

Extrusion of porous silicon nitride using different binders

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Porous silicon nitride ceramics were prepared using an extrusion process. Starch and thermoset phenol-formaldehyde resin were used as binders. The effect of the different binders on the microstructure and mechanical strength of the porous silicon nitride were investigated in detail. It is shown that the microstructure was more uniform when phenol-formaldehyde resin was used as the binder. In contrast, the pore size distribution was bimodal when starch was used. Furthermore, the flexural strength of porous Si_3N_4 using resin as the binder was higher than that using the starch.

Key words: Porous silicon nitride, Extrusion, Binders, Microstructure.

Introduction

Due to their high service temperature and excellent wear resistance, porous ceramics have gained increasing interest in many areas such as for molten metal filters, in gas separation, and as catalyst carriers [1]. In contrast to other ceramics, silicon nitride possesses good mechanical properties and excellent thermal shock resistant because of its unique fibrous interlocking microstructure consisting of elongated $\beta\text{-Si}_3\text{N}_4$ grains after sintering, which has made it attract considerable attention in the past few years [2].

Up until now, porous Si_3N_4 has been successfully prepared via partial sintering, restrained sintering, type casting, partial hot-pressing, partial forge sintering, addition of fugitive inclusions, or carbothermal nitridation of silica. Of the above fabrication routes, green bodies of porous Si_3N_4 were usually shaped by dry pressing, slip casting, or type casting [1–4]. As a result, the manufacturing efficiency is relatively low and the manufacturing cost is high, which prevents further applications in many areas. Actually, extrusion can be used to replace current shaping methods in many fields because of its high throughput. Furthermore, the manufacturing cost of porous Si_3N_4 can be lowered substantially by extrusion, which makes its widespread application possible [5–7].

In the extrusion process, binders such as clay, starch and resin play a crucial part in preparing an extrudable plastic paste. On the other hand, binders must be removed thermally from greenware before sintering. In the debinding process, different binders may have different evolution behavior, which will have large effects on the microstructure and strength of samples after the debinding. Consequently, different binders can further strongly affect the microstructure

and mechanical properties of the sintered porous Si_3N_4 . In this paper, starch and thermoset phenol-formaldehyde resin were used as binders in the extrusion of porous Si_3N_4 . The effect of different binders on the microstructure and mechanical properties of porous Si_3N_4 were investigated in detail.

Experimental Procedure

Commercially available Si_3N_4 powder was selected for use in this research. The powder has high purity, with an $\alpha\text{-Si}_3\text{N}_4$ content of > 95% and an average particle size of 1.2 μm , which was further proved by laser particle size analyzer (Rise-2008, Jinan, China). Y_2O_3 was used as a sintering aid. Starch (Tianda Co., Ltd., Tianjin, China) and a modified thermoset phenol-formaldehyde resin (2130, Xi'an resin company, China) were used as binders. In addition, castor oil was used as a lubricant and distilled water was used as the solvent for the starch. The particle size distribution of the starch was also measured by the same particle size analyzer.

When starch was used as the binder, Si_3N_4 , 5 wt% Y_2O_3 and 10 wt% starch powder were firstly dry mixed in a planetary mixer for 30 minutes. 25 wt% water and 11 wt% castor oil were added to the mixture. The mixture was then vigorously stirred for 20 minutes, providing a high-shear mixing to break up agglomerates and obtain a homogeneous paste. Then the paste was extruded through a homemade extrusion die. The diameter of the extruded rod was 8.8 mm. The extruded green rods were firstly dried at 80 °C for 10 h to remove moisture. The dried samples were thermally debinded at different temperatures to remove the starch and lubricant. Finally, the samples were sintered at 1,750 °C under a 0.2 MPa nitrogen atmosphere for 2 h.

When the binder was changed to the thermoset phenol-formaldehyde resin, because the resin is a liquid, the preparation process needed to have a few minor changes. Si_3N_4 powder and 5 wt % Y_2O_3 were mixed at first. Then 50 wt% resin and 8 wt% castor oil were added into the

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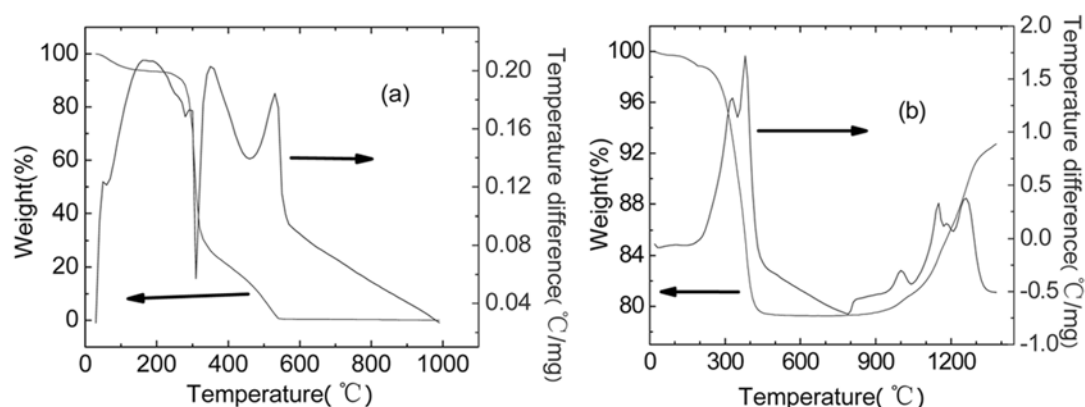


Fig. 1. TG-DSC results of starch and resin: (a) starch (b) mixture of resin and Si_3N_4

mixture to prepare the plastic batch. After vigorously stirring, the plastic batch was extruded through the die. The extruded rods were cured at 180 °C for 2 h. The following processes were the same as that when the binder was starch.

The bulk density and open porosity of the samples at different stages were measured by the Archimedes displacement method using distilled water. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted to investigate the debinding behavior of the starch and resin in a TG/DSC apparatus (SDT Q600, U.S.A.) under a flowing atmosphere. The samples after sintering were machined into test bars of $30 \times 4 \times 3$ mm for bending strength measurement. The three-point flexural strengths were measured on sample bars with a span of 16 mm at a cross-head speed of 0.5 mm/minute, using an Instron universal testing machine. Each final value was averaged over five measurements. Crystalline phases were identified by X-ray diffractometry (XRD) (Model D/MAX-2400X Rigaku Co., Ltd., Tokyo, Japan). The microstructures were characterized by a scanning electron microscope (SEM) (S-2700, Hitachi, Japan).

Results and Discussion

The measure results of particle size distributions for the starting materials showed that the average particle diameter of starch at 10 μm was much larger than that of Si_3N_4 at 1.2 μm . The resin can be dissolved in water, and the starch exists as a solid in the extrusion process. So this means that the much larger starch particles would leave larger pores in the green body after debinding than the resin would.

TG-DSC results of the starch and resin are shown in Fig. 1. Pure starch and a mixed paste of resin and Si_3N_4 were used for the thermal analysis, because of the difficulty of measuring the liquid resin. It can be seen that thermal debinding behavior of starch and resin under air were different. Starch decomposed rapidly between 250 °C and 300 °C, which corresponded to an obvious endothermal reaction. After that, the rate of decomposition was relatively moderate between 300 °C and 550 °C. In contrast, resin debound rapidly between 200 °C and 400 °C. After about

1,000 °C, the weight of samples started to increase markedly because of the passive oxidation of Si_3N_4 into SiO_2 in air [8]. However, regardless of the few differences in thermal debinding behavior, the two binders were both able to debind completely before oxidation of Si_3N_4 . So they were appropriate to be used as binders for the extrusion of Si_3N_4 .

The XRD analyses for the samples with different binders are shown in Fig. 2. After being sintering at 1,750 °C for 2 h, regardless of the great difference between binders, α - Si_3N_4 in all samples was transformed into β - Si_3N_4 completely. In addition, a small amount of $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ phase was formed due to the reaction between Si_3N_4 and Y_2O_3 .

The microstructures of sintered samples are shown in Fig. 3. All samples showed a fibrous interlocking microstructure composed of rod-like β - Si_3N_4 grains with a diameter of about 1 μm and a length of between 6 and 10 μm . Actually, the complete α - β Si_3N_4 phase transition also was confirmed by above XRD analysis. On the other hand, some remarkable differences existed in the microstructures of samples with different binders. With resin as the binder, pores were mainly uniformly formed by interlocking the

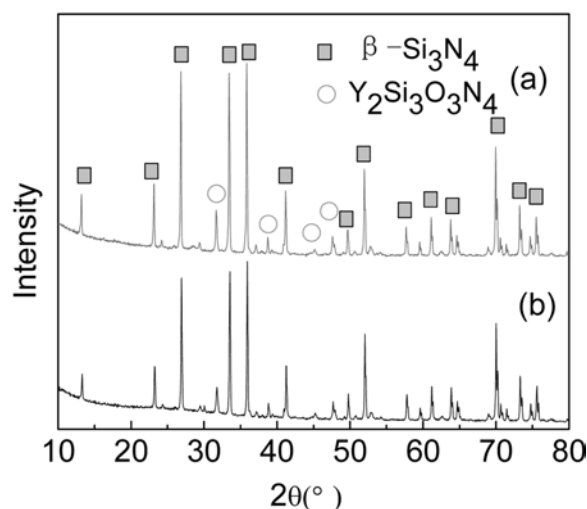


Fig. 2. XRD of the sintered samples with different binders: (a) starch (b) resin.

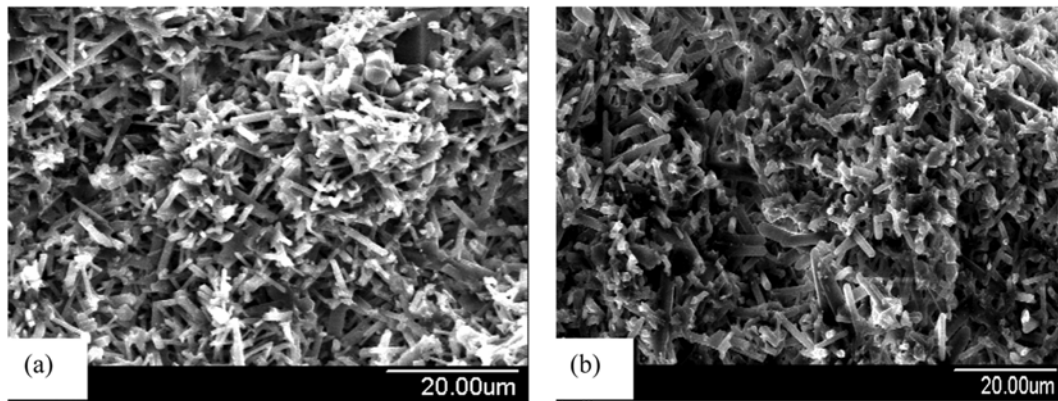


Fig. 3. Microstructures of sintered samples with different binders (a) resin (b) starch

high aspect ratio β - Si_3N_4 grains and the diameter of pores was around $1\text{ }\mu\text{m}$. However, with starch as the binder, the pore size distribution was bimodal. This means that not only the above mentioned small pores with a diameter of about $1\text{ }\mu\text{m}$ but also bigger pores with a diameter of around $5\text{ }\mu\text{m}$ existed in the samples. It is reasonable to believe that these larger pores were formed by the burn-out of starch from the samples after thermal debinding. However, the diameter of the big pores was obviously smaller than the supposed pore diameter that should be about $10\text{ }\mu\text{m}$ (starch particle diameter) after removing the starch. This phenomenon can be explained by the growth of numerous elongated β - Si_3N_4 grains which decreased the supposed pore diameter greatly.

The porosity and flexural strength of samples with different binders are presented in Table 1. Regardless of the different binders, the open porosity and bulk density have only minor differences between the two types of sample. The reason is that there was a minor difference between the volume contents of fugitive substances that can produce pores after thermal removal. However, the flexural strength of samples with resin is nearly 30% higher than that with starch. This can be mainly attributed to the uniform pore distribution in samples with the resin, which was already confirmed by SEM. Of course, the somewhat lower porosity in samples with resin also can enhance the flexural strength slightly. In addition, the current flexural strengths are compared with samples with similar porosities prepared by carbothermal nitridation in the literature in Table 1 [9]. This shows that the current strengths are similar to or higher than the results in the previous literature. So this suggests that extrusion is a promising

efficient route in fabricating porous Si_3N_4 .

Summary

Porous Si_3N_4 samples were successfully fabricated by extrusion using different binders. The type of the binder had an obvious effect on the microstructure and mechanical strength of porous Si_3N_4 . The microstructure of samples with resin as the binder was more uniform than that with starch. Consequently, the flexural strength with resin as the binder is obviously higher than that with starch. Furthermore, compared with other current preparation processes, extrusion is a promising process in fabricating porous Si_3N_4 .

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Table 1. Porosity and flexural strengths of samples with different binders

Binder	Open porosity (%)	Bulk density (g/cm^3)	Flexural strengths(MPa)
Resin	51	1.58	106
Starch	54	1.45	83
Other literature	52	-	55-100