

Low-temperature fabrication of porous SiC ceramics by preceramic polymer reaction bonding

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Abstract

Preceramic polymer polycarbosilane (PCS) and silicon carbide (SiC) powders were adopted as the starting materials for the fabrication of porous SiC ceramics. During the heat treatment process, PCS experienced an organic–inorganic transformation and acted as the bonding material between SiC particles at a low temperature of 1100 °C. The particle size of starting SiC powders and PCS content can control the pore size distribution and porosity. Fracture strength increases with higher content of PCS. Moreover, the as-fabricated porous SiC ceramics exhibit a low average coefficient of thermal expansion (CTE) of $3.4 \times 10^{-6}/\text{K}$ from room temperature to 800 °C.

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1. Introduction

Porous ceramics have been widely used in many areas, such as filters, catalyst supports, heat exchangers, electrodes, sensors, and so on [1]. Recently, porous silicon carbide (SiC) ceramics have been increasingly studied because they were proved to exhibit a unique combination of good oxidation resistance and thermal-shock resistance as well as excellent mechanical and chemical stability [2–4]. However, due to the covalent nature of Si–C bonds, SiC ceramics normally needed to be sintered at high temperatures or/and with the addition of sintering agents, which have limited the application of porous SiC ceramics. New processing routes that overcome these problems are the preceramic polymer processes, during which the polymer precursors convert into ceramic materials. These processes have the advantage of requiring unusually low temperatures (1000–1200 °C) [5]. The application areas of polymer-derived ceramics lie in a

wide range of fibers, coatings, binders, and ceramic matrix composites [6–10].

However, very little study has been reported about the application of preceramic polymer in fabricating porous ceramics [11,12]. The objective of this work is to report the method of using a kind of preceramic polymer as the bonding material to fabricate porous SiC ceramics at a temperature as low as 1100 °C. polycarbosilane (PCS; $[-\text{RSiH}-\text{CH}_2-]_n$, where R is CH_3) has been the most widely used preceramic polymer for the fabrication of SiC ceramics [8]. In our approach, PCS is used to coat the surface of SiC powders and then it experiences an organic–inorganic conversion and bonds the SiC particles during heat treatment. The structures and properties of the porous SiC ceramics are discussed.

2. Experiments

Commercially available α -SiC powders (Qinzhou Micropowders, China) and PCS (average molecule weight ≈ 1250 , National University of Defense Technology, China) were chosen as starting materials. *N*-hexane was used as solvent

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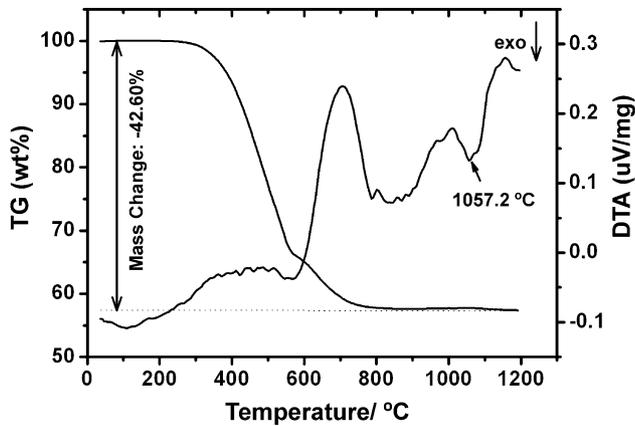


Fig. 1. TG–DTA curves of the as-received PCS at a heating rate of 10 °C/min under N₂.

for PCS. The SiC powder was dispersed in the PCS solution and further mixed; then the *n*-hexane was evaporated by blowing hot gas while stirring the paste continuously to obtain PCS-coated SiC powders. The above powders were crushed and passed through a 100 mesh sieve and then were pressed into rectangular bars under 40 MPa pressure using a stainless steel die. These specimen bars were put into a silica glass tube furnace and fired at 1100 °C for 2 h under flowing N₂.

PCS pyrolysis conversion process was investigated by TG–DTA (STA 449C, Netzsch) and XRD (RAX-10, Rigaku). Open porosity and bulk density of the porous specimens were measured by the Archimedes method. Pore size distribution was determined by mercury intrusion porosimetry (PoreSizer 9320, Micromeritics). Specimens were machined into bars of 3 mm (thickness)×4 mm (width)×40 mm (length) for three-point bending tests (AUTOGRAPH AG-I, Shimadzu) with a cross-head speed of 0.5 mm/min and a support span of 30 mm. Five specimens were tested to obtain the average strength. SEM (JSM-5600LV, JEOL) observations were conducted to examine the microstructures. The linear coefficient of

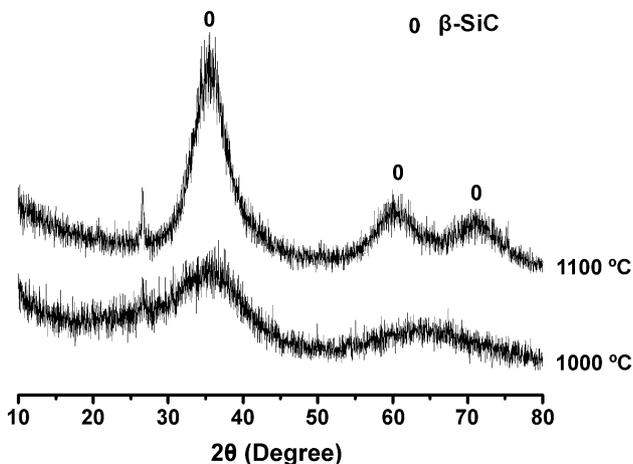


Fig. 2. XRD patterns of PCS pyrolysis products heat-treated at different temperatures.

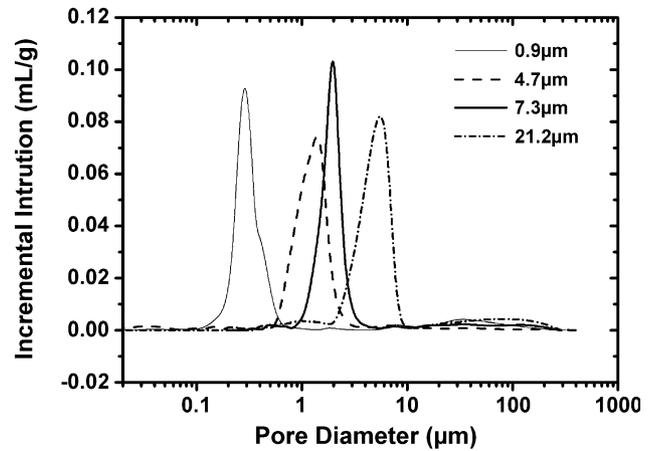


Fig. 3. Pore size distribution curves of porous SiC specimens fabricated by using four kinds of starting SiC powders with different mean particle sizes where PCS content is 9 wt.%.

thermal expansion (CTE) was measured by dilatometry (DIL 402C, Netzsch) with 5×5×25 mm specimens.

3. Results and discussion

Fig. 1 shows the TG–DTA curves of PCS, the starting preceramic polymer. PCS is a kind of preceramic polymer with a Si–C backbone. When heated in an inert atmosphere, PCS gradually cross-links and the low molecule weight species decompose, which causes weight loss. As can be seen from the TG curve, there is a total weight loss of ~42% from room temperature to 1100 °C. The major weight loss occurs from 300 to 700 °C, during which a low heating rate (1 °C/min) is necessary to avoid stress accumulation. It is shown in the DTA curve that there is an exothermic peak at 1057 °C, corresponding to the crystallization of PCS pyrolysis products, which has also been confirmed by XRD analysis. Fig. 2 is the XRD patterns of PCS pyrolysis products. PCS treated at 1000 °C yields the residue which is in an amorphous state. After 1100 °C treatment, the peaks (at $2\theta=36^\circ$, 60° , 72°) were assigned to (111), (220), (311) planes of β -SiC according to the standard JCPDS cards (29–1129). A small peak at $2\theta=26^\circ$ was also found, corresponding to the (002) diffraction peak of crystalline graphite because some residual carbon existed in the PCS pyrolysis products [8]. In the current route, the use of α -SiC powders

Table 1
Comparison of the properties of porous SiC ceramics with different content of PCS in the starting mixture

| PCS content (wt.%) | Porosity (%) | Bulk density (g/cm ³) | Fracture strength (MPa) |
|--------------------|--------------|-----------------------------------|-------------------------|
| 3 | 52.47 | 1.50 | 3.56±0.43 |
| 6 | 50.23 | 1.53 | 10.58±1.32 |
| 9 | 48.88 | 1.57 | 11.82±0.94 |
| 12 | 46.68 | 1.62 | 13.22±0.52 |
| 15 | 44.71 | 1.66 | 15.79±2.35 |

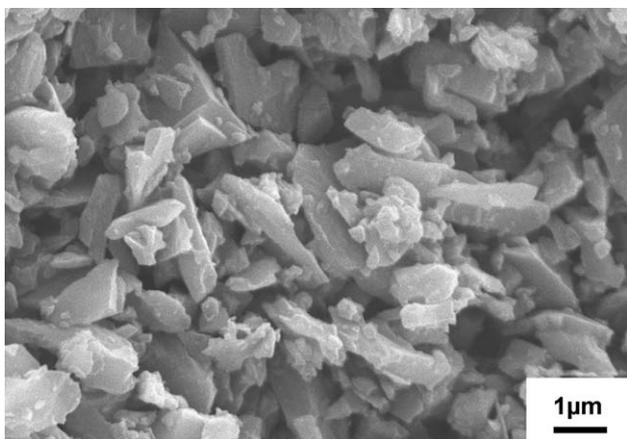


Fig. 4. SEM image of the fracture surface of the as-fabricated porous SiC ceramics specimen using 0.9 μm SiC powders and 6 wt.% PCS.

as starting materials was considered not to influence the pyrolysis behavior of PCS because SiC powder is an inert filler for PCS [9].

Porous ceramics with designed pore structures are necessary for concrete applications [1]. Larger pores can be obtained with coarser starting SiC powders and the pore size distributions of all specimens are narrowly distributed (Fig. 3). When SiC powder with the mean particle size of 21.2 μm is adopted, average pore diameter is 6.17 μm , while 0.9 μm SiC powder results in 0.26 μm pore diameter.

Table 1 shows the porosity, bulk density and fracture strength of porous SiC ceramics (SiC powder with a mean particle size of 0.9 μm was used) with different content of PCS. From these figures, the influence of PCS content is apparent. Higher content of PCS resulted in lower porosity, higher bulk density as well as higher fracture strength. As can be seen in Fig. 4, while the morphology of the SiC particles are kept unchanged, the particles have been bonded each other by PCS pyrolysis products at the contact sites and the residual pores are obvious. The joining mechanism may involve the direct formation of chemical bonds between SiC particles and the pyrolysis residual materials [13]. When PCS content was increased in the starting mixture, the bonding areas between SiC particles were larger, leading to higher strength. On the other hand, with more PCS, more space in the bulk specimens was occupied by the pyrolysis residues and, consequently, open porosity dropped while bulk density rose. Hence, the strength increase was ascribed to both the larger bonding areas between SiC particles and an improvement in density.

Moreover, it was observed that the as-fabricated porous SiC ceramics exhibited a lower average CTE of $3.4 \times 10^{-6}/\text{K}$ from room temperature to 800 $^{\circ}\text{C}$ than that of recrystallized porous SiC ceramics ($4.3 \times 10^{-6}/\text{K}$) [14]. The decrease of CTE was due to the use of PCS as the bonding material, whose shrinkage and evolution of hydrocarbon

species during the pyrolysis process could generate microcracks in the pyrolysis residual materials [9]. These microcracks were effective to accommodate thermal expansion [15]. As a result, the obtained porous SiC ceramics display a lower CTE value.

4. Conclusion

In conclusion, porous SiC ceramics were successfully fabricated through the preceramic polymer reaction bonding route at a temperature as low as 1100 $^{\circ}\text{C}$. In this process, the SiC particles were bonded to each other by the PCS pyrolysis products. The pore size of the porous specimens could be controlled by the size of starting SiC powders. Open porosity, bulk density, and fracture strength have been found to be functions of the content of PCS. In addition, the as-fabricated porous SiC ceramics exhibited a low CTE.

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