



Effect of agarose content on microstructures and mechanical properties of porous silicon nitride ceramics produced by gelcasting*

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Abstract: Porous Si₃N₄ self-reinforce ceramics were prepared by gelcasting using agarose solutions. By changing the agarose content in the slurries, the porous silicon nitride ceramics with different porosities, $\alpha \rightarrow \beta$ -Si₃N₄ phase transformation, and mechanical properties were obtained. When the agarose content changed from 0.2% to 0.8% (w/w, based on powder), the porosities increased from 10.3% to 21.4%, while the fracture strength decreased from 455 to 316 MPa and the fracture toughness decreased from 6.6 to 5.5 MPa·m^{1/2}. Many fibrous β -Si₃N₄ grains grown from the internal wall of the round pores is the typical microstructure of the gelcasting porous silicon nitride ceramic. Both elongated β -Si₃N₄ grains and suitable interfacial bonding strength contributes to high fracture toughness by favoring crack deflection and bridging. The growth mechanisms of fibrous grains resulted from the synergy of solution-diffusion-precipitation and vapor-liquid-solid (VLS).

Key words: Porous Si₃N₄ ceramics, Gelcasting, Microstructure, Mechanical properties

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1 Introduction

Advanced porous ceramics with super porosity and large surface area were widely used as filters, bio-prosthetic implants, catalyst supports, and light-weight structural materials (Soltmann *et al.*, 2003; Shqau *et al.*, 2006). Silicon nitride has a high mechanical performance even with certain levels of porosity. Porous silicon nitride is a promising candidate because of its excellent mechanical and thermal-mechanical properties (Ohji, 2008; Bocanegra-Bernal and Matovic, 2010). A number of manufacturing techniques, namely adding a fugitive substance (Díaz and Hampshire, 2004), partial sintering using a less sintering aid (Kawai and Yamakawa, 1997; Yang *et al.*, 2003), and partial hot-pressing (Yang *et al.*, 2001), have been applied to the production of porous silicon

nitride ceramics. Gelcasting is a new ceramic forming technique getting world wide attention (Gilissen *et al.*, 2000). It is a suitable technique for the fabrication of porous or dense components. Gelcasting consists of the dispersion of a kind of ceramic powder in an aqueous solution containing a gelation substance to form a stable suspension which is subsequently solidified in the mold. After sintering, material with uniform microstructure can be obtained. The purpose of this paper is to fabricate porous Si₃N₄ self-reinforce ceramics by gelcasting using agarose as a gelation and fugitive additive. By adjusting the content of agarose, the sintered porous Si₃N₄ self-reinforce ceramics with different properties were obtained.

2 Experimental

As ceramic powder, a commercial Si₃N₄ (Junyu Ceramic Co., Ltd., Shanghai, China) with a mean particle size of 0.5 μ m was used. High purity powders of Y₂O₃ and Al₂O₃ (Sinopharm Chemical Reagent

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Co., Ltd., Shanghai, China) were used as sintering additives. The initial composition (w/w) consisted of 92% Si_3N_4 , 2% Al_2O_3 , and 6% Y_2O_3 . Agarose (Kermel Chemical Reagent Co., Ltd., Tianjin, China) was used as a gelation reagent which dissolves in water at temperature above 90 °C. When the temperature falls below 40 °C, the viscosity of the agarose solution sharply increases, and then the gelation network is formed.

Si_3N_4 powder and sintering additives were added into deionized water with a dispersant. The resulting slurry was then ball milled for 24 h, and the well dispersed suspensions were heated at 60 °C. The agarose solution was prepared by dissolving the as-received agarose powder in distilled water at 90 °C and subsequently maintained at 60 °C. Then, the required content of agarose solution was added to the ceramic slurry at this temperature. The total contents of agarose were 0.2%, 0.4%, and 0.8% (w/w) with regard to dry solids. The final solid load of these slurries was fixed at 40 % (v/v).

Porous Si_3N_4 green bodies were obtained by pouring the heated slurries into polyethylene molds ($\Phi 70 \text{ mm} \times 15 \text{ mm}$). Consolidation of the slurries occurred in a few seconds, after which the green bodies were demoulded and dried in air for about 96 h. The green bodies were sintered in a high temperature sintering furnace at 1800 °C for 1.5 h under a 0.1 MPa nitrogen atmosphere. The heating rate was 10 °C/min. To avoid the decomposition of silicon nitride at high temperature, a Si_3N_4 -based powder bed was used.

The weight and volume of the sintered bodies were used to determine the porosities of the sintered samples. The measurements of flexural strength and fracture toughness were performed at room temperature. All flexural bars were machined with the tensile surface perpendicular to the freezing direction. The dimension of the specimens used for flexural strength measurement was 3 mm \times 4 mm \times 36 mm. A three-point bend fixture was used for the strength measurement and the span was 30 mm. The fracture toughness of the specimens was investigated by single edge notch bending. The dimension of the specimens was 2 mm \times 4 mm \times 30 mm and the span was 16 mm.

X-ray diffraction (XRD) was used to analyze the phase constitution of the obtained porous Si_3N_4 ceramics. The phase content of α - Si_3N_4 and β - Si_3N_4

were calculated by comparing the peak intensity (Quander *et al.*, 1997). To observe the morphologies of β - Si_3N_4 grains, the sintered bodies were etched by molten NaOH. The microstructure of the cross section was observed by a scanning electron microscope (SEM). The β - Si_3N_4 grain width was measured using the SEM micrographs. About 600 grains were measured for every single kind of sample.

3 Results and discussion

The polished cross sections of the porous Si_3N_4 ceramics produced with 0.2%, 0.4%, and 0.8% (w/w) agarose are shown in Fig. 1. The images show that a large number of pores are formed in the samples and the walls of the pores are dense. With the increase of agarose content, the number of the pores increased and the isolated pores became interconnected.

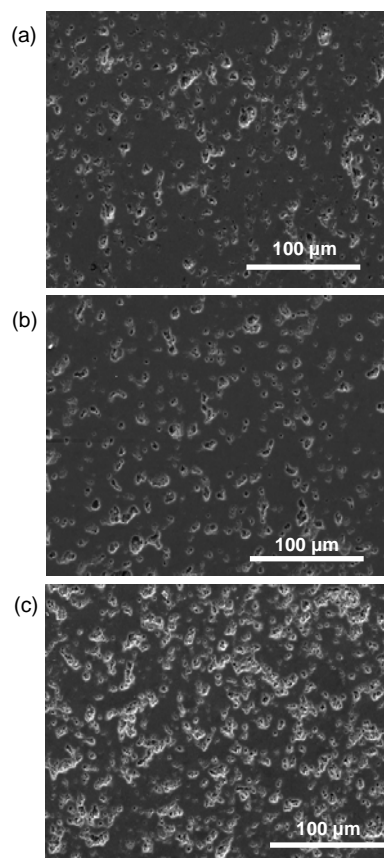


Fig. 1 Scanning electron microscope (SEM) cross-section micrographs of porous Si_3N_4 with different contents of agarose (w/w) (a) 0.2%; (b) 0.4%; (c) 0.8%

porosities of the samples are shown in Table 1. When increasing the agarose content from 0.2% to 0.8% (w/w), the porosity of the sample increases from 10.3% to 21.4%, indicating that the porosity is strongly affected by the agarose content.

Table 1 Properties of the porous Si_3N_4 with different content of agarose

Agarose (% w/w)	$\beta/(\alpha+\beta)$ (%)	Porosity (%)	Flexural strength (MPa)*	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)*
0.2	61.4	10.3	455 ± 6	6.6 ± 0.1
0.4	68.8	14.2	400 ± 7	5.8 ± 0.1
0.8	75.8	21.4	316 ± 9	5.5 ± 0.2

* Data are presented as mean \pm standard error

The XRD results show that all the investigated porous materials are composed of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$. The contents of $\beta\text{-Si}_3\text{N}_4$ phase were about 61.4%, 68.8%, and 75.8% for materials with agarose contents of 0.2%, 0.4%, and 0.8% (w/w), respectively, indicating that increasing agarose content would favor the $\alpha\rightarrow\beta\text{-Si}_3\text{N}_4$ transformation.

The typical microstructures of the obtained materials with different agarose contents are shown in Fig. 2. A few large grains are surrounded by small fibrous grains, which is the typical bimodal microstructure. Furthermore, the microstructure difference could be observed for the materials with different agarose contents. Fig. 3 shows the grain width distribution of the samples with different agarose contents, which reveals the microstructure differences. It exhibits an obvious increase in width of elongated $\beta\text{-Si}_3\text{N}_4$ grains with the increasing agarose content.

It is known that the formation and the growth of $\beta\text{-Si}_3\text{N}_4$ grains are through the solution-diffusion-reprecipitation mechanism. The additives react with SiO_2 on the surface of the Si_3N_4 grains to produce a liquid glassy phase composed of Y_2O_3 , Al_2O_3 , and SiO_2 . The growth rate of $\beta\text{-Si}_3\text{N}_4$ grains is a function of the rate of dissolution of $\alpha\text{-Si}_3\text{N}_4$ particles. Conversely, the obtained materials are porous, so vapor phase transport also contributes to anisotropic growth of $\beta\text{-Si}_3\text{N}_4$ grains (Kawai and Yamakawa, 1998). With increasing temperatures, SiO vapor was produced by the decomposition of the liquid phase $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$. The condensing of the SiO vapor

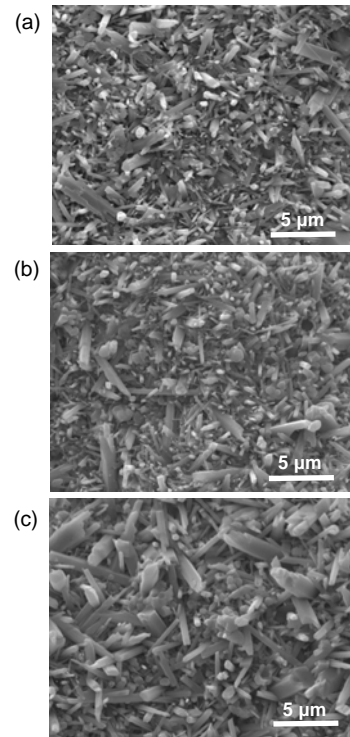


Fig. 2 Microstructure of the obtained porous Si_3N_4 ceramics with different contents of agarose (w/w) (a) 0.2%; (b) 0.4%; (c) 0.8%

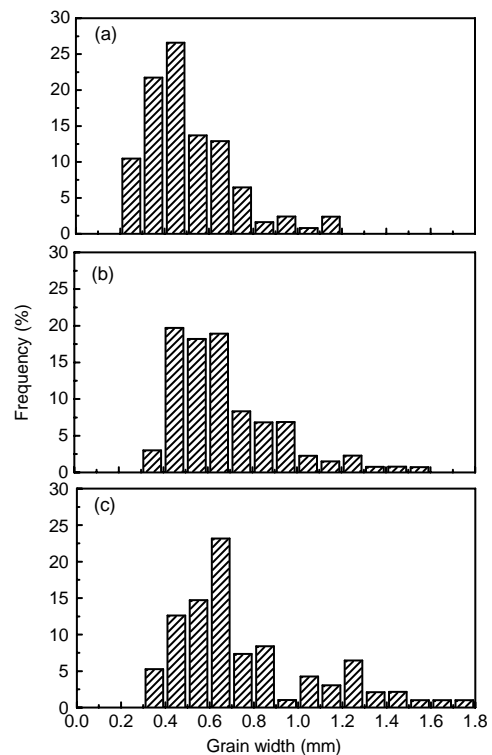


Fig. 3 Grain width distribution of porous Si_3N_4 ceramics with different contents of agarose (w/w) (a) 0.2%; (b) 0.4%; (c) 0.8%

on the surface of the existed β - Si_3N_4 grains caused the growth of the new fibrous β - Si_3N_4 grains. As shown in Fig. 1, with the increasing content of agarose, the porosity increased and the pores became interconnected. Higher interconnectivity of the pores will open paths between pores, which would favor the anisotropic β - Si_3N_4 grain growth through vapor phase transport, and resulted in higher β - Si_3N_4 contents and bigger β - Si_3N_4 grain width. The presence of some new β - Si_3N_4 whiskers grown on the surface of existed β - Si_3N_4 grain, as shown in Fig. 4a, further confirms the contribution of vapor phase transport to β - Si_3N_4 growth.

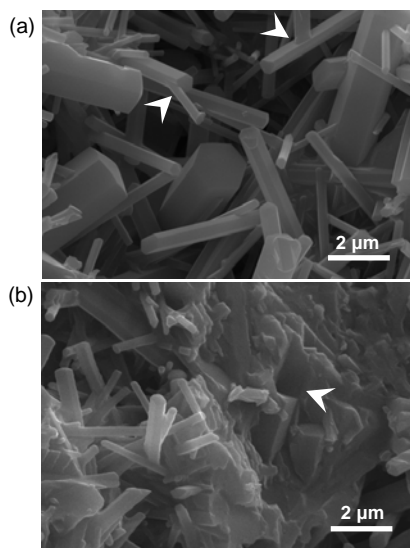


Fig. 4 Fracture morphology of obtained porous Si_3N_4

(a) New fibrous Si_3N_4 grains grown on the surface of the existed β - Si_3N_4 grain in the porous Si_3N_4 ceramic with 0.8% (w/w) agarose; (b) Typical SEM micrograph of fracture surface of porous Si_3N_4 ceramic with 0.2% (w/w) agarose

The flexural strength and fracture toughness of the obtained porous ceramics are shown in Table 1. The results indicate that the mechanical properties of the porous Si_3N_4 ceramics are strongly affected by the porosity. Increasing porosity and pore size decreases the flexural strength and fracture toughness. Elongated β - Si_3N_4 grains and suitable interfacial bonding strength contributes to high fracture toughness by favoring crack deflection and bridging (Lange, 1979; Peterson and Tien, 1995). As shown in Table 1, the sample with 0.8% (w/w) agarose content shows the lowest flexural strength and fracture toughness because it has the highest porosity. The sample with

0.2% (w/w) agarose content shows a high flexural strength of 455 MPa and fracture toughness of 6.6 $\text{MPa}\cdot\text{m}^{1/2}$ due to the low porosity, and the fine and more elongated microstructure. The mechanical properties of the obtained porous Si_3N_4 ceramics are excellent in comparison with the porous Si_3N_4 ceramics with similar porosity produced by other method (Li *et al.*, 2009). The SEM micrograph of the fracture surface reveals the fracture behavior of the investigated porous ceramics, as shown in Fig. 4b. Pullout elongated grains and residual holes left by grains could be commonly observed on the internal walls of the pores, indicating that the presence of a weak grain boundary structure is suitable for crack deflection and elongated grain pullout.

4 Conclusions

Porous Si_3N_4 ceramics were prepared by a gel-casting process using agarose as a fugitive additive. The agarose contents of the suspensions have a strong influence on porosities, $\alpha \rightarrow \beta$ - Si_3N_4 phase transformation, and mechanical properties of the resultant porous ceramics. When the agarose content changed from 0.2% to 0.8% (w/w, based on powder), the porosities increased from 10.3% to 21.4%, while the fracture strength decreased from 455 to 316 MPa and the fracture toughness decreased from 6.6 to 5.5 $\text{MPa}\cdot\text{m}^{1/2}$. The growth mechanisms of fibrous grains resulted from the synergy of solution-diffusion-precipitation and vapor-liquid-solid (VLS). Increasing agarose content would increase the porosity and lead pores interconnected. The interconnected pores were beneficial to the $\alpha \rightarrow \beta$ - Si_3N_4 phase transformation, but detrimental to the mechanical properties.

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