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Microstructure evolution process of porous silicon carbide ceramics prepared through coat-mix method

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Abstract

Porous silicon carbide ceramics were prepared through the coat-mix method and molding, carbonization and sintering process with silicon powders and phenolic resin as raw materials. The crystalline phase, microstructure, and porosity of samples treated at different stages were characterized. Results showed that the fabricated porous silicon carbide ceramics consist of pure β-SiC phase with a homogeneous structure and porosity of above 60%. Each of the processing stages, including coat-mix, molding, carbonization, and sintering, has certain contribution to the porosity of the final porous silicon carbide ceramics, in which the mole ratio of resin carbon to silicon and the molding temperature are the main factors to affect the porosity. A porosity evolution process of porous silicon carbide ceramics during fabrication process was also proposed.

Keywords: B. Porosity; Porous; Silicon carbide ceramic; Evolution process

1. Introduction

Due to a set of attractive properties, including low density, controllable porosity, large surface area, favorable permeability, high abrasion resistance, good chemical resistance, high temperature stability, low thermal expansion coefficient, high thermal shock resistance, etc. [1–3], porous silicon carbide ceramics have been widely used as filters, membranes, heat exchangers, thermal insulators, sound-absorbing materials, damping buffers, and catalyst carriers, etc. [4–6]. Many synthesis routes have been proposed for the fabrication of porous silicon carbide ceramics, including in situ reaction synthesis [7], oxidation-bonding technique [8], impregnating silicon carbide slurry into polyurethane sponge [9], gel casting process [10], chemical vapor infiltration reaction [11], coat-mix method [12], and so on. Compared with other methods, the coat-mix process combines low sintering temperature, cost-effectively, simplicity, and high output with high quality of the final products. In our previous works [13–17], the coat-mix method was developed to fabricate porous ceramics with highly pure β-SiC crystal phase, narrow pore distribution, low density, large surface area, good high temperature strength, low thermal expansion coefficient, and high thermal shock resistance, etc. The focus of present study was to investigate the crystalline phase, microstructure and porosity of porous silicon carbide ceramics prepared through coat-mix method. The microstructure evolution process of porous silicon carbide ceramics at different processing stages was also addressed.

2. Experimental

2.1. Fabrication of the porous silicon carbide ceramics

The fabrication route consists of four steps: preparation of coat-mix powder precursor with silicon powder and phenolic resin, fabrication of green compacts by heat molding, carbonization and sintering. The batches and manufacture parameters of porous silicon carbide ceramics are listed in Table 1. In a typical process, the powder precursor was prepared by coating each silicon particle with a phenolic resin envelope. Analytical ethanol was used as solvent and de-ionized water as preceptor. Then the porous silicon carbide ceramics were prepared through molding, carbonization, and sintering the coat-mix powder precursor.

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Table 1
Setup of manufacture parameters of porous silicon carbide ceramics.

Sample no.	Molar ratio of resin carbon to silicon	Molding pressure (MPa)	Molding temperature (°C)	Molding time (h)	Sintering temperature (°C)	Sintering time (h)
1	0.75	5	120	1.5	1550	1.5
2	1	7.5	160	1.5	1650	1.5
3	1.25	10	200	1.5	1750	1.5

2.2. Characterization of the porous silicon carbide ceramics

The crystalline phase of the obtained porous silicon carbide ceramics was characterized by X-ray diffraction (D/max-IIIA). The fracture surface of the fabricated porous ceramics was investigated by a scanning electron microscopy (SEM, S-3000N). The relative density and porosity of the fabricated samples were determined by Archmede's method. The theoretical density of fully densified ceramics (3.21 g/cm^3) was used as a reference to calculate the relative porosity. The pore size distribution of the porous silicon carbide ceramics was measured by mercury intrusion porosimeter (AutoPore IV 9510, Micromeritics). The residual free carbon content was investigated by a thermogravimetric/differential thermal analyzer (TG–DTA, EXSTAR6000).

3. Results and discussion

3.1. Crystalline phase of porous ceramics after different processing phases

Samples of porous silicon carbide ceramics were prepared through molding, carbonization, and sintering the coat-mix powder precursor. The typical X-ray diffraction curves of sample 2 after each treating phase are given in Fig. 1. It is shown that the green compact before carbonization and sintering is composed of silicon crystalline phase. The crystalline phase of sample after carbonization at 800 °C is also mainly silicon phase. There exists a broad diffraction peak at 2θ from 12° to 23°, which is ascribed to amorphous carbon formed by the decomposition of phenolic resin in inert atmosphere. It also can be found that there is no diffraction peak of β-silicon carbide in the sample that goes through heat treatment at 800 °C, which indicates that the reaction between carbon and silicon did not take place under this condition. After being sintered at 1650 °C, there exist five diffraction peaks of 2θ at 36°, 41°, 60°, 72° and 76°, as shown in Fig. 1(c), which are ascribed to crystalline planes (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) of β-silicon carbide. No other diffraction peaks appear in the XRD curve, which indicates that silicon and carbon reacted completely and produced pure β-silicon carbide. Considering both the molar ratio of carbon to silicon in reactant and the stoichiometric ratio of carbon to silicon in silicon carbide is 1:1, it can be concluded that all of the carbon in raw materials reacted with silicon and produced silicon carbide. There exist some small diffraction peaks before 2θ of 34° in Fig. 1(c), which are ascribed to the crystal defects such as stacking fault during the production of β-silicon carbide [18–21].

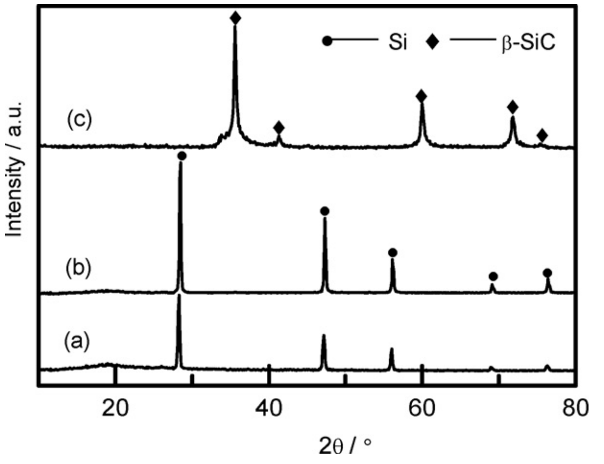

Fig. 1. XRD curves of sample 2 treated after different phases: (a) molding; (b) carbonization; and (c) sintering.

3.2. Microstructure of porous ceramics after different processing phases

Fig. 2 shows the profile microstructure of a green compact molded at pressure of 7.5 MPa, temperature of 160 °C, and time of 1.5 h. It is shown that the green compact has no obvious holes, and the porosity is low. Main reasons are listed as follows: (1) the powder precursor prepared through the coat-mix method has core–shell structure with silicon powder as the core and phenolic resin as the shell. This type of structure provides good fluidity for the powder precursor while being pressed at molding stage; therefore, the inner stress of the green compact could be reduced, causing a relatively low molding

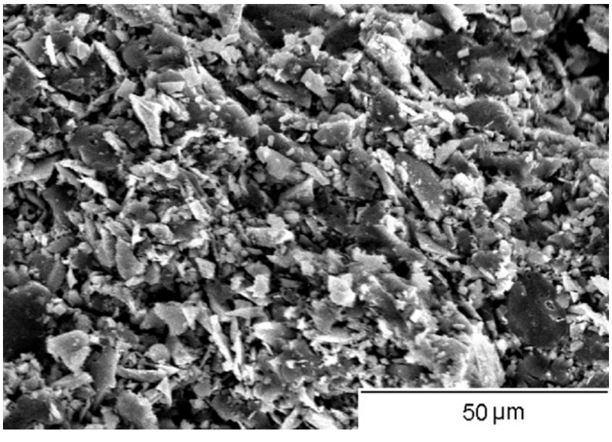

Fig. 2. Profile microstructure of sample 2 after molding process.

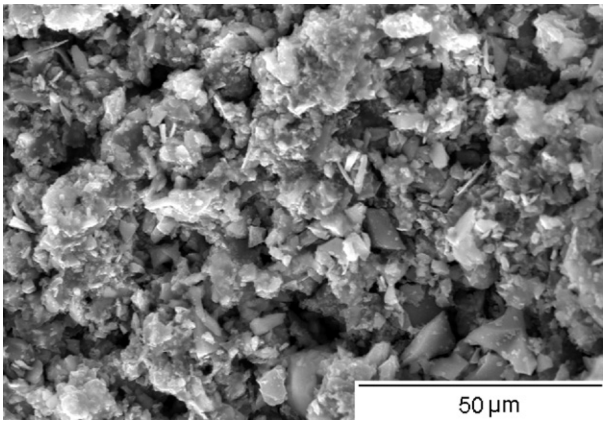

Fig. 3. Profile microstructure of sample 2 after carbonization at 7.5 Mpa, 800 °C.

pressure and relatively low porosity at the same time and (2) phenolic resin will be softened during molding, partly filling in the holes formed with the accumulation of the powdery precursor. Therefore, the molding pressure is reduced and high compactness of the material is obtained.

The profile microstructure of sample 2 after the carbonization process at 7.5 Mpa, 800 °C is shown in Fig. 3. Compared with compact sample (Fig. 2), sample 2 after the carbonization process has very different microstructure. The porosity significantly increases and a sharp decrease of density could be detected on the macro-level. This change is mainly ascribed to the decomposition of resin and the release of the gas mixture generated in the reaction.

Fig. 4 is the profile microstructure of sample 2 after sintering at 1650 °C for 1.5 h. Compared with Fig. 2, it is evident that the microstructure of this sample is remarkably changed. The porous silicon carbide ceramics formed after sintering have a uniform microstructure. The pores have an average diameter of approximately 5 μm, distributing in a very narrow range, and they connect with each other, making up a construction of interpenetration. It can be estimated that the walls of pores are dense with their thickness to be about 1 μm, and this microscopic framework may result in certain strength on macro level, which is a considerable factor for the porous silicon carbide ceramics to be extensively employed in industry. The density of porous silicon carbide ceramics bulk decreases significantly and the porosity increases concomitantly.

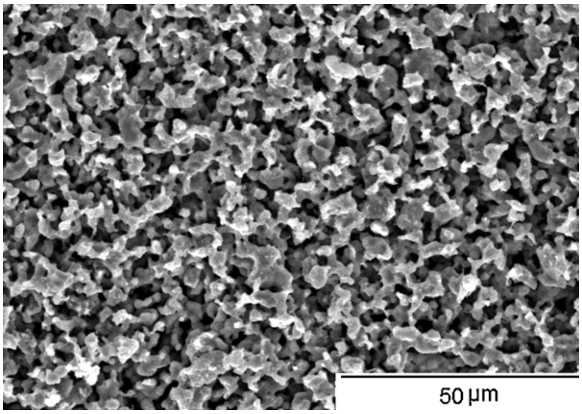

Fig. 4. Profile microstructure of sample 2 after sintering at 1650 °C for 1.5 h.

3.3. Porosity of porous ceramics after different processing phases

As mentioned above, the preparation process of porous silicon carbide ceramics by silicon powder/barium-phenolic resin precursor with core–shell structure mainly involves the following phases: molding, carbonization, and sintering. The porosity of porous silicon carbide ceramics versus different processing phases is shown in Fig. 5. Results show that all of the processing phases contribute the porosity of final porous silicon carbide ceramics and the porosity of porous silicon carbide ceramic increases after the treatment process of molding, carbonization, and sintering.

3.3.1. Molding process

It is indicated in Fig. 5 that pores exited originally in the body of the green compacts after molding, while the porosity is relatively low: sample 1 (5.67%) > sample 2 (4.16%) > sample 3 (3.52%). The formation of these pores is ascribed to the accumulation of powder precursor during molding process. The increase of porosity, as well as the decrease of density from sample 3 to sample 1 is due to the increase of molding pressure, molding temperature and molding time, though the change is small compared with the ones between two stages of the whole process. The core–shell structure of silicon/barium phenolic resin powder precursor prepared through coat-mix method has good liquidity and dispersive characteristics at chosen temperature, therefore, relatively dense compact could be prepared at lower molding pressure.

3.3.2. Carbonization process

The porosities of sample 1, sample 2 and sample 3 after the carbonization process are 16.42%, 28.78%, and 25.46%, respectively. Compared with the green compacts, the porosities

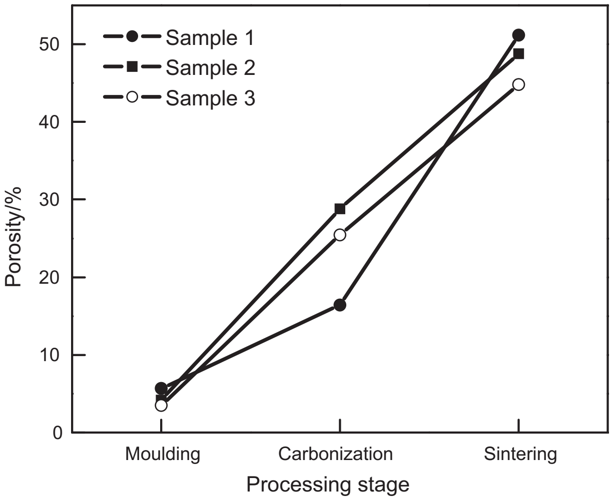

Fig. 5. The porosity of porous silicon carbide ceramics versus different processing.

of samples after carbonization increased obviously. During the carbonization process in an inert atmosphere at 800 °C, the barium phenolic resin decomposed to resin carbon and a gas mixture, leaving a large amount of pores. It is inferred that the porosity goes up with the increase of mole ratio of barium phenolic resin to silicon in the powder precursor.

3.3.3. Sintering process

The porosities of sample 1, sample 2 and sample 3 after the sintering process are 51.16%, 48.82%, and 44.78%, respectively. During the sintering process, hyperthermal liquid silicon can infiltrate the micropores of porous resin carbon, driven by capillary force, and the generation of silicon carbide is a process with a reduction in total volume [22–25]. As listed in Table 2, the theoretical density of resin carbon, silicon, and silicon carbide are 2.26 g cm^{-3}, 2.33 g cm^{-3}, and 3.21 g cm^{-3}, respectively. The molar mass of resin carbon, silicon, and silicon carbide are 12 g mol^{-1}, 28 g mol^{-1}, and 40 g mol^{-1}, respectively. The theoretical molar volumes of resin, silicon, and silicon carbide are 5.3 cm^3 mol^{-1}, 12.1 cm^3 mol^{-1}, and 12.5 cm^3 mol^{-1}, respectively.

The stoichiometry of carbon reacting with silicon to generate silicon carbide is 1/1, and the total volume change caused when one unit molar of resin carbon reacts with one unit molar of silicon can be described as:

$$\Delta V = V_{\mathrm{Si}} + V_{\mathrm{C}} - V_{\mathrm{SiC}} \tag{1}$$

The total volume reduction fraction of this reaction should be calculated by Eq. (2):

$$\Delta P = \left(1 - \frac{V_{\mathrm{SiC}}}{V_{\mathrm{Si}} + V_{\mathrm{C}}}\right) \times 100\% = \frac{\Delta V}{V_{\mathrm{Si}} + V_{\mathrm{C}}} \times 100\% \tag{2}$$

According to Eq. (2), the total volume reduction fraction of one unit molar resin carbon reacts with one unit molar silicon to generate one molar silicon carbide is 28.2%. It is the main reason to make the porosity of porous silicon carbide ceramic further increase during the sintering process.

After the sintering process, the net porosity increase of sample 1, sample 2, and sample 3 are 34.74%, 20.04%, and 19.32%, respectively, and this disparity is due to the different resin carbon-to-silicon molar ratios of different ceramic samples.

If the molar ratio of resin carbon to silicon is *x*/1, the volume fraction of resin carbon and silicon in samples after the carbonization process are:

$$V_{\mathrm{C}} = (1 - V_1) \times \frac{5.3x}{12.1 + 5.3x} \tag{3}$$

$$V_{\mathrm{Si}} = (1 - V_1) \times \frac{12.1}{12.1 + 5.3x} \tag{4}$$

where, V_{C} and V_{Si} are the volume fraction of resin carbon and silicon in samples after the molding and carbonization process, respectively; V_1 is the porosity of samples after the molding and carbonization process.

Table 2
The physical chemical parameters of carbon, silicon, and silicon carbide.

Matter	Theoretical density (g cm^{-3})	Molar mass (g mol^{-1})	Molar volume (cm^3 mol^{-1})
Si	2.33	28	12.1
C	2.26	12	5.3
SiC	3.21	40	12.5

(1) When the molar ratio of resin carbon to silicon in samples equals to the stoichiometry of the silicon carbide reaction, *i.e.* $x = 1$, all resin carbon and silicon take part in the reaction and form silicon carbide during the sintering process. Therefore, for the porous silicon carbide ceramics production, the volumes fraction of resin, carbon, and silicon carbide are:

$$V_{\mathrm{C}} = 0 \tag{5}$$

$$V_{\mathrm{Si}} = 0 \tag{6}$$

$$V_{\mathrm{SiC}} = (1 - V_1) \times \frac{12.5}{12.1 + 5.3x} = 0.718(1 - V_1) \tag{7}$$

In which V_{SiC} is the volume fraction of ceramic samples after the sintering process. Because all the silicon of samples took part in the reaction, the sintering process did not change the porosity of samples, and the theoretic porosity porous silicon carbide ceramics can be calculated by Eq. (8).

$$P = 1 - 0.718(1 - V_1) \tag{8}$$

In which P is the porosity of ceramic samples after the sintering process. In Section 3.3.2, the porosity of sample 2 after molding and carbonization (V_l) is 28.78%, thereby, the theoretic porosity of sample 2 after the sintering process calculated by Eq. (8) is 48.86%, very close to the experimental value (48.82%).

(2) When the molar ratio of resin carbon to silicon in samples is less than the stoichiometry of the silicon carbide reaction, *i.e.* $x < 1$, all the resin carbon took part in the reaction and form silicon carbide during the sintering process, while excess silicon will remain in the last ceramic samples. Therefore, in the last prepared porous silicon carbide ceramics, the volume fractions of resin, carbon, and silicon carbide are:

$$V_{\mathrm{C}} = 0 \tag{9}$$

$$V_{\mathrm{Si}} = (1 - V_1) \times \frac{12.1(-x)}{12.1 + 5.3x} \tag{10}$$

$$V_{\mathrm{SiC}} = (1 - V_1) \times \frac{12.5x}{12.1 + 5.3x} \tag{11}$$

Based on the analysis above, when the molar ratio of resin carbon to silicon in the green compacts was less than the stoichiometry of the silicon carbide reaction, *i.e.* $x < 1$, all of resin carbon reacted and generated silicon carbide after the sintering process.

Besides, the survival excess silicon will degrade the performance of porous silicon carbide ceramics and

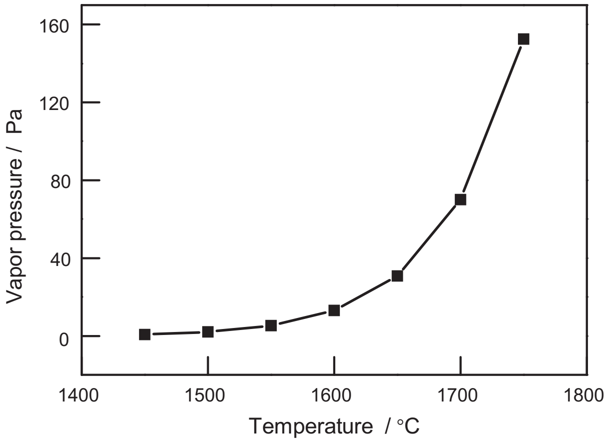

Fig. 6. The function curve of saturation vapor pressure of liquid silicon versus temperature.

influence their application in the fields with high temperature and other rigorous circumstances. The saturation vapor pressure of liquid silicon should be more than the vapor pressure of vacuum furnace so that all remain silicon could be removed. In this paper, the vapor pressure of vacuum furnace is chosen to be 0.5 Pa. The saturation vapor pressure of liquid silicon will increase rapidly with the increase of the sintering temperature, their mathematical relationship can be described by Eq. (12) [26].

$$\log P = \frac{-27404}{T} + 15.55 \tag{12}$$

According to Eq. (12), which is shown diagrammatically in Fig. 6, the saturation vapor pressures are 5.22 Pa, 30.81 Pa, and 152.65 Pa at temperature of 1550 °C, 1650 °C, and 1750 °C, respectively. It is indicated that all of the excess silicon can be removed successfully in the sintering process, and highly pure porous silicon carbide ceramic products could be obtained.

Therefore, when the molar ratio of resin carbon to silicon in the green compacts was less than the stoichiometry of the silicon carbide reaction, the theoretical porosity of porous silicon carbide ceramic after the sintering process can be calculated by Eq. (13).

$$P = 1 - (1 - V_1) \times \frac{12.5x}{12.1 + 5.3x} \tag{13}$$

The porosity of sample 1 after the molding and carbonization (V_l) is 16.42%, then the theoretic porosity of sample 1 after the sintering process calculated by Eq. (13) is 51.26%, very close to the experimental value (51.16%).

(3) When the molar ratio of resin carbon to silicon in samples is more than the stoichiometry of the silicon carbide reaction, *i.e.* $x > 1$, all silicon in the green compact take part in the reaction and form silicon carbide after the sintering process, while excess resin carbon will remain in the last ceramic samples. Therefore, in the last prepared porous silicon carbide ceramics, the volumes fraction of resin, carbon, and silicon carbide are:

$$V_{\mathrm{C}} = (1 - V_1) \times \frac{5.3(x-1)}{12.1 + 5.3x} \tag{14}$$

$$V_{\mathrm{Si}} = 0 \tag{15}$$

$$V_{\mathrm{SiC}} = (1 - V_1) \times \frac{12.5}{12.1 + 5.3x} \tag{16}$$

Part of resin carbon remained in samples after the sintering process. In this case, the theoretical porosity of porous silicon carbide ceramic after the sintering process can be calculated by Eq. (17).

$$P = 1 - (1 - V_1) \times \frac{5.3(x-1)}{12.1 + 5.3x} - (1 - V_1) \times \frac{12.5}{12.1 + 5.3x} \tag{17}$$

For sample 3 after the carbonation process, if the molar ratio of resin carbon to silicon and the porosity V_1 are introduced into Eq. (17), then the theoretical porosity of sample after the sintering process can be calculated to be 44.95%.

4. Conclusions

Porous silicon carbide ceramics were prepared through the coat-mix method and molding, carbonization and sintering process with silicon powders and phenolic resin as raw materials. Results showed that: (1) Powder precursor has core–shell structure, with silicon particle as the core and barium phenolic resin as the shell. Dense green compacts could be obtained at relatively low temperature. (2) Each processing stage makes certain contribution to the porosity of the final porous silicon carbide ceramic productions: at molding process, it is mainly due to the accumulation of powdery precursor; at carbonizing process, it is mainly due to the decomposition of calcium phenolic resin; and at sintering process, it is mainly due to the volume reduction in the silicon carbon reaction. (3) The mole ratio of resin carbon to silicon and molding parameters are the main factors to affect the porosity of porous silicon carbide ceramics.

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