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SYNTHESIS OF POROUS SILICON NITRIDE WITH UNIDIRECTIONALLY ALIGNED CHANNELS USING EXTRUSION METHOD

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Porous silicon nitride (Si_3N_4) ceramics with highly ordered and unidirectionally aligned channels were fabricated by extrusion method using nylon fibers as the pore forming agent. The microstructure, mechanical properties and gas permeability were investigated. The results showed that the added nylon fibers were mostly converted to pores, the average pore diameter was approximately 19.5 μm and shrank about 22 % from the size of original pore former (25 μm) during sintering. The porosity and gas permeability increased and the 3-point bending strength decreased proportionally with increasing the nylon fiber content. When the nylon fiber content increased to 20 wt. %, the porosity, bending strength and gas permeability of the extruded samples with uni-directionally aligned pores were higher than those of non-extruded sample with random pores. For the extruded samples, the resulting porous silicon nitride ceramics showed a high gas permeability owing to their uni-directionally oriented structure.

INTRODUCTION

Silicon nitride (Si_3N_4), as one of the most important structural ceramics, has a superior toughness, high strength, high decomposition temperature, good resistance to corrosive environments and low coefficient of friction [1]. Porous Si_3N_4 ceramic with unidirectionally aligned channels is given a great deal of attention due to its potential applications, such as catalyst carriers and separation filters, which need a high permeability while maintaining good mechanical properties [2, 3].

One of the main challenges in the fabrication of porous ceramic is to control the size, distribution and connectivity of the pores to improve the permeability. Some attempts have been reported to fabricate porous ceramics with unidirectionally aligned pores (channels) using extrusion [4, 5], filament winding [6], electrophoretic deposition [7], biomimetic process [8], slip casting [9], gel casting [10] and freeze drying methods [2, 11, 12]. Among these methods mentioned above, extrusion process is specially adapted for the mass production of regular and constant cross-section bodies. It is also used for the preparation of porous ceramics with unidirectionally aligned channels. Such a highly oriented microstructure can be obtained by the uniform convergent flow of the matrix, which induces the rearrangement of the fiber orientations in the extrusion die. Therefore, porous ceramics with unidirectionally aligned channels are fabricated by extrusion method when the flammable fibers are used as the pore-forming agent [13]. Since the porous microstructure is controlled, the resulting porous ceramics have very high permeability and high mechanical strength.

For the applications of porous Si_3N_4 ceramics with unidirectionally aligned channels, it is essentially important to tailor the shape, morphology and orientation of pores as well as the porosity and the size distribution of pores during extrusion. However, there is little report on the influence of fiber content on the microstructure and properties of porous Si_3N_4 ceramics with unidirectionally aligned channels. Thus, the flammable nylon fibers were used as the pore-forming agent in the present work, the effect of fiber content on the microstructure and mechanical properties of porous Si_3N_4 ceramics with the aim of achieving improved knowledge of the accurate control of the microstructure and obtaining the high-performance porous Si_3N_4 ceramics with unidirectionally aligned channels.

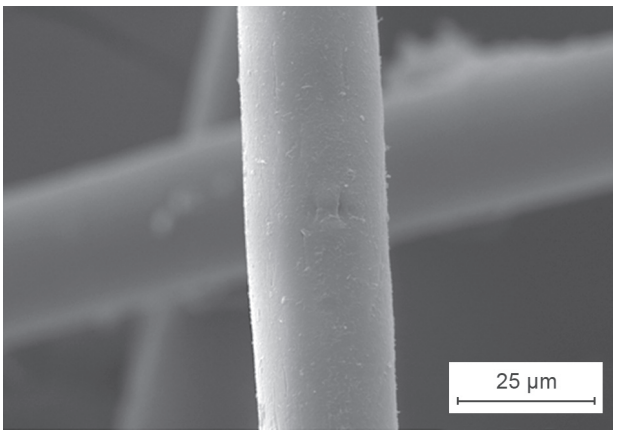


Figure 1. SEM of nylon fibers.

EXPERIMENTAL

Preparation of samples

High purity 95 wt. % α-Si_3N_4 powder (Junyu Co. Ltd., Shanghai, China) was used as the starting powder. 5 wt. % yttria powder (Rong ri da Co. Ltd., Zibo, China) was used as sintering additives. Nylon fibers (see Figure 1, 0 ~ 30 wt. %) with an average diameter of 25 μm and length of 2 mm (Hongyu Co. Ltd., Jiamusi, China) were chosen as the pore-forming agent. 20 wt. % hydroxypropyl methylcellulose (HPMC), 5 wt. % polyethylene glycol (PEG), 5 wt. % castor oil and a drop or two propanetriol were used as the binder, plasticizer, lubricant and defoamer respectively. The mixture was kneaded with 25 - 30 wt. % distilled water and placed in a sealed container for 24 h. The resulting paste was molded using a self-made piston extruder (Figure 2a). A schematic diagram was shown in Figure 2b. The extruded green bodies were dried at 90°C for 48 h in an oven. The organic compounds (binder, plasticizer and ant blocking agent) were removed from the green bodies by heating at 690°C for 3 h in air. After removal of the organic compounds, the green bodies were sintered in a graphite resistance furnace (High multi-5000 Fijidempa Co. Ltd., Osaka, Japan) at 1750°C under a nitrogen-gas pressure of 0.3 MPa. The heating rate was 10 - 20°C·min^{-1} and holding time was 2 h.

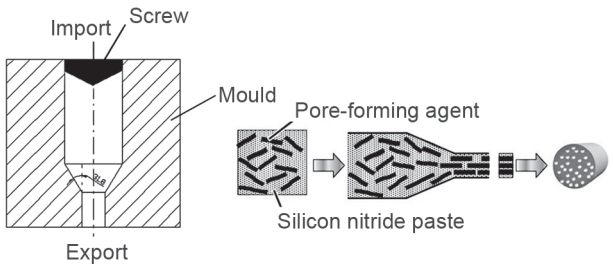


Figure 2. Schematic diagram of a laboratory extruder and schematic for obtaining porous silicon nitride ceramics with oriented cylindrical pores by the extrusion method.

Characterization of samples

The open porosities of the sintered samples were measured by Archimedes displacement method using distilled water. Crystalline phases were identified by an X-ray diffractometry (XRD, D/MAX-2400X, Rigaku Co., Tokyo, Japan) using Cu Kα radiation. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Q600, USA) were carried out for the extruded pastes in air with a heating rate of 10°C·min^{-1} from 0 to 1200°C. The microstructure of as-sintered samples was characterized by a scanning electron microscope (SEM, JSM-35C, JEOL, Tokyo, Japan). The specimens were machined into test bars measuring 25 mm × 4 mm × 3 mm, for bending-strength measurement. The permeability of the porous ceramics was evaluated using Equation 1:

$$\Delta P = \frac{\eta L}{\mu A} Q \qquad (1)$$

where P is the pressure drop from entrance to exit of the sample, μ is the Darcy's permeability, η is the dynamic viscosity of the fluid, A and L are the cross-sectional area and the thickness of the sample, Q is the flow rate. The gas permeametry equipment and measuring calculation method used in this study is referred to the Isobe document [14]. The dynamic viscosity η of air used in our experiment is 1.8×10^{-5} Pa·s.

RESULTS AND DISCUSSION

DSC-TGA analysis

Figure 3 shows DSC and TGA analysis of green body(extruded pastes). The TGA curve showed a gradually downward trend from 200°C to 800°C with 21.98 % weight loss due to desorption of physically absorbed water, combustion of the nylon fibers and decomposition of organic compounds (HPMC, PEG and propanetriol). The exothermic peak in the DSC curve at 316°C and 691°C could be mainly attributed to the

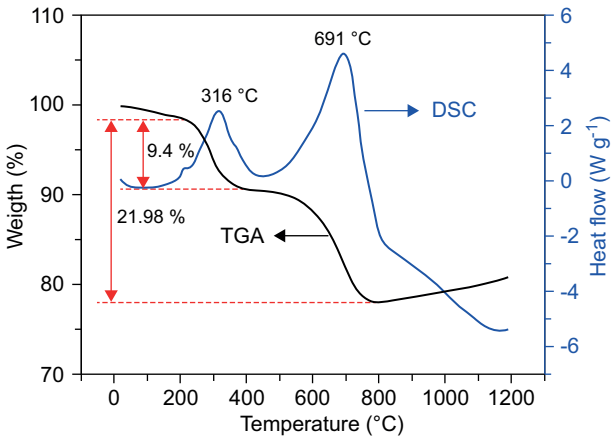


Figure 3. The DSC-TGA curve of green body.

combustion of nylon fibers and decomposition of organic compounds respectively. Based on the above analysis, the appropriate temperature chosen for the removal of organic compounds was 690°C, and the holding time was 3 hours for better debinding.

Microstructure

Figure 4 shows a SEM micrograph of the cross section of the non-extruded sample with 20 wt. % nylon fibers. Many cylindrical pores formed by burn-out of fibers presented a random three-dimensional orientation. Figure 5 shows SEM micrographs of the cross-section of the samples with 20 wt. % nylon fibers, a) perpendicular to the extrusion direction, b) parallel to the extrusion direction, c) and d) high magnification figures. The microstructures (Figure 5a and b) showed

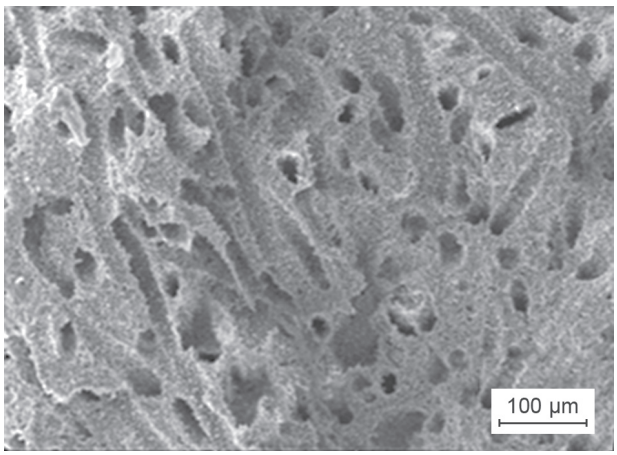
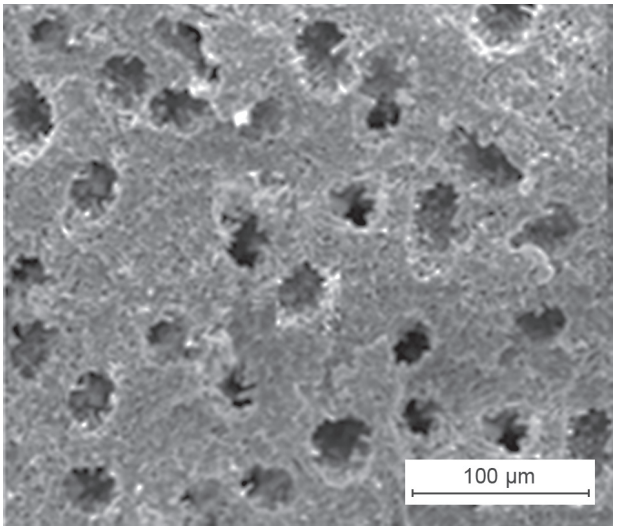
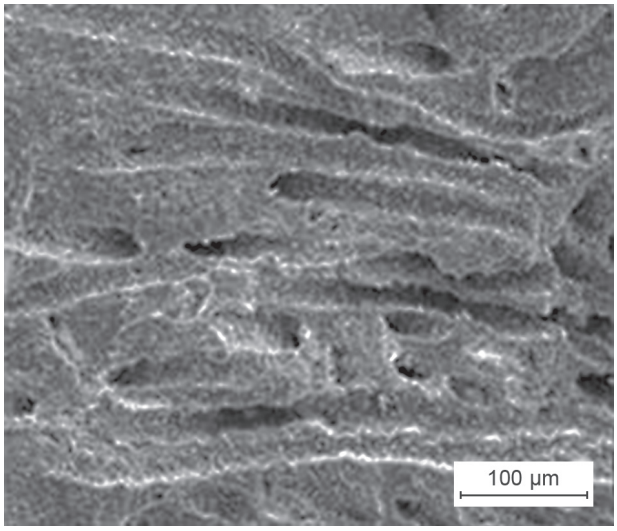


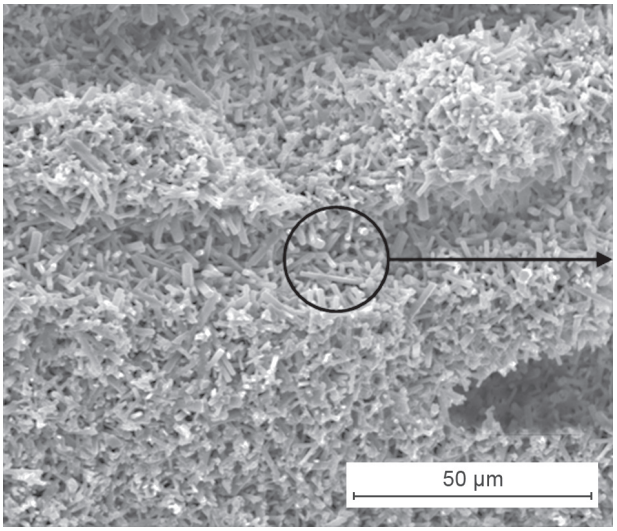
Figure 4. SEM micrograph of the cross section of the non-extruded sample with 20 wt. % nylon fibers.



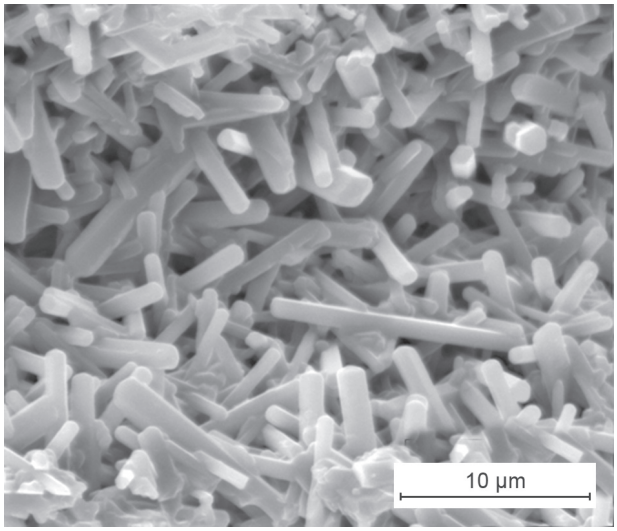
a)



b)



c)



d)

Figure 5. SEM micrographs of the cross-section of the samples with 20 wt. % nylon fibers: a) perpendicular to the extrusion direction, b) parallel to the extrusion direction, c) and d) high magnification figures.

highly oriented cylindrical pores parallel to the extrusion direction. These pore shapes can be attributed to the fiber shape. The average observed pore diameter was approximately 19.5 μm and shrank about 22 % from the size of original pore former (25 μm) during sintering. Also in this case, a remarkable β-Si_3N_4 grains growth from the internal walls of the open channel was observed (Figure 5c and d). The fibrous grains seemed to be thinner and longer, this suggested phase transformation and grain growth were concluded to occur through a solution–reprecipitation mechanism that was controlled by the interfacial reaction [15]. And interestingly, unlike fibrous β-Si_3N_4 grains within channels walls, β-Si_3N_4 grains in channels grew sufficiently to interlock with each other, this may be due to β-Si_3N_4 grains in channels having enough space to fully grow into length fibers protruding into the internal space of channels. This interlocked microstructure generated the secondary pore structure with pore size of several micrometers.

Mechanical properties

Figure 6 shows the relationship between the fiber contents, porosities and 3-point bending strength of extrusion and non-extruded samples. The porosity increased and the 3-point bending strength decreased proportionally with increasing the nylon fiber content, it can be considered that the added nylon fibers were mostly converted to pores after sintering. Comparing the two samples, it was found that the porosity of the extruded sample was higher than that of the non-extruded sample, when the amount of nylon fibers was added before 15 %, the 3-point bending strength of the non-extruded samples was higher than that of the extrusion samples, the main reason was due to the lower porosity of non-extruded samples, when the addition amount exceeded 20 %, although the porosity of the extrusion samples was higher than that of the non-extruded samples, the bending strength of the extrusion samples was higher than that of the non-extruded samples, the main reason was that the long and straight pathways observed in the SEM micrographs of extrusion samples (Figure 4 and 5). On the other hand, the above-mentioned special microstructure (Figure 5d) with fibrous grains would not only decrease the channel size, but also create various kinds of pores, this also explained why the pore diameter shrank about 22 % from the size of original pore former (25 μm) during sintering.

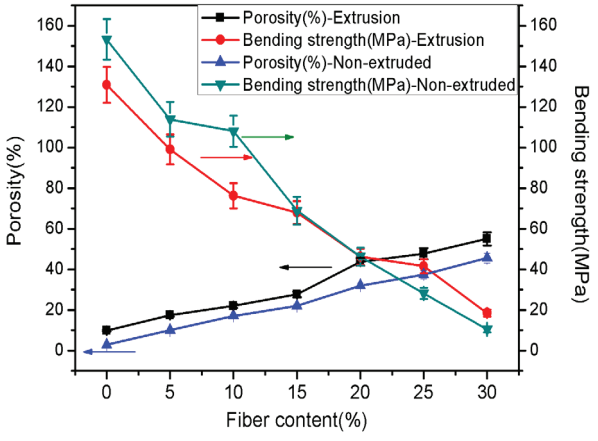


Figure 6. The relationship between the fiber contents, porosities and 3-point bending strength of extrusion and non-extruded samples.

Gas permeability

Figure 7 shows the relationship between the porosity and permeability of extrusion samples. The permeability of the obtained ceramics increases from 1.72 × 10^{-15} to 5.83 × 10^{-13} m^2 as the average porosity increases from 18.39 to 55.03 %. The calculated values were obtained from Equation 2 [16].

$$\mu = \frac{d^2}{32} P \qquad (2)$$

The permeability of extrusion samples with uni-directionally aligned pores showed slightly lower permeability from that of the calculated values. However, the permeability of the present sample with 43.75 % porosity (2.98 × 10^{-13} m^2) was higher than that of non-extruded sample with 44 % porosity and 3.05 × 10^{-5} m^2 permeability. And the gas permeability of the extrusion samples with uni-directionally aligned pores was higher than that of non-extruded sample with random pores. The main reason was due to the channels uniformly distributed, highly ordered and unidirectionally aligned structure of extrusion samples, and the above-mentioned special microstructure with fibrous grains and various types of pores (Figure 6d), which appeared to effectively enhance the gas permeability. Isobe et al. [14] have

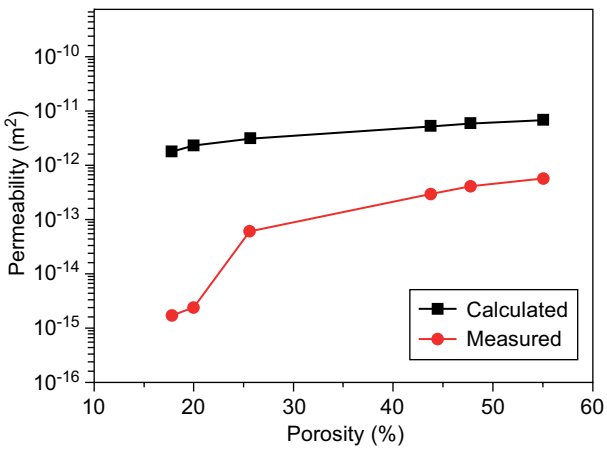


Figure 7. Permeability of the extruded porous silicon ceramics as a function of porosity.

confirmed that the permeability values of conventional porous alumina ceramics of random type are about 10^3 times lower than the ideal value, and the gas permeability of the extrusion samples is higher than that of the conventional samples.

CONCLUSIONS

Porous silicon ceramics with unidirectionally aligned channels pores extended in the extrusion direction were prepared using nylon fibers as the pore forming agent. Nylon fibers with an average diameter of 25 μm and length of 2 mm were elongated and connected by the extrusion process. These elongated nylon fibers were converted to through-hole pores after sintering at 1750°C for 2 h. The average observed pore diameter was approximately 19.5 μm and shrank about 22 % from the size of original pore former (25 μm) during sintering. The porosities of these porous silicon ceramics increased proportionally with increasing nylon fibers content, and the samples showed a high porosity and gas permeability owing to their uni-directionally pores oriented structure.

Acknowledgments

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