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Preparation and characterization of porous, biomorphic SiC ceramic with hybrid pore structure

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Abstract

Bio-carbon template (charcoal) was prepared by carbonizing pine wood at 1200 °C under vacuum, and was impregnated with phenolic resin/SiO_2 sol mixture by vacuum/pressure processing. Porous SiC ceramics with hybrid pore structure, a combination of tubular pores and network SiC struts in the tubular pores, were fabricated via sol–gel conversion, carbonization and carbothermal reduction reaction at elevated temperatures in Ar atmosphere. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) were employed to characterize the phase identification and microstructural changes during the C/SiO_2 composites-to-porous SiC ceramic conversion. Experimental results show that the density of C/SiO_2 composite increases with the number of impregnation procedure, and increases from 0.32 g cm^{-3} of pine-derived charcoal to 1.5 g cm^{-3} of C/SiO_2 composite after the sixth impregnation. The conversion degree of charcoal to porous SiC ceramic increases as reaction time is lengthened. The resulting SiC ceramic consists of β-SiC with a small amount of α-SiC. The conversion from pine charcoal to porous SiC ceramic with hybrid pore structure improves bending strength from 16.4 to 42.2 MPa, and decreases porosity from 76.1% to 48.3%.

Keywords: Wood; Sol–gel process; SiC; Porosity

1. Introduction

Biomorphic porous ceramics prepared from wood is a novel kind of porous ceramics, is comprised of elongated tubular cells with diameter of some to hundreds micrometers aligned with the axis of tree trunk, and cannot be prepared by the traditional technologies for fabricating porous ceramics. Up to now, the technologies for preparing ceramic materials from wood include molten silicon infiltration,[1] reactive infiltration of Si contained vapors,[2] infiltration-pyrolysis of metallic alkoxide,[3] polymeric precursors,[4] sol–gel/carbothermal reduction method,[5] and infiltrating ceramic/oxidation method,[6] etc. However, either porosity or strength of the products prepared by the above-mentioned methods is not satisfying. Among them, the sol–gel/carbothermal reduction method has some advantages such as low cost, easy procedure, and allowing lower temperatures of synthesis and high pure resultant, and can retain the structure and morphology of starting carbonaceous materials very well.[7,8] The corresponding resultants are usually single-phase carbide ceramics with high porosity, and possess poorer mechanical properties because the reaction to form SiC consumes partial carbonaceous pore struts in charcoal.

To obtain highly porous SiC ceramic with desirable high strength, in the present paper, a new processing is designed, namely, phenolic resin/SiO_2 sol mixture is used to substitute traditional oxide impregnants (SiO_2 or TiO_2 sols). Phenolic resin/SiO_2 sol mixture was infiltrated into pine-derived charcoal by vacuum/pressure impregnation process, forming phenolic resin/SiO_2 gel/charcoal composite after gelling and drying. The phenolic resin/SiO_2 gel/charcoal composite is converted into porous SiC ceramic via carbonizing in vacuum and carbothermal reduction reaction in Ar atmosphere at high temperatures, which not only retains the tubular pore

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structure and strut thickness of pine charcoal very well, but also possesses network SiC struts formed in the tubular pores. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM) were employed to characterize the phase identification and microstructural changes during the carbothermal reduction reaction.

2. Experimental procedure

2.1. Material preparation

Dried pine wood was shaped, and subsequently carbonized at 1200 °C for 4 h in vacuum in a graphite heater furnace with low heating ramp of ≤5 °C/min, resulting in a porous biocarbon template (charcoal). Silica sol was prepared from tetraethoxysilane [$Si(OC_2H_5)_4$, TEOS] purchased from Xi'an Chemical Reagent Co. (Xi'an, China) by the same sol–gel process as that described elsewhere.[5] In the present work, the concentration of silica sol was equal to 20% by weight. The solid content and viscosity of resol phenolic resin (101#, Xi'an Resin Co., Xi'an, China) are 80% and 2.5 Pa s (25 °C), respectively. Phenolic resin before being mixed with silica sol is diluted by water, and its viscosity is tested by a rotating viscometer (NDJ-1, Shanghai Balance Co., Shanghai, China). The TGA curve of phenolic resin was studied in our another paper.[9]

Charcoal was placed in an infiltration vessel. The vessel was evacuated and held for 3 h, and then backfilled with phenolic resin/silica sol mixture with a weight ratio of 1:5, following by raising the pressure in the vessel to a high atmosphere pressure of 1.5 MPa with 6 h hold. Then, the silica sol/phenolic resin mixture contained in charcoal was gelled and cured at 120 °C for 8 h, resulting in phenolic resin/silica/charcoal composite. The treatment process was repeated several times to increase the phenolic resin and silica contents in the composite.

Carbothermal reduction reaction of the above-mentioned composites was carried out in Ar atmosphere in a graphite heater furnace at 1200–1600 °C for 1–4 h to form porous SiC ceramic with hybrid pore structure. Fig. 1 summarizes the processing scheme.

2.2. Characterization

The morphological changes of the starting materials during the carbon/silica composite material-to-porous SiC ceramic conversion were observed and analyzed by scanning electron microscopy (SEM, Hitachi, S-2700) operated at 20 kV and 20 mA. X-ray diffraction (XRD) was measured on a D/MAX-RA X-ray diffractometer to determine the crystalline phases formed during carbothermal reduction reaction, using nickel filtered Cu Kα radiation produced at 35 kV and 20 mA. Fourier transform infrared spectroscopy (FT-IR) studies were performed with a Fourier transform infrared spectrometer (AVATAR 360 FT-IR, Nicolet) in the wavenumber range of 4000–400 cm^{-1}.

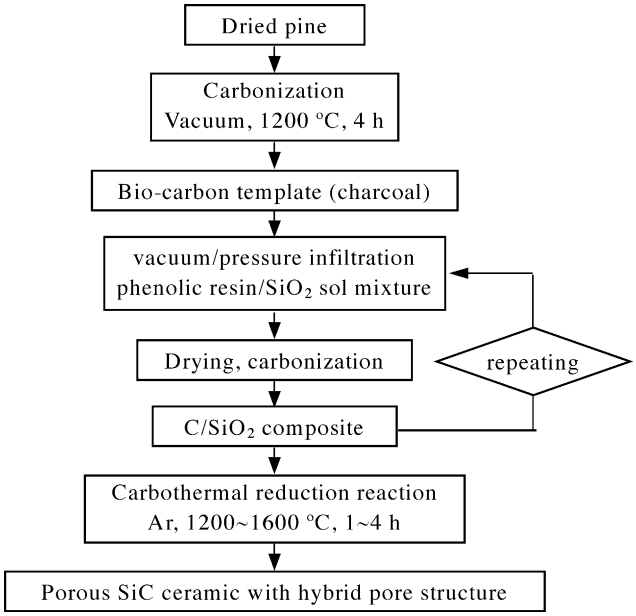

Fig. 1. Processing scheme of manufacturing SiC ceramic with hybrid pore structure from pine by carbothermal reduction reaction.

The samples' density and porosity was measured by water displacement method based on the Archimedean principle. Three-point bending strength was measured with a SANS-CMT 5104A universal testing machine using a span of 20 mm and a crosshead speed of 0.5 mm/min. The dimensions of the rectangular bar samples were about 4 mm × 5 mm × 30 mm.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of charcoal and the products obtained from C/SiO_2 composites by sintering at different temperatures for 4 h are shown in Fig. 2. It can be seen from Fig. 2a that the two broad peaks centered at around 25° and 44° are corresponding to (0 0 2) and (0 0 4) peaks of carbon,[10] indicating that charcoal is amorphous. After C/SiO_2 composite was heated at 1200 °C (Fig. 2b), no diffraction peaks due to SiC phase appear, but many peaks for cristobalite are observed. At the same time, the high baseline suggests that much amorphous carbon and SiO_2 exit. In the XRD pattern of the products prepared at 1400 °C (Fig. 2c), the peaks for β-SiC phases at $2\theta = 35.34°$ ($d = 0.254$ nm) are observed together with the peaks for amorphous carbon and cristobalite, indicating that the carbothermal reduction reaction to form SiC occurred. However, in the XRD pattern of the products obtained at 1600 °C (Fig. 2d), the peaks due to amorphous carbon and cristobalite nearly completely disappear, and only the peaks for major phase β-SiC and second phase α-SiC exit. The results reported in literature also show that preparing SiC

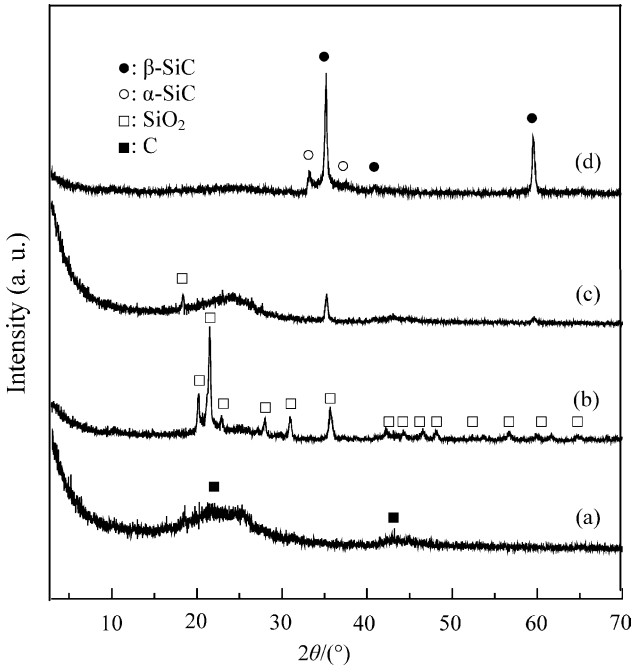

Fig. 2. Powder XRD patterns of (a) charcoal and the products obtained from C/SiO_2 composites at (b) 1200 °C, (c) 1400 °C and (d) 1600 °C for 4 h.

by carbothermal reduction reaction usually produces a minor amount of α-SiC.[7,11]

3.2. FT-IR analysis

Fig. 3 shows the FT-IR spectra of C/SiO_2 composite and its corresponding products obtained at different temperatures for 2 h. In the FT-IR spectrum of C/SiO_2 composite (Fig. 3a), the absorption peak at 3440 cm^{-1} is attributed to stretching vibrations of Si–OH bond in SiO_2 gel and O–H bond in absorbed water.[12] The absorption bands at 3000–2800 and 1600 cm^{-1} are ascribed to C–H structure and C=C bond and its conjugation in charcoal,[13] respectively. The peaks at 1090, 800 and 460 cm^{-1} are ascribed to antisymmetric and symmetric stretching vibrations of Si–O–Si and Si–OH bonds.[14] The peak of Si–O bond at 1090 cm^{-1} may shield the peaks attributed to antisymmetric stretching vibrations of C–O–C bond, C–C in-plane stretching vibration of condensed nuclear hydrocarbon, or the peak of C–H bond in charcoal.[15] The distinguished behavior of individual C=O bands (at 1710 and 1740 cm^{-1}) for wood does not appear in the spectra. When the C/SiO_2 composite was sintered at 1200 °C, the above-mentioned peaks significantly decrease or disappear except the peaks ascribed to Si–O–Si bond, and no new absorption peaks appear, indicating that condensation reaction in SiO_2 sol is completed after sintering, but carbothermal reduction reaction still does not start. In the FT-IR spectrum of the products fabricated at 1400 °C (Fig. 3c), the intensity of peaks ascribed to Si–O bond decrease, the peak due to C=C bond in charcoal disappears, and two new peaks at 825 and 950 cm^{-1} appear, which are ascribed to the Si–C fundamental stretching vibration,[16] indicating that carbothermal reduction reaction occurred. In the FT-IR spectrum of the products fabricated at 1600 °C (Fig. 3d), the peaks assigned to Si–O bond become very small, and nearly only the peaks ascribed to Si–C bond exist, suggesting that carbothermal reduction reaction is nearly completed.

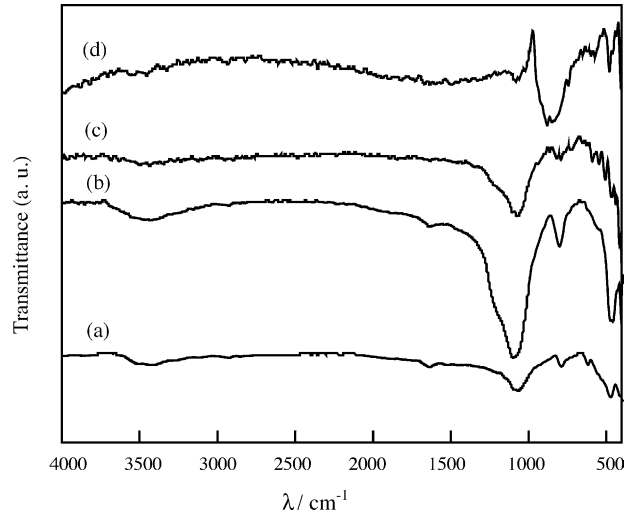

Fig. 3. FT-IR spectra of (a) C/SiO_2 composite and resulting products prepared at (b) 1200 °C, (c) 1400 °C and (d) 1600 °C for 2 h.

3.3. SEM analysis

The SEM micrographs of pine-derived charcoal and C/SiO_2 composite are shown in Fig. 4. As shown in Fig. 4a, the microstructure of pine charcoal shows hollow channels of nearly same diameter that originate from tracheid cells parallel to the axis of tree. The average diameter of the cells was 20 μm. Most of the cellular pores show a round or elliptic shape.

After pine charcoal is impregnated with phenolic resin/SiO_2 sol mixture, and subsequent gelling, curing and carbonization for several times, the tubular pores in charcoal are filled with SiO_2 and carbon from phenolic resin. When the above treatment processing is repeated two times (Fig. 4c), carbon/SiO_2 composite only distributes in the partial tubular pores of charcoal, existing in form of tube or rod. The tubular pores are completely and uniformly filled up with carbon/SiO_2 composite when the treatment processing is repeated six times (Fig. 4d).

Silica content in C/SiO_2 composite may be controlled by the number of treatment processing. The relationship between the density of C/SiO_2 composite and the number of treatment processing is shown in Fig. 5. It can be seen that the density of pine charcoal is 0.32 g cm^{-3}, and the density of C/SiO_2 composite quickly increases as the number of impregnation procedure increases. The density of C/SiO_2 composite increases to 1.46 g cm^{-3} after the fifth impregnation, subsequently tardily increases owing to high viscosity of phenolic resin/SiO_2 sol mixture and the "bottle-neck" effect of the

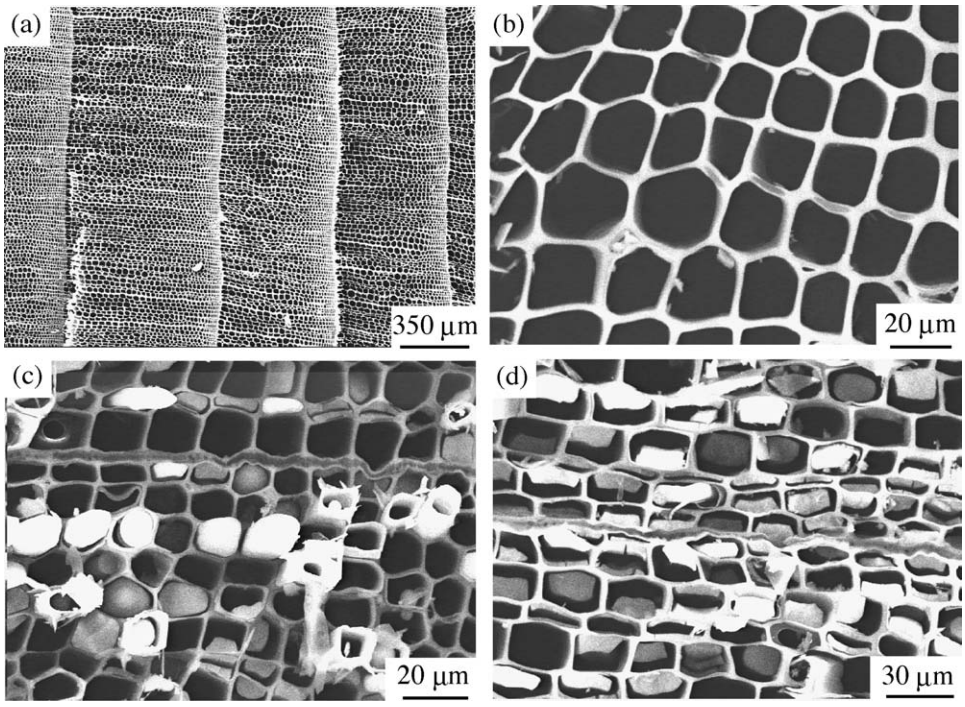

Fig. 4. SEM micrographs of (a and b) pine charcoal and C/SiO_2 composites obtained by heating pine charcoal impregnated with phenolic resin/SiO_2 mixture (c) two times and (d) six times at 1000 °C for 4 h.

tubular pores, and finally becomes nearly constant after the impregnation procedure is repeated six times.

Fig. 6 shows the SEM micrographs of porous SiC ceramics prepared from pine charcoal impregnated with SiO_2 sol and phenolic resin/SiO_2 sol mixture by carbothermal reduction reaction at 1600 °C for 4 h. It is seen that porous SiC ceramic prepared from pine charcoal impregnated with SiO_2 sol is of a microstructure pseudomorphous to pine charcoal, and its tubular pore walls are composed of SiC particles with typical diameter of less than 2 μm. But the tubular pore walls are much thinner than those of pine charcoal, and possess lots of pores with hundreds nm and some micrometers in diameter (Fig. 6a). However, porous SiC ceramic prepared from pine charcoal impregnated with phenolic resin/SiO_2 sol mixture not only retains the same tubular pore microstructure and pore wall thickness as pine charcoal, but also possesses SiC foams formed in the tubular pores (Fig. 6b). For the latter porous SiC ceramic, the tubular pore walls and the struts of the SiC foams in the tubular pores are composed of SiC particles, and are dense (Fig. 6c). The microstructure may significantly improve the mechanical properties of the resulting porous SiC ceramic with hybrid pore structure. A schematic model for forming mechanism of porous SiC ceramic with hybrid pore structure is given in Fig. 7, giving an example with a tubular pore.

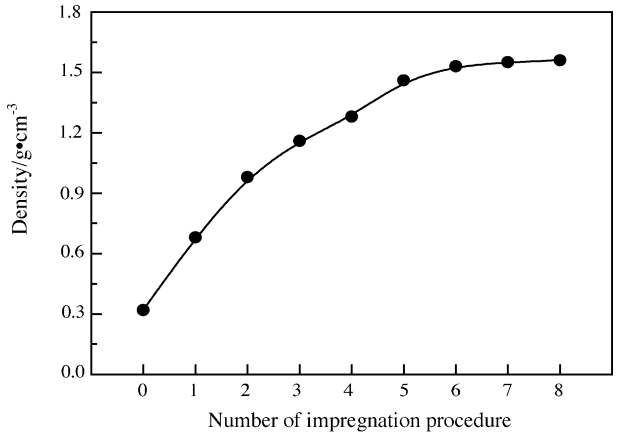

Fig. 5. Relationship between density of C/SiO_2 composite and number of impregnation procedure.

3.4. Bending strength and porosity of porous SiC ceramic with hybrid pore structure

The bending strength and porosity of porous SiC with hybrid pore structure prepared from pine by carbothermal reduction reaction strongly depend on the number of impregnation procedure, as shown in Fig. 8. As can be seen, the bending strength and porosity of pine charcoal are 16.4 MPa and 76.1%, respectively. After two impregnation procedures, the bending strength and porosity of the resulting porous SiC ceramic are 24.7 MPa and 63.2%, respectively. Compared with pine charcoal, bending strength increases, and porosity decreases, because carbonaceous tubular pore struts of charcoal were converted into SiC struts and new SiC foams formed in the tubular pores, respectively. Bending strength further increases, and porosity continues to decrease as the number

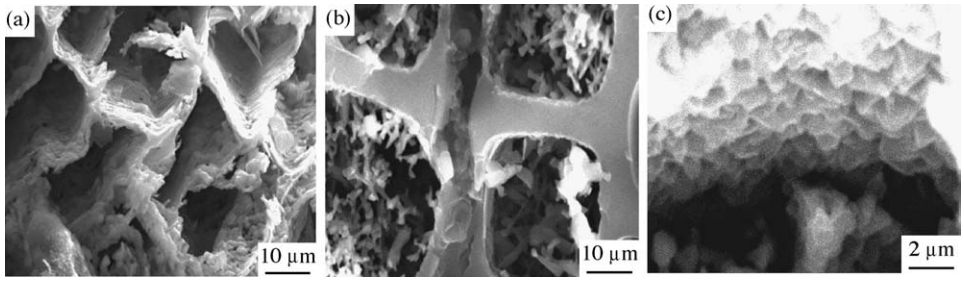

Fig. 6. SEM micrographs of porous SiC ceramics prepared from pine charcoal impregnated with (a) SiO_2 sol and (b) phenolic resin/SiO_2 sol mixture. (c) A high-magnification SEM image of a typical pore in (b).

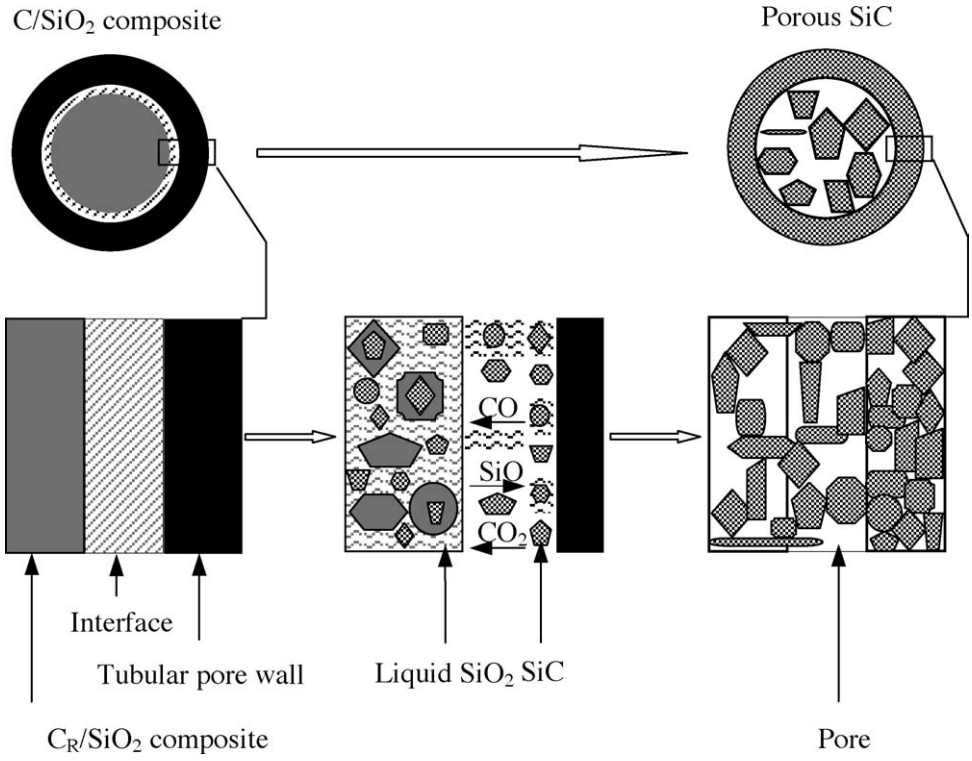

Fig. 7. A schematic model for forming mechanism of porous SiC ceramic with hybrid pore structure. C_R represents carbon from phenolic resin.

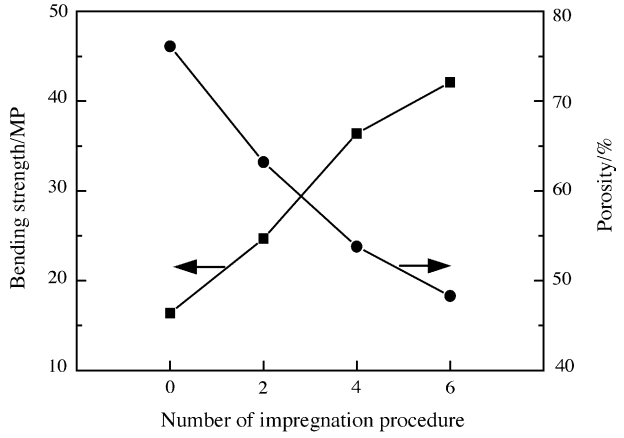

Fig. 8. Effects of number of impregnation procedure on bending strength and porosity of the resulting porous SiC ceramic with hybrid pore structure sintering at 1600 °C for 4 h.

of impregnation procedure increases. The bending strength of porous SiC ceramic with hybrid pore structure reaches 42.2 MPa, and its porosity decreases to 48.3% after the impregnation procedure is repeated six times. The conversion of charcoal to porous SiC ceramic with hybrid pore structure improves bending strength two to three times, and reduces porosity 27.8%. The bending strength of porous SiC ceramic with hybrid pore structure fabricated in this research is much higher than that (<2 MPa) of biomorphic porous SiC ceramic from beech by carbothermal reduction,[17] and the porosity is comparable. The main reason for the above-mentioned results is the formation of hybrid pore structure. In addition, In the case of infiltrating charcoal with SiO_2 sol, carbon needed for carbothermal reduction reaction only comes from the tubular pore walls in charcoal, which results in the volatilization of nearly two-thirds of the carbon mass of charcoal and makes tubular pore walls become thin and high porosity, lead-

ing to poor mechanical property. However, in the infiltrating charcoal with phenolic resin/SiO_2 sol mixture case, carbon needed for carbothermal reduction reaction comes from both the tubular pore walls of charcoal and phenolic resin-derived carbon in the tubular pores, and then there is not observable effect on the thickness of tubular pore walls in the resulting porous SiC ceramic.

4. Conclusions

1. Porous SiC ceramic with hybrid pore structure was fabricated by carbonizing and sintering phenolic resin/charcoal/SiO_2 composites at high temperatures, which were prepared by infiltrating phenolic resin/SiO_2 sol mixture into pine charcoal via vacuum/pressure impregnation procedure. The resulting porous SiC ceramic is composed of major crystal phases β-SiC with a small amount of α-SiC.
2. The density of C/SiO_2 composite increases with the number of impregnation procedure, and increases from 0.32 g cm^{-3} for pine charcoal to 1.5 g cm^{-3} after the sixth impregnation.
3. The conversion from pine charcoal to porous SiC ceramic with hybrid pore structure improves bending strength from 16.4 to 42.2 MPa, and reduces porosity from 76.1% to 48.3%.

Acknowledgements

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