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Fabrication and characterization of nanoporous SiO_2 ceramics via pyrolysis of silicone resin filled with nanometer SiO_2 powders

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Abstract

Mesoporous SiO_2 ceramics are fabricated by pyrolysis of silicone resin filled with nanometer SiO_2 powders in air at 1273 K. With the increase of shaping pressure, open porosity and average pore size decrease, while bulk density and fracture strength are improved. The fracture surface of porous SiO_2 ceramics was observed.

Keywords: C. Strength; D. SiO_2; Silicone resin; Mesoporous ceramics; Pore size

1. Introduction

Nanoporous especially mesoporous silica has many unusual properties such as a low dielectric constant, a low thermal conductivity, high specific surface area, and good thermal stability. Therefore, it has become increasingly attractive to use mesoporous silica in catalyst, optical, microelectronic, adsorption, and so on [1–3].

Up to now, the fabrication of nanoporous silica is greatly dependent on the sol–gel process [4–6]. Although the sol–gel technique offers several processing advantages over many material production methods, mainly due to purity, homogeneity and modifications of material properties by changing fabrication parameters, the sol–gel process has its intrinsic disadvantages such as extraordinary high volume shrinkage, long time for gelation and drying, and difficulty in preparing non-oxide ceramics and porous thick monolithic bodies.

Recently, much attention has been paid to the manufacture of porous ceramic materials via pyrolysis of preceramic polymers for its advantages such as processing versatility (e.g., plastic forming ability), lower processing temperature, high purity, and preparation of metastable phases unachievable by conventional methods [7–12]. Besides macroporous ceramics, micro-/mesoporous ceramics can be obtained from preceramic polymer pyrolysis due to the evolution of volatile species [8–10]. Although high volume shrinkage also occurs during polymer-ceramic conversion resulting from a pronounced density increase, the incorporation of inert/active fillers has been demonstrated to be an effective method to reduce the shrinkage [13,14]. Therefore, it is feasible to fabricate nanoporous thick monolithic bodies via preceramic polymer pyrolysis.

In this paper, nanoporous silica ceramics were fabricated via pyrolysis of silicone resin with nanometer SiO_2 powders as fillers, and the pore structure and strength was investigated.

2. Experiment

A flake silicone resin with a trade mark of DC249 was selected as the precursor to SiO_2. Amorphous SiO_2 powders with a specific surface area of 380 m^2/g (Zhejiang Ultrafine Powders & Chemicals Co., LTD., PR China) were used as inert fillers. The mixtures of DC249 (40 vol%) and SiO_2 powders (60 vol%) were ball-milled in acetone for 12 h to increase the homogeneity. After drying in an oven and being sieved through a 100-mesh screen, the powders were pressed into rectangular specimens under different pressures. Then the specimens were cured in air at 523 K for 6 h and pyrolyzed at 1273 K for 1 h with a heating rate of 5 K/min in a muffle.

The pyrolysis behavior of cured DC249 in air was investigated by thermal gravimetric analysis (TG, STA

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449C, Netzsch) with a heating rate of 10 K/min. The pyrolyzates of DC249 were characterized by FTIR (Fourier transform, Nicolet 360) and XRD (Siemens-D500). Mercury intrusion method (PoreSizer 9320, Micromeritics) was employed to characterize porosity, average pore size, pore size distribution, and bulk density. The specific surface area was determined by nitrogen adesorption/desorption at 77 K (Quantachrome Monosorb). For flexural strength testing, the obtained porous ceramics were cut into bars with a size of 3 mm (thickness) × 4 mm (width) × 35 mm (length). The flexural strength was tested by a three-point bending method with a span of 30 mm and a cross-head speed of 0.2 mm/min, using a universal testing machine (Instron-1342). Each data point was an average of five values. After flexure tests, SEM (JSM-5600LV, JEOL) was employed to observe the fracture surfaces of porous ceramics.

3. Results and discussion

TG was used in analyzing the thermal decomposition of silicone resin in air, and the results are shown in Fig. 1. It can be seen that silicone resin can be stable to ~723 K in air. In the temperature range of 723–973 K, there is a 40% mass loss. At $T > 973$ K, no obvious mass loss is observed.

The pyrolyzates of silicone resin in air were characterized by FTIR and XRD, and the results are shown in Figs. 2 and 3, respectively. The peaks located at about 1130 cm^{-1}, 800 cm^{-1} and 470 cm^{-1} are ascribed to stretching vibration of Si–O–Si. In combination of the XRD pattern, it is deduced that the pyrolyzates of silicone resin in air are amorphous SiO_2.

Table 1 shows the effects of shaping pressure on the properties of porous SiO_2 ceramics. With the increase of shaping pressure, open porosity and average pore size decrease. As a result, bulk density and fracture strength are improved. As shown in Fig. 4, the sample with high shaping pressure shows dense and glassy fracture surface. With decreasing shaping pressure, the fracture surface becomes rough and loose with obvious cracks.

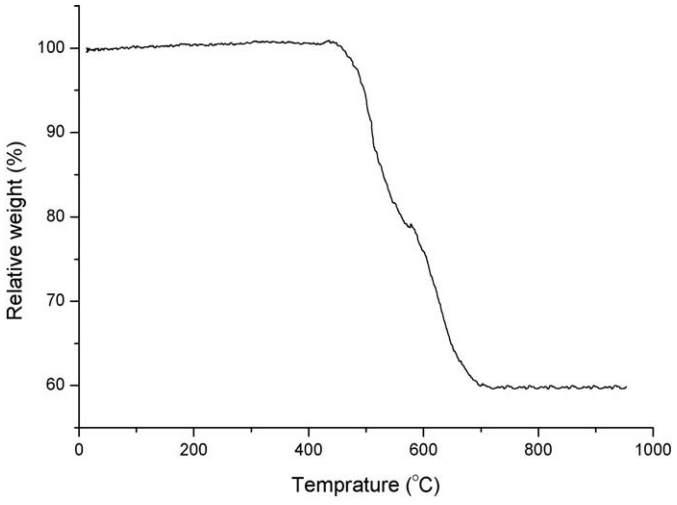

Fig. 1. TG curve of silicone resin in air with a heating rate of 10 K/min.

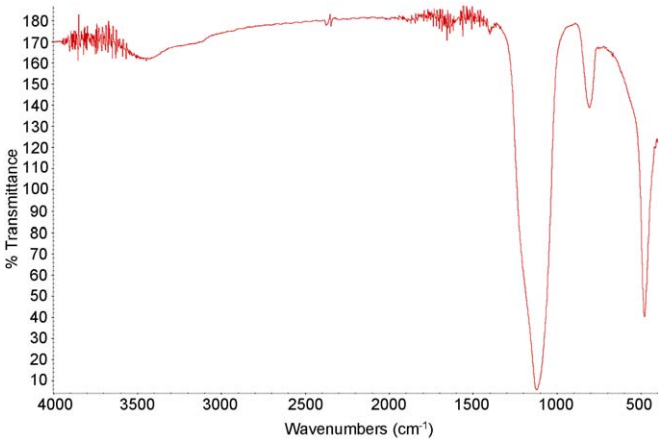

Fig. 2. FTIR spectrum of pyrolyzates of silicone resin in air.

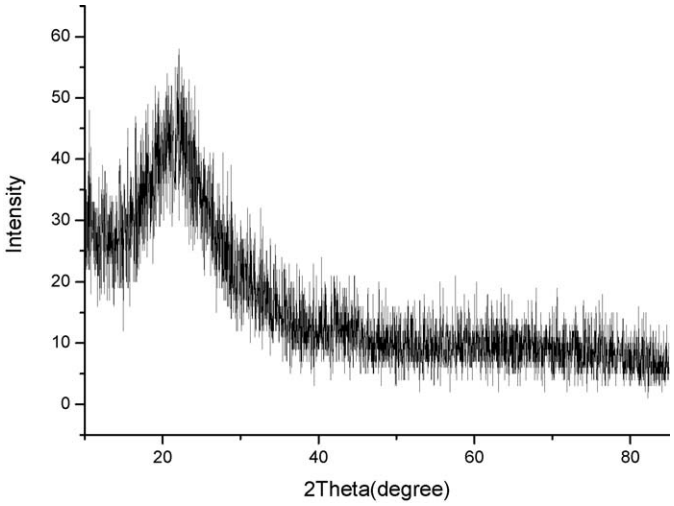

Fig. 3. XRD pattern of pyrolyzates of silicone resin in air.

As demonstrated in Fig. 5, the pore size of all samples is in the range of 9–50 nm. Therefore, mesoporous SiO_2 ceramics are obtained by pyrolysis of silicone resin filled with nanometer SiO_2 powders in air. Due to high porosity and mesopores, the sample shaped with a pressure of 11 MPa shows a specific surface area of 403.7 m^2/g. In Fig. 5, it is also indicated that larger shaping pressure results in narrower pore size distribution.

Since significant gas evolution accompanies the polymer-to-ceramic conversion, it is very likely to produce nanoporous ceramics from pyrolysis of preceramic polymers. However, it has been found that some transient porosity developed in the

Table 1
Effects of shaping pressure on the properties of porous SiO_2 ceramics.

Shaping pressure (MPa)	Bulk density (g/cm^3)	Open porosity (%)	Fracture strength (MPa)	Average pore size (nm)
43	1.109	54.22	14.49 ± 0.17	16.5
22	0.934	65.55	7.63 ± 2.22	23.2
11	0.792	71.85	3.93 ± 0.37	26.2
6	0.675	81.23	–	28.1

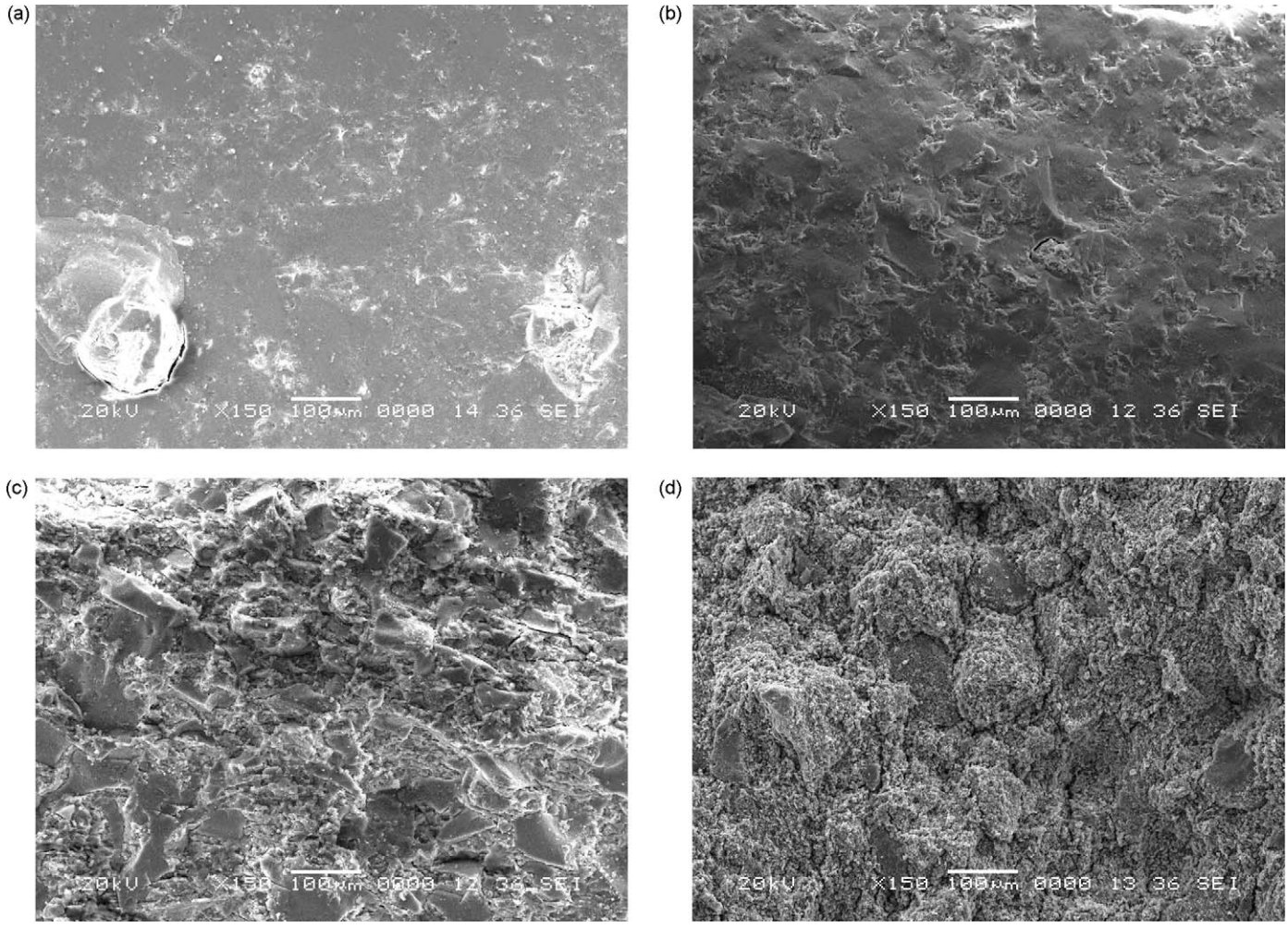

Fig. 4. SEM images of fracture surfaces of porous SiO_2 ceramics shaped by different pressures: (a) 43 MPa, (b) 22 MPa, (c) 11 MPa, (d) 6 MPa.

preceramic matrix due to polymer decomposition and gas evolution would close up when pyrolysis temperatures above 873 K are reached, resulting in sharply decrease in specific surface area and total pore volume [8,9]. When nanometer SiO_2 particles are introduced, the elimination of porosity and shrinkage are hindered by the presence of this solid phase which regularly shows no volume change. As a result, the mesopores can survive the polymer-to-ceramic conversion even after pyrolysis at high temperature.

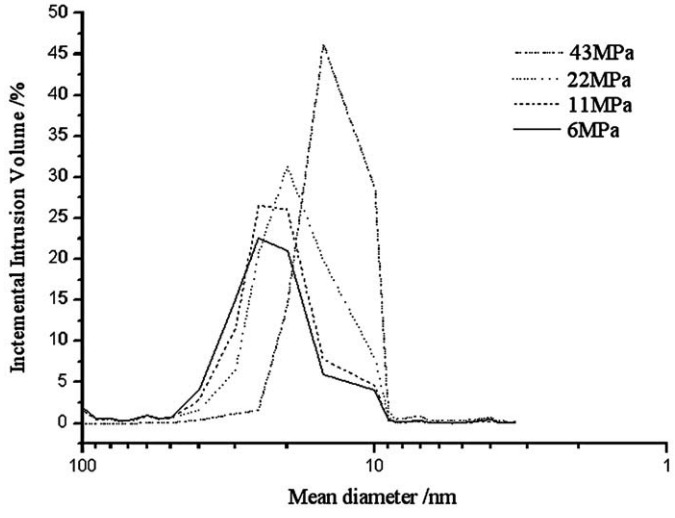

Fig. 5. Effects of shaping pressure on the pore size distribution of porous SiO_2 ceramics.

4. Conclusion

Mesoporous SiO_2 ceramics are obtained by pyrolysis of silicone resin filled with nanometer SiO_2 powders in air. Shaping pressure has great influence on pore size distribution, average pore size, open porosity and flexural strength of mesoporous SiO_2 ceramics. The effects of heating rate, maximum pyrolysis temperature, content and size of SiO_2 fillers on the pore structure and mechanical and physical properties are being under investigation.

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References

[1] X.W. Liu, J.W. Li, L. Zhou, D.S. Huang, Y.P. Zhou, Adsorption of CO_2, CH_4 and N_2 on ordered mesoporous silica molecular sieve, Chem. Phys. Lett. 415 (4–6) (2005) 198–201.

[2] A. Jain, S. Rogojevic, S. Ponoth, N. Agarwal, I. Matthew, W.N. Gill, P. Persans, M. Tomozawa, J.L. Plawsky, E. Simonyi, Porous silica materials as low-*k* dielectrics for electronic and optical interconnects, Thin Solid Films 398–399 (2001) 513–522.

[3] B.N. Nair, T. Yamaguchi, T. Okubo, H. Suematsu, K. Keizer, S.I. Nako, Sol-gel synthesis of molecular sieving silica membranes, J. Membr. Sci. 135 (2) (1997) 237–243.

[4] Y. Liu, L.Y. Zhang, X. Yao, C.N. Xu, Development of porous silica thick films by a new base-catalyzed sol–gel route, Mater. Lett. 49 (2) (2001) 102–107.

[5] A.M.M. Santos, W.L. Vasconcelos, Properties of porous silica glasses prepared via sol–gel process, J. Non-Cryst. Solids 273 (1–3) (2000) 145–149.

[6] G.M. Wu, J. Wang, J. Shen, T.H. Yang, Q.Y. Zhang, B. Zhou, Z.S. Deng, B. Fan, D.P. Zhou, F.S. Zhang, A new method to control nano-porous structure of sol–gel-derived silica films and their properties, Mater. Res. Bull. 36 (12) (2001) 2127–2139.

[7] P. Colombo, Engineering porosity in polymer-derived ceramics, J. Eur. Ceram. Soc. 28 (2008) 1389–1395.

[8] M. Wilhelm, C. Soltmann, D. Koch, G. Grathwohl, Ceramers – functional materials for adsorption techniques, J. Eur. Ceram. Soc. 25 (2005) 271–276.

[9] H. Schmidt, D. Koch, G. Grathwohl, P. Colombo, Micro-/macroporous ceramics form preceramic precursors, J. Am. Ceram. Soc. 84 (10) (2001) 2252–2255.

[10] P. Colombo, E. Bernardo, Macro- and micro-cellular porous ceramics from preceramic polymers, Compos. Sci. Technol. 63 (2003) 2353–2359.

[11] P. Colombo, E. Bernardo, L. Biasetto, Novel microcellular ceramics from a silicon resin, J. Am. Ceram. Soc. 87 (1) (2004) 152–154.

[12] J. Zeschky, T. Höfner, C. Arnold, R. Weißmann, D.B. Hourlier, M. Scheffler, P. Greil, Polysilsesquioxane derived ceramic foams with gradient porosity, Acta Mater. 53 (2005) 927–937.

[13] E. Bernardo, P. Colombo, S. Hampshire, Advanced ceramics from a preceramic polymer and nano-fillers, J. Eur. Ceram. Soc. 29 (2009) 843–849.

[14] F. Griggio, E. Bernardo, P. Colombo, G.L. Messing, Kinetic studies of mullite synthesis from alumina nanoparticles and a preceramic polymer, J. Am. Ceram. Soc. 91 (8) (2008) 2529–2533.