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Original Research

Porous SiC ceramics fabricated by quick freeze casting and solid state sintering

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ABSTRACT

Porous SiC ceramics with uniform microstructure were fabricated by quick freezing in liquid nitrogen and solid state sintering. Poly (vinyl alcohol) (PVA) was added as binder and pore morphology controller in this work. The microstructure and mechanical properties of porous SiC ceramics could be controlled by the composition of the aqueous slurries. Both solid content of the slurries and PVA content impacted on the pore structures and mechanical properties of the porous SiC ceramics. The solid content of slurries and PVA content varied from 60 to 67.5 wt% and 2–6 wt%, respectively. Besides, the grain morphology of ceramics was also tailored by changing the sintering temperature from 2050 to 2150 °C. Porous SiC ceramics with an average porosity of 42.72%, flexural strength of 59.28 MPa were obtained at 2150 °C from 67.5 wt% slurries with 2 wt% PVA.

1. Introduction

The SiC ceramics and their composites possess wide ranges of applications, such as catalyst [1] supports, thermo-structural application [2] filters for hot gas or molten metal [3–5] and inorganic fillers [6,7] due to its excellent high temperature strength, chemical stability, and oxidation resistance [8,9]. Generally, the properties of porous ceramics strongly depend on the character of materials as well as the microstructures. The pore structure such as pore size, distribution and orientation can be controlled by the fabrication process. Thus, the fabrication method is of great importance in obtaining porous SiC ceramics with optimized properties.

Nowadays, a number of manufacturing techniques have been utilized for the production of porous SiC ceramics, such as reaction bonding method [10–13]; recrystallization method [14]; infiltration technique [15]; sol-gel and carbothermal reduction processing [16]; adding pore-forming agent [17] and the aqueous gelcasting method [18]. However, another widely-used method called freeze-drying, also known as lyophilization has been put forward to prepare porous SiC ceramics. When aqueous solutions are utilized, the ice crystals as pore-forming agent is environment-friendly and the remove process of the solvent will not bring impurities into the samples [19]. Moreover, the pore structure can be controlled by the freeze conditions [20].

However, the porous SiC ceramics manufactured through the freeze-casting generally underwent a freezing temperature of −10 to −70 °C [21,22], which led to the slow growth of ice crystals to large dimensions and also led to nonuniform distribution of pores. By the quick freezing, the ice crystals can be nucleated immediately and the sizes of ice crystals are controlled smaller. In addition, highly aligned pore structure can be achieved through this method. Porous SiC ceramics fabricated through quick freezing in liquid nitrogen and solid state sintering have rarely been reported yet. The comprehensive researches on this method will provide an attractive perspective on manufacturing porous SiC ceramics with homogenous pore structures and excellent mechanical properties.

In the present work, ice was used as mold and porogen for preparation of SiC ceramic green bodies with highly aligned pore structure. The extremely low temperature for quick freezing was provided by liquid nitrogen. The microstructures and performances of porous SiC ceramics were investigated as functions of solid content and PVA content. The solid state sintering was conducted at various temperatures to investigate the effect of temperature on the growth of SiC grains. The flexural strength, morphology, and porosity of porous SiC ceramics were characterized.

2. Experimental procedure

2.1. Starting materials

The starting powder was commercially available SiC powder (d_{50}=0.5 μm, α-phase, FCP15C, Sika Tech., Lillesand, Norway). B_4C powder (d_{50}=1.0 μm, Mudanjiang Jingangzuan Boron Carbide Co.,

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Ltd., China) and C powder (d_{50}=0.2 μm, Shanghai Coking & Chemical Development, Shanghai, China) were used as the sintering additives in the solid-state-sintering process. The weight percentages of C and B_4C powder based on the SiC powder were 2.5 wt% and 0.5 wt%, respectively. Tetramethylammonium hydroxide (TMAH, Taixing Haoshen Chemical Trading CO., Ltd., China) was used as dispersant agent, and the weight percent of TMAH based on the SiC powder was 0.6 wt%. Poly(vinyl alcohol) (PVA, Sinopharm Chemical Reagent Co., Ltd., China) was used as binder and pore morphology controller. The PVA was dissolved in deionized water to make a solution with concentration of 8 wt% at first. Polyethylene glycol (PEG400, Sinopharm Chemical Reagent Co., Ltd., China) and glycerol (Sinopharm Chemical Reagent Co., Ltd., China) was used as plasticizing agents. The weight percentages of PEG and glycerol based on the SiC powder were 5 wt% and 5 wt%.

2.2. Fabrication procedure

The SiC suspensions with initial solid contents of 60 wt, 62.5 wt%, 65 wt%, 67.5 wt% were prepared by mixing SiC powder with sintering additives and dispersant agent in the distilled water. The suspensions were ball-milled by planetary ball mill for 1 h at a rotation speed of 300 r/min. Further ball-milling in planetary ball mill for 2 h at the same speed was continued after adding plasticizing agents and poly(-vinyl alcohol) water solution to achieve homogenous slurries. The ratios of PVA to the SiC powder were fixed at 2 wt%, 4 wt%, and 6 wt%. The samples obtained from these slurries were named as showing in Table 1. Antifoaming agent would be used if bubbles were generated in the ball-milled process.

The homogenous slurries were poured into steel moulds with dimension of 50.0×50.0×50.0 mm^3. Then, the moulds with slurries were immersed into the liquid nitrogen for quick freezing. The frozen samples were obtained within about 2–5 min and were transferred to the lyophilizer (YB-FD-20D, Shanghai Yibei, Ltd., China) for 36 h to remove the ice crystals. The condensator temperature was −58 °C and the drying oven was 50 °C with a vacuum degree of 1 Pa. Before sintering, the freeze-dried green bodies were heated up in vacuum to 600 °C for 2 h to remove the organic additives. Finally, the samples were divided into three batches, which were sintered at 2050 °C, 2100 °C, and 2150 °C for 2 h in Ar atmosphere, respectively.

2.3. Characterization

The specimens were machined to a dimension of 3.0×4.0×36.0 mm^3 to test the flexural strength at room temperature via the three-point bending test (Model AUTOGRAPHAG-I, Shimadzu Co. Ltd., Japan) with a support distance of 30.0 mm and a cross-head speed of 0.5 mm min^{-1}. The open porosities of sintered SiC ceramics were measured by the Archimedes method. Pore size distributions were characterized by the mercury porosimetry (Model Pore Sizer 9320, Micromeritics, Norcross, GA, USA). Morphologies of the fracture surface of porous SiC ceramics were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Akishima, Japan).

Table 1
Compositions of studied samples come from different slurries.

Name	Initial solid content wt%	PVA content wt %	final solid content wt%
60S2P[a]	60	2	49.84
62.5S2P	62.5	2	51.55
65S2P	65	2	53.24
67.5S2P	67.5	2	54.91
67.5S4P	67.5	4	48.45
67.5S6P	67.5	6	43.35

[a] S denotes solid content and P denotes PVA.

3. Results and discussion

3.1. Effect of solid content on the properties of porous SiC ceramics

The pore structures in ceramics were replicated from the ice crystals. It was found that the pore channels became narrower as the solid content increased. Fig. 1 shows the microstructure of porous SiC ceramics sintered at 2050 °C with solid content increasing from 60 wt% to 67.5 wt%. The pores structure of SiC ceramics were generated during the freezing process through the growth of ice crystals. The SiC particles in the slurries are squeezed by the advancing ice fronts during the freezing process. The particles will be squeezed along with the solid/liquid interface until the compression force is countered by the force created by the particles concentration. The force from particles is the osmotic force from the osmotic pressure of the suspension, Π. The osmotic pressure in a well-dispersed suspension can be molded with a modified Carnahan-Starling equation [23,24].

$$\Pi(\Phi) = \frac{kT}{V_p}\left(\frac{\Phi(1 + \Phi + \Phi^2 - \Phi^3)}{(\Phi_m - \Phi)^3}\right)$$

where Φ_m is the volume fraction particles at maximum packing, Φ is the solid content of the suspension, k is Boltzmann's constant and V_p is the volume of a single particle.

Notice that the Π(Φ) will increase with Φ as the suspension becomes more concentrated. Further concentration is prevented as long as Φ reaches the value of Φ_m. In our work, the Φ is below the value of Φ_m that the osmotic pressure will increase with increasing the solid content. Thus the growth of ice crystals encounters more resistance as the higher concentrated SiC suspension. Noah O. Kiyosh et al. [25] have also proved that the sizes of the dendrite pores are inversely proportional to particle volume fraction in the suspension.

Fig. 1 shows the fracture surface of porous SiC ceramics sintered at 2050 °C with different solid contents. The micrographs were obtained by scanning electron microscopy. Pores were uniformly distributed on the fracture surface from different samples. With the increasing of the solid content in the slurries, the SiC ceramics proved to have lower porosity and smaller pore size, which contributed to the improvement in mechanical properties. Fig. 2 shows the porosity and flexural strength of porous SiC ceramics sintered at 2050 °C. With solid content increasing from 60 wt% to 67.5 wt%, the porosity decreased from 61.47% to 54.27% and the flexural strength increased from 18.1 MPa to 30.63 MPa.

3.2. Effect of PVA content on the properties of porous SiC ceramics

The addition of PVA water solution into the slurries affects the final solid content of the slurries and also changes the viscosity of the slurries. The viscosity of SiC ceramic slurries tend to decrease with the reduction of solid content. However, the results were different from the expectation. Although the final solid content of the slurries decreased with increasing PVA content, the viscosity of slurries increased. Fig. 3 shows the effect of PVA content on the viscosity of SiC slurries with the solid content of 67.5 wt%. The viscosity of 67.5 wt% SiC slurries increased with increasing PVA content from 2 wt% to 6 wt% due to the hydrodynamic coupling between free PVA molecules and SiC particles. High amount of PVA in the slurries should be avoided for the probable flocculation caused by the interaction between PVA molecules and SiC particles.

The flexural strength and porosity of porous SiC ceramics sintered at 2050 °C from 67.5 wt% slurries are presented in the Fig. 4. With increasing the PVA content from 2 wt% to 6 wt%, the porosity increased from 54.27% to 67.96% and flexural strength decreased from 30.63 MPa to 14.13 MPa. The PVA have two roles in the work. Firstly, PVA was used as binder to enhance mechanical properties of SiC green bodies. In addition, the PVA in the slurries was used to