

Processing, microstructure and mechanical properties of porous silicon nitride by a slip casting method using petroleum coke as pore former

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In this study, porous Si_3N_4 ceramics were obtained by a slip casting method which would be easier applied in industry. The most stable and dispersing aqueous suspension was obtained from a solid slurry content of 56.2%, a carboxymethyl cellulose concentration of 0.3% as the adhesive and 0.05% glycerol as the defoamer. Petroleum coke was used as pore-former, and at the same time, it was helpful for the stability of the suspension. The burning-out of the petroleum coke seemed to be an economical way for increasing the porosity of porous Si_3N_4 . After sintering at 1,800 °C for 2 h, samples with a pore size about 10 μm , porosities of 45-60%, and flexural strength of 52.0-112.1 MPa were obtained.

Key words: Pore former, Slip casting, Aqueous suspension.

Introduction

Porous Si_3N_4 is a prominent filtering material due to its excellent mechanical, high-temperature thermal and chemical stability. Many studies have been devoted into the molding methods of porous Si_3N_4 , such as compression molding, injection molding, isostatic pressing, slip casting and extrusion. Also it is clear that people have paid more attention to slip casting and extrusion recently, as these two methods are easy to apply in industry [1, 2]. As we all know, the key factor in slip casting is the stability and dispersing of the aqueous suspension. However, studies have shown that a pure Si_3N_4 suspension was not well-dispersed and stable because of its grain size, morphology, isoelectric point and other properties [3], and other low density grains can improve the properties of the suspension, such as petroleum coke. At the same time, petroleum coke is a cheaper and more easily attainable pore-former than organic whiskers and active carbon [4].

The objective of the present study is to investigate the influence of petroleum coke additions on the suspension, formation of green bodies, burning-out temperature, properties and microstructure of sintered Si_3N_4 porous ceramics. On the other hand, sintering conditions are also very important, hence the properties and microstructure of Si_3N_4 are discussed by adjusting the sintering temperature.

Experimental Procedures

In this study, the starting powder consisted of 92 wt% Si_3N_4 (Shanghai, China, mean size, 1 μm),

5 wt% Y_2O_3 (grade fine C, mean size, < 1 μm) and 3 wt% Al_2O_3 (particle size, 3.6 μm). 20%, 30%, 40% and 50% petroleum coke by weight as the pore former were added in addition. Powders were mixed together with various weight contents of petroleum coke (97.3% C, mean size, 10 μm). Differential scanning calorimetry thermal analyses (DSC) and thermogravimetric analyses (TGA) of the petroleum coke were conducted in a TG/DSC apparatus (SDTQ 600, TA Co., Ltd., America) at a heating rate of 10 K/minute from room temperature to 1,000°C in an air atmosphere. An aqueous suspension of Si_3N_4 /petroleum coke powder mixtures with a solid content of 56.2 wt% using 0.3 wt% carboxymethyl cellulose (viscosity, 800-1200) as a deflocculant, 0.05wt% glycerol as an anti-blowing agent was prepared by planetary milling for 2.5 h in a polyethylene bottle. A $\text{NH}_3\text{H}_2\text{O}$ solution was added to adjust the pH value to 10.5. The corresponding viscosities were measured using a rotational viscometer (NDJ-1, Shanghai Jinjke Industrial Co., Ltd., China) at 12 r.p.m.

Drain casting was performed in a gypsum mold after aging for 12 h. The slip-cast supports were allowed to dry at room temperature for 3h, then dried at 60 °C for 4 h, and finally dried at 120 °C to evaporate the distilled water. The density of the green bodies was measured by the Archimedes displacement method using kerosene. The bodies after the slip casting process were fired in a furnace (High multi-5000 Fijidempa Co. Ltd., Osaka, Japan) at different sintering conditions under an atmosphere of 3atm nitrogen. The density and open porosities were measured by the Archimedes displacement method. Specimens were subjected to measurements of flexural strength in which $30 \times 4 \times 3 \text{ mm}^3$ test specimens were employed using a three-point bending method with a span of 16 mm at a cross-head speed of 0.5 mm/minute (Instron 1195, Instron Co., England). XRD (D/MAX-34) and SEM (JSM-35C,

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JEOL, Japan) were used for phase identification and morphological observations, respectively.

Results and Discussion

Slip rheology and performance of green bodies

The performance of green bodies was mainly influenced by the stability of the Si_3N_4 aqueous suspension. More stable, well-dispersed and non-sedimentation suspensions are helpful for slip casting, and ceramic green bodies with a better performance were prepared by this casting route. Pure Si_3N_4 sediments easily because of its higher density (3.2 g/cm^3) and smaller particle size ($1 \mu\text{m}$) which caused the Si_3N_4 particles to have lower buoyancy than their gravity settling, and the result was the sedimentation of Si_3N_4 particles in the suspension. Thus the Si_3N_4 suspension without petroleum coke was less stable and easy to settle and stratify during aging process, the rheology of the suspension was improved by the addition of the petroleum coke.

The apparent viscosity of Si_3N_4 /petroleum coke slips with a solid content of 56.2 wt% are shown in Fig. 1. With the addition of petroleum coke, the viscosity increased from 1025 to 2532 mPa·s. The petroleum coke particles had a better suspension property due to their lower density (1.98 g/cm^3) and larger particle size ($10 \mu\text{m}$). In the suspension different sizes particles co-existed, which could help prevent sedimentation. On the other hand, with a further increase of petroleum coke content, there was more contact between petroleum coke particles, resulting in large stresses needed to overcome the viscosity [4]. The results showed that the highest addition of petroleum coke was 50 wt%, more would increase the viscosity, and a higher viscosity suspension had lazy flow properties, which would be against carrying out slip casting. Also a petroleum coke content of 60 wt% was tested, and the green bodies had no strength after burning-out the petroleum coke.

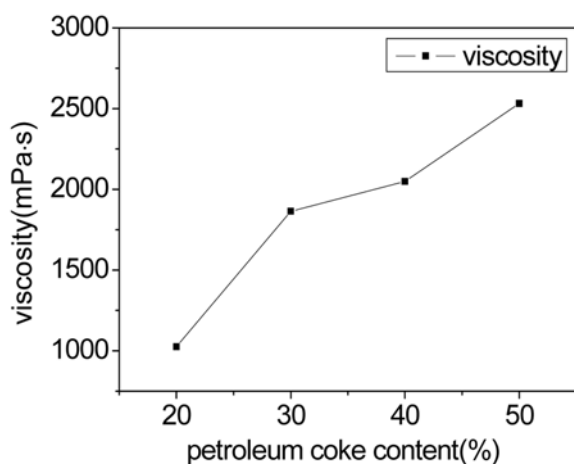


Fig. 1. The curve of Si_3N_4 suspension viscosity with different petroleum coke contents.

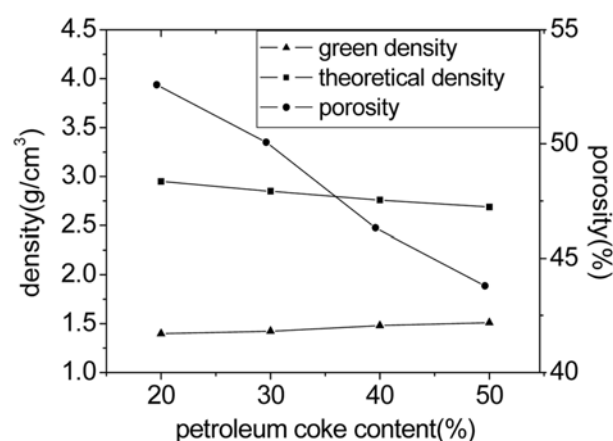


Fig. 2. The porosity, green density and theoretical density of green bodies with different petroleum coke contents

The porosity, green sheet density and theoretical density of green bodies with different petroleum coke contents are shown in Fig. 2. The increase of petroleum coke content could lead to a decrease of the theoretical density and porosity, but an increase of the green sheet density. This could be explained by the fact that as the viscosity increased with the increase of petroleum coke content, and the Si_3N_4 suspension became more stable, this resulted in a homogeneous slip casting and a slower drying process. Finally the green bodies obtained were dense and the green density increased, while the porosity decreased.

The thermal analysis results of petroleum coke are shown in Fig. 3. It could be concluded that the weight loss happened at 600°C which was due to the carbon in the petroleum coke. With the carbon burning, the heat was generated. And the heat would support combustion of the residual C in petroleum coke. As a result, there was no need to increase the temperature to 850°C at which the weight loss was most. In order to burn off petroleum coke in the green bodies, we chose 650°C as the debinding temperature, and 3 h for keeping in order to save energy.

Sintering behavior and mechanical properties

SEM micrograph of porous Si_3N_4 with a 50 wt%

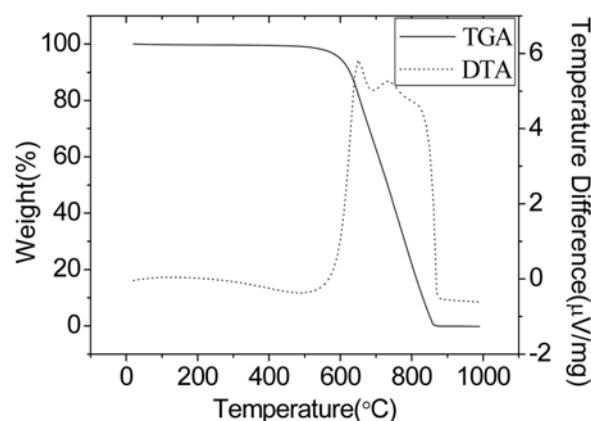


Fig. 3. TG-DTA curves of petroleum coke.

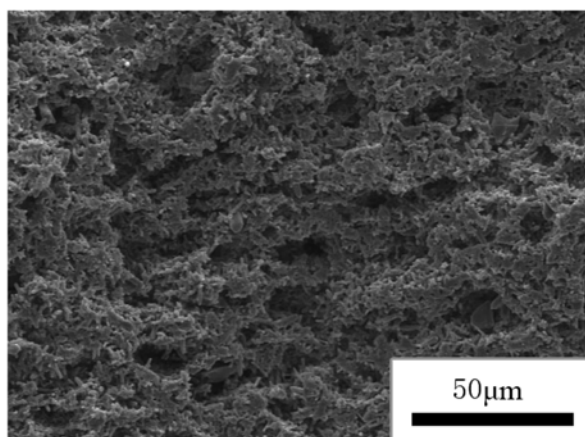


Fig. 4. SEM micrograph of porous Si_3N_4 ceramic after sintering at 1,750 °C for 2 h with a petroleum coke content of 50%

petroleum coke addition is shown in Fig. 4. The microstructures showed that large pores could be found evenly distributed in the matrix. The pores were formed by the burnout of petroleum coke, and their shapes could be attributed to the shape of the petroleum coke particles. The average pore diameter observed was 10 μm , and the pores were connected to each other because of the high petroleum coke loading, which gave a high permeability.

Fig. 5. showed the differences in the microstructure of porous Si_3N_4 sintered at 1,750 °C with an increase in the petroleum coke content. The quantities of pores in the matrix region increased, the pores became connected, while the average pore size decreased a little. With an increase in the addition of the petroleum coke content, after the burning-out process, the quantities of pores in the green bodies increased, the final quantities of pores in sintered Si_3N_4 increased and the pores were connected

with each other, which can give better filtration. Also with an increase in the pores, the volume shrink during the burning-out and sintering processes increased, which could cause a decrease of the mean pore size.

The microstructures of the porous Si_3N_4 ceramics with 20 wt% petroleum coke after sintering at different temperatures are shown in Fig. 6. It could be concluded that $\beta\text{-Si}_3\text{N}_4$ grains were formed and developed with an increase of the sintering temperature.

The XRD results showed that there were only $\beta\text{-Si}_3\text{N}_4$ peaks when the sintering conditions were 1,750 °C for 2 h, which conformed that the phase transformation had finished. Because of the large amount of sintering additions, the content of the glass phase was large. When a sample was sintered at 1,750 °C, the viscosity of the glass phase was too high, and growing the $\beta\text{-Si}_3\text{N}_4$ grains was difficult, the final aspect ratio was lower, and the samples were denser, as a result, the porosity decreased. Because the flexural strength of porous ceramics decreases exponentially with the porosity [5], the flexural strength was the highest for this sample. But compared with the other two sintering temperature, when the content of petroleum coke was the same, the porosity of the porous Si_3N_4 sintered at 1,750 °C was less, which was not good for applying for filtration. Very fine, fibrous and higher aspect ratio $\beta\text{-Si}_3\text{N}_4$ grains were obtained, and good network type pores appeared at 1,800 °C, which was helpful in gaining a higher porosity and flexural strength. This could be explained because the viscosity of the glass phase at 1,800 °C was advantageous for producing high aspect ratio $\beta\text{-Si}_3\text{N}_4$ grains. However, when the sintering temperature was increased to 1,850 °C, coarse and elongated $\beta\text{-Si}_3\text{N}_4$ grains dominated, the degree of densification increased, the porosity decreased, and with the grain growth, the diameter of grains increased,

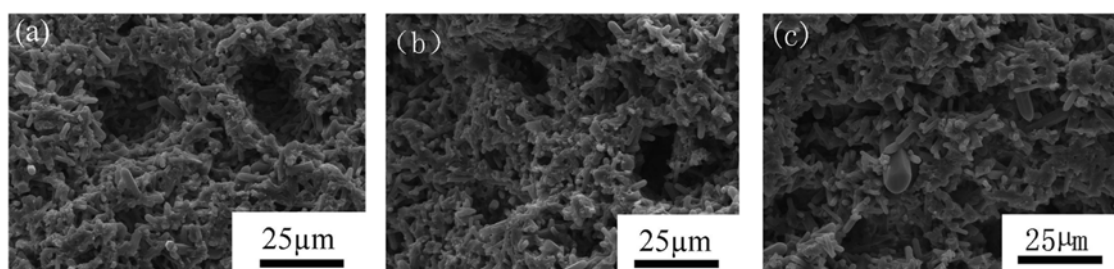


Fig. 5. SEM micrograph of porous Si_3N_4 sintered at 1,750 °C with (a) 30 wt%, (b) 40 wt%, (c) 50 wt% petroleum coke as the pore-former.

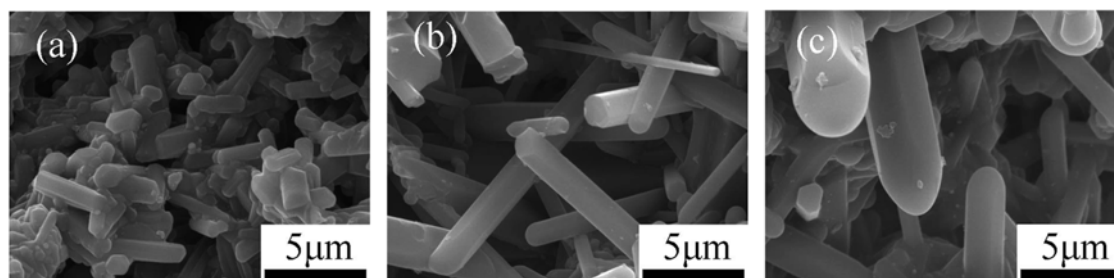


Fig. 6. SEM micrograph of porous Si_3N_4 ceramic with 20 wt% petroleum coke sintered at (a) 1,750 °C, (b) 1,800 °C, (c) 1,850 °C, for 2 h, respectively.

Table 1. Variations in the porosity and flexural strength with different sintering conditions and different petroleum coke contents

Petroleum coke content (%)	20		30		40		50	
Sintering condition	P _o (%)	σ _f (MPa)	P _o (%)	σ _f (MPa)	P _o (%)	σ _f (MPa)	P _o (%)	σ _f (MPa)
1,750 °C / 2 h	37.1	154.3	41.6	131.1	45.6	129.7	49.2	82.4
1,800 °C / 2 h	45.0	112.1	49.9	78.86	57.5	64.7	59.4	52.0
1,850 °C / 2 h	40.7	106.0	47.7	79.2	49.5	68.9	55.1	63.3

*P_o-Porosity; σ_f-Flexural strength.

this would make the flexural strength decrease [6]. As shown in Table 1, the values of porosity and flexural strength of porous Si₃N₄ ceramics with 50 wt% petroleum coke content after sintering at 1,800 °C for 2 h were about 59.4% and 52.0 MPa, respectively. These outstanding mechanical properties would have a beneficial effect on filtration [7].

Conclusions

In the slip casting of porous Si₃N₄ ceramics, the addition of petroleum coke could not only increase the stability of the suspension which caused the resulting green bodies to have excellent performance, but also acted as the pore former. After burning-out the pore former, large pores existed in the matrix. Also with an increase of the petroleum coke content, the number of large pores increased and became evenly distributed, which would be of benefit for filtering. Excellent mechanical properties and microstructures were obtained when the sintering conditions were 1,800 °C for 2 h. With the content of petroleum coke ranging from 20% to 50%, porous Si₃N₄ ceramics, with 45-60% porosity and 52.0-112.1 MPa flexural strength, respectively,

were obtained.

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