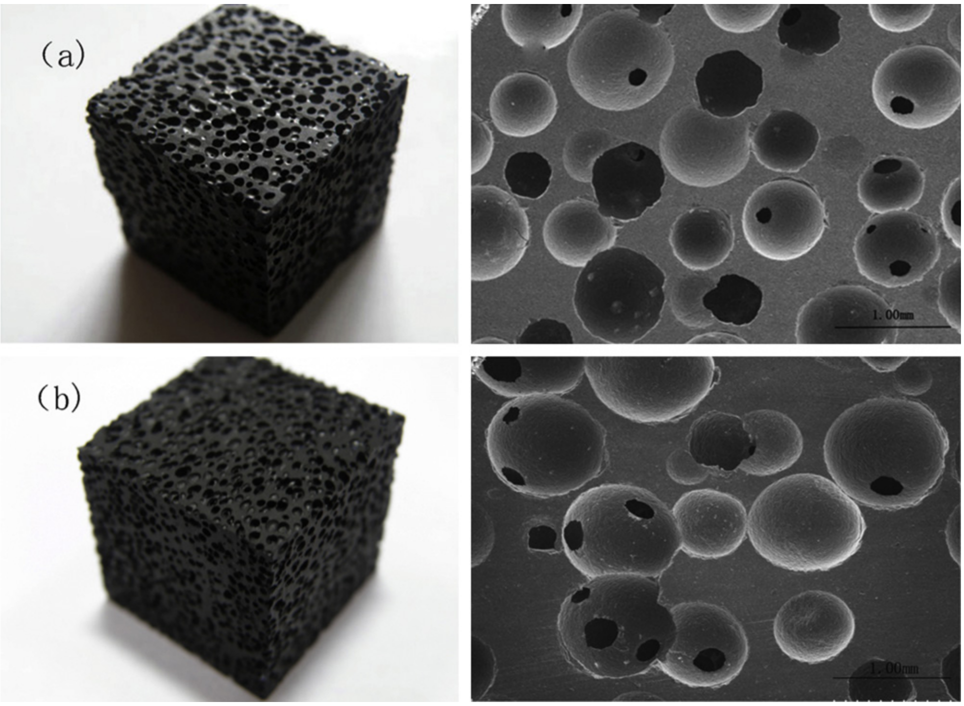

Fig. 2. Macro-photographs (left) and typical fracture surfaces (right) of the porous ceramics with different type of filler. (a) SiOC and (b) SiC.

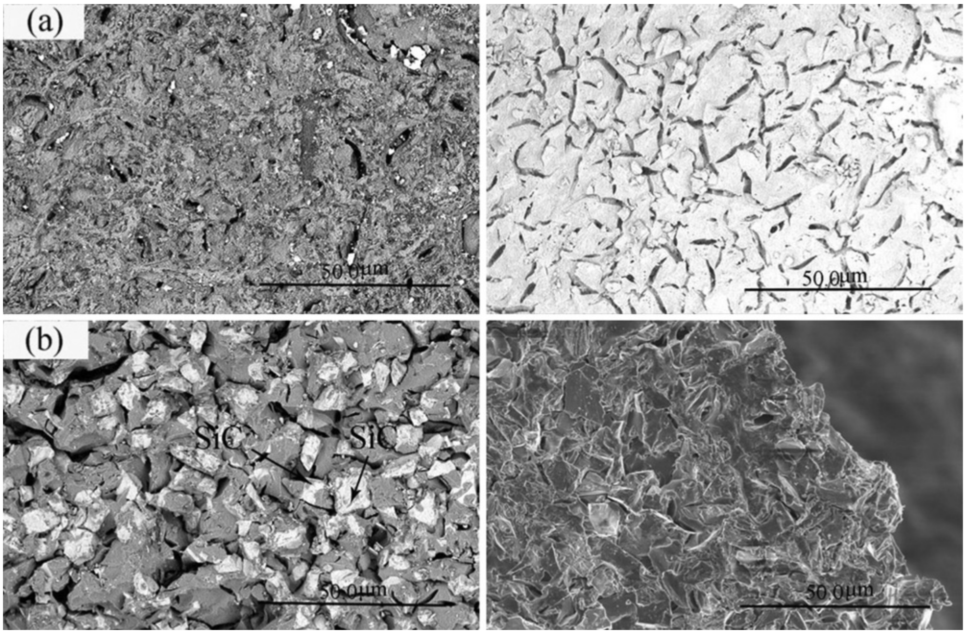

Fig. 3. Morphologies of porous ceramics with different type of fillers before (left) and after (right) oxidation (1200 °C). (a) SiOC and (b) SiC.

Table 3
Comparison of the oxidation properties of porous ceramics with different variety of fillers under different oxidation temperature.

Variety of fillers	Oxidation temperature (°C)	Mass loss rate (%)	Strength reserved ratio (%)
SiOC	800	3.96	50.07
	1000	9.25	46.23
	1200	14.46	43.63
SiC	800	4.67	75.25
	1000	10.83	55.26
	1200	10.32	46.58

strength of the former was higher too. This may result from the higher rigidity and elastic modulus of SiC fillers than SiOC fillers.

Table 3 shows the oxidation behavior of the porous ceramics with different fillers under different oxidation temperatures. As shown, the compressive strength of both specimens decreased with increasing oxidation temperature. Comparing of the strength reserved ratio of porous ceramics with two different fillers, the porous ceramics with SiC fillers showed better oxidation resistance. It can be explained that using the SiC powders as fillers, the oxidation products of the SiC was SiO_2 glass. This oxidation process could retard the mass loss of porous ceramics. In addition, the SiO_2 glass might work as an adhesive at the high temperature, which could make the cell struts (wall) become densified (Fig. 3). As a result, the oxidation resistance of the porous ceramics with SiC fillers was better than the ones with SiOC powders as fillers.

4. Conclusions

Highly porous SiOC ceramics were fabricated in a single step manufacturing process, using in situ foaming of different mean particle size of SiC fillers loaded silicone resin DC217. The following conclusions can be drawn from the present investigation:

(1)With the mean particle size of SiC fillers increasing from 5 μm to 10 μm, the total porosity of the porous ceramics increased from 52.3% to 63.7%, the open porosity increased from 36.3% to 56.8%, respectively, and the compressive strength increased from 19.8 MPa to 27.3 MPa. But, the porosity, mean cell size and compressive strength of the porous ceramics showed no evident changes when the filler size increased from 10 μm to 15 μm. The porous ceramics with the filler size exceeded 5 μm could have a well-defined and regular pore structure.

(2) Comparing with the porous ceramics which were fabricated under the same condition with the SiOC powders as fillers, the cell morphology was similar. But the compressive strength and the oxidation resistance of porous ceramics with SiC powders as fillers were much better.

Acknowledgement

The authors are grateful to Natural Science Foundation of China (91116001) for financial support.

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