Porous SiC Ceramics with Controllable Porosity Achieved by Micro-sized Powder through Recrystallization Sintering

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Abstract: Porous silicon carbide (SiC) ceramics with various porosity and pore size were successfully fabricated by adjusting the particle size and content of fine powder via recrystallization sintering process. The effects of the addition of fine powder with different particle size on the micromorphology of porous SiC ceramic and the flexural strength were investigated. With the increase of the fine powder content from 5wt% to 20 wt%, the porosity and pore size decrease, and the crystal grains gradually become larger and tend to round. The neck area among grains increases, leading to the improvement of flexural strength. The mechanism for promoting the sintering of porous SiC ceramics lies in the evaporation-condensation process of fine powder at high temperature. The finer particles are easier to be evaporated to promote the growth of coarse grain and the development of grain neck, so that the porosity and pore size were smaller, and the flexural strength was enhanced. At the addition of F4 powder of 20 wt%, the porous SiC ceramics with the porosity and MFP size of 39.1% and 1.38 μm respectively, and the flexural strength of 54.49MPa were obtained.

1. Introduction

Porous SiC ceramics have been widely applied in aerospace, energy, environmental protection and chemical industries due to their excellent advantages, such as high hardness, high thermal conductivity, low thermal expansion coefficient, good oxidation and corrosion resistance, and excellent mechanical properties [1-6]. Porous SiC ceramics are ideal materials for high-temperature gas filtration and dust removal, which play a critical role in the preparation of diesel vehicle exhaust particle traps [7,8]. However, this doesn’t only depend on the physical properties of porous SiC ceramics, but also takes into account the microstructure, such as porosity, pore size, and spatial framework structure [9]. Therefore, it is an urgent need but also a significant challenge to prepare porous SiC ceramics with controllable microstructure.

The pore structure, porosity and mechanical properties can be effectively modulated by the adjustment of the raw material particle size, the degree of roundness of the particles, the sintering temperature and sintering aids [10]. The B₄C additive can induce the conversion from 6H-SiC to 4H-SiC at high temperature, which promotes the formation of platelet crystal grains and increases the bending strength [11,12]. Li et al. [13] reported the porous SiC ceramics with high flexural strength (104.3 MPa) and high gas permeability (air permeability 4.6x10⁻¹⁴ m²) prepared by adjusting the particle size of SiC powders when Al₂O₃ and Y₂O₃ were added as sintering aids. Liu et al. [14] obtained porous SiC ceramics characterized by narrow pore size distribution, high porosity and high bending strength after spheroidizing the irregularly shaped raw materials. Simultaneously, the addition of pore formers, such as carbon black, graphite, starch, polyvinyl alcohol and oxides, is available for an effective control of the
pore size and porosity [15-17], but these additives will introduce impurity phases. High-purity porous SiC ceramics were fabricated by the addition of silicon nitride additive (Si$_3$N$_4$) [18,19]; Si$_3$N$_4$ decomposed to Si and N$_2$ at high temperatures, which increased the porosity and adjusted the pore size. In addition, pure porous silicon carbide ceramics with high porosity were fabricated through recrystallization sintering by using the evaporation-condensation process [20,21].

In this paper, porous SiC ceramics with different initial SiC particle sizes were prepared through recrystallization sintering. The effects of the initial SiC particle size on the porosity, pore size, phase composition, microstructure and flexural strength of porous SiC ceramics were investigated.

2. Experiment

Porous SiC ceramics were prepared by using SiC powders (purity>99.9 %; Pingdingshan Yicheng New Material Co., Ltd. Henan, China) with different initial particle sizes as raw materials and Polyvinylpyrrolidone (PVP; K-30; (C$_6$H$_9$NO)$_n$; purity≥99.9 %; Shanpu Chemical Co., Ltd., Shanghai, China) as the binder. Coarse powder (F1; 15.6 μm) and fine powder (F2, F3, F4) D$_{50}$ of 8.7 μm, 3.5 μm and 1.8 μm, respectively were added according to Tab. 1. The SiC powders were accurately weighed and milled in absolute ethanol for 4h at 200 rpm to obtain the homogeneous slurries which were then dried, ground, and dry pressed under 60 MPa to fabricate green bodies. The green bodies were subsequently sintered at 2300 ℃ for 2h under the protection of argon gas with high purity. Porous silicon carbide ceramics were obtained at the completion of the sintering process.

The porosity and average pore size were measured by using the Archimedes drainage method and capillary flow aperture analyzer (poroluxTM 500, Promet Co., Ltd. Germany), respectively. The phase analysis was performed by X-ray diffraction (XRD-6100, Shimadzu Corporation, Japan). And the microstructure and morphology were observed by using scanning electron microscope (SEM, SU-3500, Hitachi Limited, Japan). The flexural strength was characterized by using three-point bending method.

| Sample number | Fine powder content (wt %) | PVP (wt %) |
|---------------|---------------------------|------------|
|               | A (F2 / F1)               | B (F3 / F1) | C (F4 / F1) |               |
| 1             | 5                         | 5          | 5          | 1             |
| 2             | 10                        | 10         | 10         | 1             |
| 3             | 15                        | 15         | 15         | 1             |
| 4             | 20                        | 20         | 20         | 1             |

3. Results and discuss

3.1 Porosity and average pore size

Figure 1 shows the influence of fine powder content on porosity and average pore size. It is observed that the porosity and MFP size of the sintered samples decrease with the increase of the fine powder content from 5 wt% to 20 wt%. And the larger the particle size of the fine powder added (D$_{50}$ (F2) > D$_{50}$ (F3) > D$_{50}$ (F4), the larger the porosity and MFP size. The maximum porosity (44.5 %) and MFP size (1.57 μm) were obtained at the fine powder content of F2 of 5 wt%. On the contrary, in the case that F4 fine powder at 20 wt% was added, the porosity and MFP size were the minimum, i.e., 39.1% and 1.38 μm, respectively. Therefore, it is an effective way to regulate the porosity of porous SiC ceramics through adjusting the particle size and content of fine powder.

3.2 Phase composition

The XRD patterns of the porous SiC ceramics sintered at 2300 ℃ are displayed in Figure 2. Compared with the standard card PDF-# 72-0018, the phase composition of the sintered samples in the groups of
A, B and C are all in the 6H-SiC crystal form. The result indicates that the addition of F1, F2 and F3 fine powders did not change the phase composition of the samples during sintering because no phase transformation occurred. In addition, with the increase of the content of F1, F2 and F3 fine powders from 5 wt% to 20 wt%, the phase of porous SiC ceramic samples was still in the 6H-SiC crystal form, and no other impurity phases were prepared.

Figure 1 The influence of fine powder particle size and content on porosity (a) and MFP size (b).

Figure 2 XRD patterns of sintered samples with different formulations

3.3 The microstructure of porous SiC ceramics
Figure 3 exhibits the SEM images of the cross-section of the samples in Group C. Irregular grains were formed in the sample with the F4 fine powder content of 5 wt% [Figure 3(a)]. The size
distribution was uneven, and the average size of the coarse grains was about 16.2 μm. At the F4 fine powder content of 10 wt% [Figure 3(b)], the neck area among crystal grains increased, and the average size of the coarse grains was about 16.7 μm. At the F4 fine powder content of 15 wt% [Figure 3(c)], the increase of the neck area between the grains facilitates the tight connection of the grains, and the average grain size was about 18.3 μm. At the same time, in addition to the fracture of the sample in the neck between the coarse particles, the intergranular fracture also occurred inside the coarse particles. When the F4 fine powder content was 20 wt% [Figure 3(d)], the grains tended to be more round, the size of the coarse grains increased significantly, and the average size was about 20.3μm.

The cross-sectional SEM images of the three groups of samples with the fine powder content of 20 wt% are displayed in Figure 4. With the addition of fine powder of F2 [Figure 4(e)], irregular coarse grains and small grains with high sphericity coexisted in the sample, the average size of coarse grains and small grains was 15.8μm and 6.8μm, respectively. In the case of the fine powder of F3 [Figure 4(f)], a small amount of small grains existed in the sample, while the neck area between the coarse grains increased with the average size of about 19.1 μm. When the fine powder was F4 [Figure 4(g)], no small crystal grains existed in the sample, and the average size was about 20.3 μm. It can be seen from the results, the smaller the particle size of the fine powder, the easier it is to disappear, promoting the growth of coarse grains and the development of the neck between coarse grains.

**Figure 3** SEM images of the cross-section of samples in Group C (F4 / F1). Fine powder content (a, b, c, d; 5 %, 10 %, 15 %, 20 %)

**Figure 4** The cross-sections SEM images of the three groups of samples with 20 wt% fine powder content (e, F2 / F1; f, F3 / F1; g, F4 / F1)
3.4 The flexural strength of porous SiC samples

The flexural strength of the sintered samples is demonstrated in Figure 5 as a function of the starting particle size and the fine powder content. With the addition of F2 fine powder, the flexural strength slightly increased from 20.30 MPa to 28.69 MPa. By contrast, their flexural strength was enhanced by 2.2 times (from 24.26 MPa to 54.49 MPa) at the addition of F3 fine powder. And there was an increase of 1.5 times (from 36.16 MPa to 54.49 MPa) in flexural strength for the samples fabricated with F4 fine powder. Therefore, the maximum flexural strength (54.49 MPa) was obtained at the F4 fine powder content of 20 wt%. These results show that both the decrease in fine powder particle size and the increase in fine powder content in the formula contribute to the enhancement of the flexural strength of porous SiC ceramics.

![Figure 5](image)

**Figure 5** Relation diagram of flexural strength of samples with different formulations

3.5 The formation mechanism of SiC grain microstructures

Porous SiC ceramics was formed by recrystallization sintering at 2300 °C. Just as the interpretation of the complicated electroceramic grain spatial distribution via building the grain connection models about fractal nature analysis [22-24], herein, the sintering model about particles with different particle size [Figure 6] was created to analyze the evaporation-condensation process at high temperature. Figure 6 presents the formation mechanism of SiC grain microstructures. When the sample is fabricated with F2 fine powder [Figure 6(a) ~ Figure 6(b)], the bulges of large particles and fine particles with high surface energy at high temperature are evaporated preferentially to produce gaseous products (Si, Si2C, SiC2, etc.) [Figure 6(a)], resulting in the larger local vapor pressure. Driven by the vapor pressure difference, the gaseous products migrated to the necks among grains and the surface of the large particles to recrystallize, thereby forming SiC [Figure 6(b)] [25,26]. The formation of the sintered necks and the growth of coarse grains are promoted in porous SiC ceramics. The fine particles are more likely to evaporate, which makes the fine grains become round, resulting a size reduction of the fine grains. Therefore, there are some small crystal grains with high sphericity and coarse grains in the porous SiC ceramics. For the sintered samples with the addition of F3 or F4 fine powder, the formation mechanism of SiC grain morphologies is shown in Figure 6 (a) and Figure 6 (c). Compared with the F2 fine powder, the particle size of the F3 or F4 fine powders is smaller. The fine particles are almost completely evaporated to produce gaseous products at high temperature, leading to an increase
in the neck area of grains and the coarse grain size, which is consistent with the micromorphology shown in Figure 4. With the increase of the F3 or F4 fine powder content, the concomitant increase of gaseous products during sintering process promotes the development of the neck and the growth of grains, resulting in the tighter connections between grains and the reduction of porosity. However, it is conducive to the enhancement of flexural strength.

Figure 6 Schematic diagram of SiC grain growth mechanism

4. Conclusion
Recrystallized porous SiC ceramics with controllable porosity were fabricated at 2300 °C by regulating the fine powder particle size (F2, F3 or F4) and fine powder content. The effects of the addition of F2, F3 or F4 fine powder on microstructure and flexural strength were investigated. The conclusion is drawn as follows:

1) The addition of fine powder with a larger particle size (D_{50} (F2) > D_{50} (F3) > D_{50} (F4)) leads to higher porosity and larger average pore size of porous SiC ceramics. With the increase of the content of fine powders from 5 wt% to 20 wt%, the porosity and average pore size of porous SiC ceramics are reduced.

2) Although fine powders with different particle sizes and contents were added, the main crystal phase 6H-SiC of porous silicon carbide ceramics remained unchanged. The evaporation-condensation process of SiC powder led to the formation of microstructure. The increase of the addition of fine powders promoted the development of the necks and the growth of the grains, resulting in the larger neck area among grains and more rounded coarse grains. And the smaller the fine powder particle size, the easier to evaporate and recrystallize for the formation of SiC.

3) Both the decrease in fine powder particle size and the increase in fine powder content in the formula contribute to the enhancement of the flexural strength of porous SiC ceramics. With the addition of F4 fine powder of 20 wt%, the maximum value of flexural strength of 54.49 MPa was obtained.

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