Fabrication and characterization of hierarchical porous SiC ceramics via gelcasting and carbothermal reduction between carbon and SiO

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With phenolic resin as carbon source, ethylene glycol as solvent and pore-forming agent, and silicon monoxide as pore-forming agent and silicon source, a kind of light hierarchical porous silicon carbide (SiC) ceramics with adjustable pores was prepared by gelcasting, carbonization and carbothermal reduction. With the addition of silicon monoxide in the green body from 13 to 49%, the porosities increased from 66 to 89%, the densities and thermal conductivity are as low as 0.36 g·cm⁻³ and 0.29 W·m⁻¹·K⁻¹. The macropores are mainly determined by the addition of silica particle size, which increases from 9.2 to 39.5%, while the micropores and mesopores, ranging from 56.8 to 49.5%, are mainly determined by the pyrolysis of resin carbon source. When the porosity of porous SiC is 75%, the compressive strength of 7.83 MPa can be reached. The prepared porous SiC ceramics possessed light, good thermal insulation and other properties, which can be further improved by changing the shape and size of the added SiO particles. In addition, different from using polycarbosilane as preceramic polymer, the porous SiC ceramics with complex shape and uniform microstructure can be prepared via gelcasting, which will reduce the production costs and broaden its application.

Key-words : SiC ceramic, Hierarchical pores, Gelcasting, Adding pore-making agent, Carbothermal reduction

1. Introduction

Porous silicon carbide (SiC) ceramics with low density, large specific surface area, excellent thermal shock and oxidation resistance, as well as high temperature and chemical corrosion resistance, are widely used as filter, thermal insulation, separation membranes, catalyst supports, bio-ceramics and other component materials.¹⁻³ So far, there are many preparation methods for porous SiC ceramics, including organic foam impregnation,⁴ foaming,⁵ adding pore-making agent,⁶ solid-state sintering,⁷ extrusion molding,⁸ sol–gel,⁹,¹⁰ and gelcasting.¹¹

The pore size of porous SiC ceramics prepared by organic foam impregnation mainly depends on the structural sizes of the pore and the coating thickness of the slurry.⁹ The foam impregnation speed of foaming method is fast and a lot of gas is produced in a short time, which will produce large bubbles, blanket collapse and nonuniform phenomenon, hence it is difficult to control the process conditions.⁵ The method of adding pore-making agent can control the pores size, shape and porosity by adding pore-making agents with different shapes, particle sizes and contents.⁶ For solid-state sintering, the shape, size and distribution of powder particles, the content and types of various additives, and sintering temperature all have direct influence on the formation, porosity, pore size and distribution of microporous bodies.⁷ Extrusion requires accurate design of the shape and size of the pore in the porous metal mold, and it cannot produce porous materials with complex structures and small pore sizes.⁸ The sol–gel reaction process is easy to control, and the uniformity and purity of the products are relatively high, which is suitable for preparing nanometer separation membrane.⁹,¹⁰ Gelcasting is through the crosslinking of organic monomers to achieve ceramic molding, and the choice of gel system directly determines the molding performance of ceramic slurry, structure uniformity, strength and machinability of ceramic body.¹¹

The hierarchical porous structure has low density, large surface area, abundant pore hierarchy and anisotropy.¹² Within the porous structures, it has good mechanical tolerances, and the load-bearing materials can be dispersed at different length scales to avoid fracture during compression. In addition, the hierarchical pores can effectively extend the heat transfer path and hinder the heat conduction of the gas. At the same time, if the micropore sizes in the hierarchical pores are smaller than the main molecular size in air, the energy exchange efficiency and thermal conductivity between the gas molecules will be reduced.¹,¹³ The size and shape of the pores are usually controlled by the addition of foaming agent, pore-making
agent or braided printing, and they can be controlled as needed.\textsuperscript{14}

Carbothermal reduction reaction is also frequently used to prepare porous ceramics, due to its simple process and resultant high porosities. J. M. Qian et al. prepared highly porous SiC ceramic with woodlike microstructure at 1400–1600 °C by carbothermal reaction of charcoal/silica composites in static argon atmosphere.\textsuperscript{15} M. R. Youm, et al. prepared SiO\textsubscript{2}–C preforms with relatively high surface areas using the modified sol–gel process, and the surface area was an important factor for promoting SiC formation by carbothermal reduction.\textsuperscript{16} In these reports, SiO\textsubscript{2} was used as reactant and SiO vapor can be formed through reaction between SiO\textsubscript{2} and C. To obtain high porosity, Q. Zhi et al. applied a novel carbothermal reduction–nitration reaction between light preform of die-pressed carbon nanotubes and SiO vapor provided from outside of samples to prepared highly porous Si\textsubscript{3}N\textsubscript{4} ceramics, and a high porosity of 73% was achieved, respectively,\textsuperscript{17} but the reaction process was dependent on the penetration of SiO. In our previous experiments of preparation of porous SiC through carbothermal reduction, porous carbon bodies with porosities ranging from 60 to 70% were successfully prepared through pyrolysis of phenolic resin with addition of ethylene glycol. And in order to further increase the porosity and form hierarchical pores for the porous SiC ceramics, a novel process that direction addition of SiO particles in the phenolic resin is proposed in this paper, and the SiO can not only participate carbothermal reduction reaction with the porous carbon to produce porous SiC, but also result in hierarchical pores through formation of macropores after volatilization of the extra SiO.

In this experiment, a kind of light hierarchical porous SiC ceramics with adjustable pores was prepared by gelcasting of slurry containing phenolic resin and SiO which were used as carbon and silicon source respectively, and the SiO particle was also performed as pore-forming agent. The porosities and sizes of micropores and mesopores are determined by the proportion of each raw material in the gel system and the pyrolysis temperature. Porous carbon body reacts with the sublimated SiO gas to obtain porous SiC ceramics at high temperature. Effects of SiO contents and sintering temperature were investigated, the macropores left by sublimation at high temperature gradually increase from 9.2 to 39.5%, and the porosities of porous SiC also increased from 66 to 89%. What’s more, the pore size and porosity were adjustable. Compared with porous SiC produced by polycarboxylane, it is cheaper and more convenient for practical production and application.

\section*{2. Experimental procedure}

Phenolic resin with the carbon residue rate of 62.5% (2130°, Xi’an Resin Factory Co., Ltd., China), ethylene glycol [(CH\textsubscript{2}OH\textsubscript{2}, AR, 99.5%, Tianjin Fuyu Fine Chemical Co., Ltd., China), silicon monoxide (SiO, Shanghai Chaowei Nano Technology Co., Ltd., China), in turn, were added to a beaker, using magnetic stirrer to stir 3 h, and the benzenesulfonyl chloride (C\textsubscript{6}H\textsubscript{5}ClO\textsubscript{2}S, AR, 99%, Tianjin Fuyu Fine Chemical Co., Ltd., China) was added to continue stirring for another 0.5 h to mix the slurry uniformly, then the slurry was kept in vacuum state with 10 min. The mass ratio of phenolic resin and ethylene glycol was 1:1, and the mass ratios of SiO changed from 13 to 49%. Benzenesulfonyl chloride was used as a curing catalyst with a dosage of 6%. After vacuumizing, the slurries were kept at 70 °C for 24 h, followed by increasing to 150 °C at a rate of 2 °C/min, and the curing body was obtained after soaking 16 h at 150 °C. Subsequently, the samples were heated to 800 °C at 2 °C/min, then to 1100 °C at 1 °C/min with a flowing N\textsubscript{2} atmosphere, finally soaking for 4 h to obtain performs containing carbon and SiO.

In the furnace (High Multi-5000, Fujidempa Co., Ltd., Osaka, Japan), the SiO powder was placed below the graphite paper, while the body was placed on the graphite paper with large holes, and the body was sintered under 1700 °C for 4 h with a constant argon gas pressure of 0.225 MPa. To be specific, the SiO powder located under the graphite paper and inside the carbon body is sublimated into SiO vapor at high temperature and then reacts with the carbon body to form silicon carbide. The heating rate from room temperature to 1200 °C was 20 °C/min, and the heating rate from 1200 °C to the final sintering temperature was 5 °C/min.

The porosity and density were measured by Archimedes method. The phase constituents of SiC powder were determined by X-ray diffractometer (XRD, XPert Pro 3040160, Panalytical B.V., Netherlands), with Cu K\textsubscript{α} radiation. The fracture microstructures were observed and analyzed by laser scanning confocal microscope (VK-9700K, Keyence Co., Ltd., Japan). The thermal diffusivity (α) and specific heat capacity (Cp) of specimens (size: 10 mm × 10 mm × 2 mm) were measured by a Thermal Properties Analyzer (FlashlineTM-5000, Anter Corporation, Pittsburgh, PA) at room temperature. The thermal conductivity (λ) of the SiC samples was calculated according to the equation: λ = ρ × α × Cp. Compression properties (size: 4.5 mm × 4.5 mm × 12.5 mm) were measured by universal testing machine (Instron 5944, Instron Co., London, UK) at a constant cross head speed of 0.5 mm/min at room temperature. Due to the sample limitation, only sample with addition of 22 wt % SiO was measured for comparison. Thermal gravimetric analysis (TGA) was performed by using a TA SDT Q600 TGA-DSC instrument, at a ramping rate of 10°C·min\textsuperscript{-1} under an air environment.

\section*{3. Results and discussion}

Figure 1 shows the XRD pattern of porous silicon carbide prepared by sintering at 1700 °C with the porosity of 82%. No residual silica, carbon and other peaks have been identified, only β-SiC has been identified, indicating that the reaction between carbon and silicon monoxide has been fully completed. The 2θ of the five strong peaks are 35.70, 41.33, 60.01, 71.98, and 75.36, respectively, which
are consistent with the (111), (200), (220), (311), and (222) crystal planes of $\beta$-SiC. The peaks of $2\theta = 33.53$ is caused by stacking faults in $\beta$-SiC.\(^{15}\)

**Figure 2(a)** is microstructure of the porous SiC prepared at 1700 °C with the porosity of 82%. The green body is composed of carbon obtained from resin pyrolysis and added silicon monoxide. At 1500–1800 °C, the silicon monoxide particles in the body and those placed at the bottom of the crucible first sublimate to form silicon monoxide vapor, and then in-situ carbothermic reaction with carbon in the body is carried out to produce porous silicon carbide. The body shape is almost unchanged, and the shape of silicon monoxide particles determines the shapes of the macropores, while no further machining is performed for the silicon monoxide selected in this experiment. In addition, the pores of carbon body are mainly formed in the gelation reaction stage of the resin slurry. By curing, there are cross-linking and interconnecting three-dimensional pores in the body. After pyrolysis, the body size changes slightly, and a large number of micropores and mesopores are formed in the body. The micropores and mesopores formed by resin pyrolysis, and the macropores left by the sublimation of added silicon monoxide, constitute the hierarchical pores in porous silicon carbide. What’s more, the shape, size and number of macropores can be changed by the shape, size and content of silicon monoxide particles added to the body, while the micropores and mesopores are changed by the ratio of phenolic resin and ethylene glycol.

Figures 2(b) and 2(c) are enlarged images in different magnification and Fig. 2(d) is parts of Fig. 2(a), and their specific positions are marked in Fig. 2(a). Figure 2(b) is the microstructure of the pore wall. The thickness is mainly related to the distances among the SiO particles. Figure 2(c) is a cross-sectional microstructure of SiC at magnification of 30,000 times, and the particle sizes are mainly between 100–200 nm. The pore diameters are mainly distributed at 50–130 nm, which is depended on the ratio of phenolic resin to ethylene glycol. Figure 2(d) shows a small amount of SiC whiskers generated during carbothermic reduction, located in few macropores. When the reaction reaches a certain temperature and pressure, SiO gas reacts with CO to form SiCw, SiO(g) + 3CO(g) → SiCw(s) + 2CO2(g), and the reaction can be controlled by adjusting the partial pressure of CO gas.\(^{18,19}\)

**Figure 3** shows the mass ratios of SiO in the body to pyrolytic C and the change of density of porous SiC with contents of SiO. **Figure 4** shows the porosities of macro-

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**Fig. 1.** XRD pattern of porous SiC prepared at 1700 °C with the porosity of 82%.

**Fig. 2.** Microstructure of porous SiC prepared at 1700 °C with the porosity of 82% at different parts and magnification ratios. (a) 1,500 times (b) 30,000 times, wall of pore (c) 30,000 times, cross-section (d) 30,000 times, a small amount of SiCw formed in macropores.
pores, micropores and mesopores, and porous SiC prepared at different mass ratios of SiO at 1700 °C. According to the reaction: \[ \text{SiO(g)} + 2\text{C(s)} \rightarrow \text{SiC(s)} + \text{CO(g)}, \] complete reaction can be performed for the mass ratio of SiO to pyrolytic C of 1.83 (mass ratio of SiO is 36%). As SiO particles are also placed under the samples in crucible, although the mass ratio is less than 1.83, the reaction can also be completed. The extra amount of SiO in the body can also vaporate, leaving small number of macropores. When the ratio is greater than 1.83, the volatile amount of SiO in the body increases with the ratio, and the porosity also increases. With the amount of SiO added to the body increasing from 13 to 49%, the macropores left by sublimation at high temperature also gradually increase from 9.2 to 39.5%, so the porosity of porous SiC increases from 66 to 89%, while the density decreases from 1.10 to 0.36 g cm\(^{-3}\). When the SiO in the body is less, it has no significant effect on pyrolysis. What’s more, the distance among the particles is larger and the dispersion is uniform, so the pores formed by sublimation at high temperature are more uniform. With the increasing of the amount of addition, the porosities of macropores and porous SiC increase faster while the density decreases rapidly. With further addition of SiO particles, their distribution become poor with further reduction of the particle distance and agglomeration of a few particles. After pyrolysis, it is easier to form three-dimensional interconnecting pores resulting in reduced porosity of micropores and mesopores. However, when the mass ratio of SiO to pyrolytic C is greater than 1.83 (mass ratio of SiO is 36%) in the case of complete reaction, the escape amount of SiO from the body increases with the increase of the ratio, the total porosity increases slowly. Finally, when the decline rate of the content of micropores and mesopores slows down as a result of the formation of three-dimensional interconnecting pores to a certain limit while the content of macropores still increases, the increase rate of porosity of porous SiC is further accelerated.

Figure 5 shows the thermal conductivity of porous SiC at different porosities. With the porosity increasing, the thermal conductivity decreases gradually. For the porous ceramics with the hierarchical pore structure, thermal conductivity is not only related to the total porosity, but also to the proportion of different pores. With the mass ratio of SiO from 31 to 49%, the porosities of the micropores and mesopores are decreased from 58.8 to 49.5% after organic matter pyrolysis gradually, and that of macropores are increased from 23.2 to 39.5% attributed to the remaining of pores after the SiO sublimation in porous SiC. These jointly form hierarchical pores, and prolong the heat transfer path and hinder the heat conduction of gas. What’s more, the pore size of nanopores formed during resin pyrolysis is smaller than the average free path (about 70 nm) of the major molecules in the air, so it is difficult to contact with the air, resulting in lower energy exchange efficiency and lower thermal conductivity between gas

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**Fig. 3.** Mass ratios of SiO in the body to pyrolytic C and densities of porous SiC prepared at different mass ratios of SiO at 1700 °C.

**Fig. 4.** Porosities of macropores, micropores and mesopores, and porous SiC prepared at different mass ratios of SiO at 1700 °C.

**Fig. 5.** Thermal conductivity of porous SiC at different porosities prepared at 1700 °C.
molecules. F. X. Alvarez et al. also demonstrated that the thermal conductivity was lower for higher porosity and for smaller pore radius, as a consequence of phonon ballistic effects. Therefore, with the rapid increasing number of macropores and the slow decreasing number of micropores and mesopores, although the total porosity is increased continually, the decreasing rate of thermal conductivity of porous SiC decreases gradually.

Figure 6 shows the TGA curve of SiC with the porosity of 82% in air, and the thermal stability of porous SiC is further studied through thermogravimetric analysis. From room temperature to 700 °C, its mass remained almost constant. During 700−1100 °C, due to the small particle size and large specific surface area of porous SiC, SiC and O2 in air rapidly undergo passive oxidation reaction to form SiO2 layer. What’s more, the particle size increases and occupies part of the pore. The specific reaction is as follows: 2SiC(s) + 3O2(g) → 2SiO2(s) + 2CO(g). During 1100−1250 °C, the SiC surface is covered with a SiO2 layer, which slows down the rate of further SiO2 formation and the mass increase rate. With the change of porous SiC mass from the original 100% to the ultimate 142%, the density increased from 0.58 to 0.83 g·cm−3, while the porosity decreased from 73 to 42%.

Table 1 lists the compressive strength and phase composition of sample with addition of 22 wt% SiO and some representative porous SiC with similar porosities.

![Figure 6](https://doi.org/10.1021/acsami.7b07735 (2017).)

Table 1. Compressive strength and phase composition of sample with addition of 22 wt% SiO and some representative porous SiC with similar porosities

| Sample | Porosity (%) | Compressive strength (MPa) | Phase composition | Reference |
|--------|--------------|---------------------------|------------------|-----------|
| 22 wt% SiO | 75 | 7.83 | β-SiC | this work |
| R1     | 70 | 2.5  | SiC-Si  | 22        |
| R2     | 74.1 | 1.0 | SiC-SiO2 | 23        |
| R3     | 75.9 | 1.6  | β-SiC  | 24        |

4. Conclusion

A kind of light porous silicon carbide ceramic material with adjustable pores was prepared by gelcasting, carbonization and carbothermal reduction. The SiO added in the body is not only acted as the reactant but also the pore-making agent, and the porosity of porous SiC is changed from 66 to 89% by SiO addition from 13 to 49%. The macropores are mainly determined by the addition of silica particle size, which increases from 9.2 to 39.5%, while the micropores and mesopores pores, ranging from 56.8 to 49.5%, are mainly determined by the pyrolysis of resin carbon source. The lowest density and the thermal conductivity of porous SiC with porosity of 89% are 0.36 g·cm−3 and 0.29 W·m−1·K−1, respectively. High compressive strength of 7.83 MPa can be reached for the porous SiC sample with porosity of 75%. The porous SiC ceramics with complex shape and uniform microstructure can be prepared via gelcasting, which will reduce the production costs and broaden its application.

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