JOURNALOF

Ceramic Processing Research

Fabrication of porous Si_3N_4 ceramics with controlled porosity by milling of fibrous α -Si₃N₄ powder

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Porous Si_3N_4 ceramics with varied porosities were prepared by liquid phase sintering of fibrous α -Si₃N₄ powder with different morphology after ball milling. The influence of the ball milling time on porosity, shrinkage, microstructure and mechanical properties of Si₃N₄ ceramics were investigated. With increasing of the ball milling time from 0 h to 24 hrs, the mean length and aspect ratio of the fibrous α -Si₃N₄ particles decreased dramatically, resulting in the porosity of porous Si₃N₄ ceramics decreased from 55.6% to 19.3%. With the decreased length of the fibrous α -Si₃N₄ particles, microstructures with decreased aspect ratio of β -Si₃N₄ grains were formed, as a result of increased nuclei number and limited grain growth of the β -Si₃N₄ grains. The flexural strength varied from 62 MPa to 205 MPa could be obtained attributed to the synergy effect of porosity and microstructure.

Key words: Fibrous α -Si₃N₄, Porous ceramics, Porosity, Flexural strength.

Introduction

Porous silicon nitride (Si₃N₄) ceramics have been focus of interesting research in the field of porous materials due to its excellent mechanical strength, good chemical resistance, high thermal shock resistance, and so on. [1-5] Various processing techniques have been developed to fabricate porous Si₃N₄ ceramics such as tape casting, freeze-drying and carbothermal nitridation of silica. [6-9] Particularly, extensive efforts have been devoted to control the porosity of the ceramics, resulted in improved properties and function of porous Si₃N₄ ceramics. Equiaxed α -Si₃N₄ powder was generally used as raw material for liquid sintering of porous silicon nitride ceramics, whose porosity can be controlled by either using partial sintering [10, 11], fugitive substance, [12, 13] or addition of sintering additive [14, 15] and carbon [16]. These processes were sensitive to sintering condition and properties of the introduced materials, so it was difficult to control the porosity of the ceramics for a wide range. On the other hand, some rod-like â-Si₃N₄ seed used in original powder also influences the densification and microstructure of sintered β-Si₃N₄ ceramics. [17-19] Compared with α -Si₃N₄ powder, the rod-like β-Si₃N₄ seed only underwent grain growth during sintering process, so the anisotropy of the β -Si₃N₄ grains could be maintained.

In some case, α -Si₃N₄ particles with fibrous morphology can be fabricated via direct nitridation of

silicon powder in a flowing hydrogen/ nitrogen stream over a temperature of 1623 K. [20, 21] When the fibrous particles were used as raw material, the porous material had a network structure and resulted in numerous pores by the interconnection of fibrous particles. [22, 23] Recently, we have obtained porous Si₃N₄ ceramics with various porosities by addition of fibrous α -Si₃N₄ powder into the equiaxed α -Si₃N₄ powder, and the porosity was increased with the increasing content of the fibrous α -Si₃N₄ powder. [24] The mixing of the two kinds of powder was complex due to the intention of keeping the fibrous morphology, so if the fibrous particles can be ground directly to get different particle size, it will be easy to control the porosity of the green body as well as the sintering body by the stocking of the fibrous particles with varied aspect ratio.

In the present work, fibrous α -Si₃N₄ powder with high aspect ratio was ball milled for different times together with 5 wt% Y₂O₃ as sintering additive, to obtain porous β-Si₃N₄ ceramics with controlled porosities. The influences of morphology of the fibrous α -Si₃N₄ particles on densification, porosities, microstructure and mechanical properties of the porous Si₃N₄ ceramics were characterized.

Experimental

Fibrous α -Si₃N₄ powder (Chaowei Nano Technology Co. Ltd., Shanghai, China) was used as raw material, and Y₂O₃ (Yuelong Rare Material Co., Ltd., Shanghai, China) as the sintering additive. The powder mixtures of 95 wt% α -Si₃N₄ and 5 wt% Y₂O₃ were wet milled with high-purity zirconia balls in anhydrous alcohol for 0 ~ 24 hrs in alumina tank, keeping the rotation speed

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at ~ 200 rpm. The mass ratio of original powder: alcohol: zirconia balls was 1:3:5. After ball milling, the obtained slurries were dried by a rotary evaporator and sieved through a 150 µm screen, then the powder mixtures were pressed to form rectangular bars with a size of 5 mm × 5 mm × 50 mm by uniaxial pressing. The green bodies were sintered in a furnace (Highmulti-5000, Fujidempa Co. Ltd., Osaka, Japan) at 1750 °C for 2 hrs, at a nitrogen-gas pressure of 0.3 MPa, with heating rate of 15 °C /min.

The porosities of green bodies and sintered samples were obtained by measuring their weight and dimension and Archimedean method, respectively. The crystallinephases presenting in the materials were determined by Xray diffraction (D/MAX-2400X, 40 kV, 40 mA, Cu Ka, Rigaku Co., Tokyo, Japan). Microstructures of the sintering bodies were characterized by investigation of the fracture surface on scanning electronic microscope (SEM, JSM-7000F, JEOL, Japan). Grain width and length were obtained from the individual grains in the SEM photographs. More than 200 grains were measured statistically for each sample by image analysis software (Nano Measure 1.2). The samples were machined to bending test bars with a size of $3 \text{ mm} \times 4 \text{ mm} \times 50 \text{ mm}$. The tensile surface was ground on an 800-grit diamond wheel and the edges were beveled to reduce the effect of edge cracks. The flexural strength was measured by using three-point bending testing method in universal testing machine (Instron1195, Instron Co., U.K.) with a span of 16 mm at a cross-head speed of 0.5 mm/min.

Results and Discussion

Morphology of fibrous α -Si₃N₄ powders after ballmilling process

Fig. 1 shows the SEM images of fibrous α -Si₃N₄ powder after ball milling for different times. The microstructure difference could be distinguished from the samples, especially for the particle length and aspect



Fig. 1. SEM micrograph of fibrous Si_3N_4 powder after different milling time: (a) 0 hr, (b) 4 hrs, (c) 12 hrs, (d) 24 hrs.



Fig. 2. Particle length distribution of the fibrous Si_3N_4 powder after different milling time.

Table 1. Mean particle length and aspect ratio for fibrous Si_3N_4 powder after different milling time.

Ball milling time/h	0	4	12	24
Mean particle length/µm	5.5	2.0	1.7	1.0
Aspect ratio	7.94	3.66	2.58	1.90

ratio. Evidently, the original fibrous α -Si₃N₄ powder was consisted of a large amount of elongated particles with a remarkably large particle size and high aspect ratio. As the ball milling time increased, the content of large elongated fibrous α -Si₃N₄ particles decreased and the mean particle length became smaller. When the powder was ball milled for 12 hrs, numerous small particles were dominated beside some elongated fibrous α -Si₃N₄ particles. The powder after 24 hrs milling showed a uniform microstructure in which no large particles were observed. In comparison with the less effect of long milling time on the particle size and morphology, the short time was more effective for reducing fibrous α -Si₃N₄ particle size by milling.

Fig. 2 demonstrates the relationship between the particle length distribution and the ball milling time. Table 1 summarizes the mean particle length and aspect ratio of fibrous α -Si₃N₄ powder with different ball milling time. It can be seen that the original fibrous α -Si₃N₄ particles have mean particle length of $\sim 5.5 \,\mu\text{m}$ and aspect ratio of 7.94 which are much longer than other samples. After ball milling with 4 hrs

and 12 hrs, the α -Si₃N₄ particles demonstrated relatively uniform size, and the particle length and aspect ratio of the fibrous α -Si₃N₄ particles decreased to 2.0 µm, 3.66 and 1.7 µm, 2.58 respectively. The ball milling treatment resulted in not only broken of the aggregate in the original powder, but also fracture of the fibrous α -Si₃N₄ fiber particle. When the milling time was 24 hrs, the obtained particles had mean particle length of ~ 1.0 µm and the lowest mean aspect ratio of 1.90.

Sintering behavior and microstructure of porous Si₃N₄ ceramics

Densification and phase transformation

Fig. 3 shows the green porosities, linear shrinkages and bulk porosities of the porous Si_3N_4 ceramics after sintering at 1750 °C for 2 hrs. High porosity of 59.6% was obtained for the green body using the original fibrous α -Si₃N₄ powder, and it decreased to 53.4% as the ball milling time increased to 24 hrs. For the original powder, the elongated fibrous particles with high aspect ratio interlocked each other and a large amount of pores could be developed inside the green body. With the fracture of the fibrous particles after ball milling treatment, the porosities decreased, due to the relatively compacted packing of the refined fibrous



Fig. 3. Porosity and linear shrinkage versus milling time for the porous Si_3N_4 ceramics: (a) green porosity, (b) sintering porosity and linear shrinkage.



Fig. 4. XRD patterns of fibrous Si_3N_4 powder and porous Si_3N_4 ceramics by sintered at 1750 °C, 2 hrs: (a) original fibrous Si_3N_4 powder, (b) porous Si_3N_4 ceramics from fibrous powder after 24 hrs milling.

particles.

After sintering, the samples prepared by the ball milled particles exhibited considerably increased shrinkage and decreased porosity. Although the porosity of green body was only changed within a small range $(59.6\% \sim 53.4\%)$, the shrinkage of the ceramics increased from 2.2% to 14.1%. It was indicated that the morphology of α -Si₃N₄ particles had a significant effect on the densification behavior. The densification during liquid phase sintering was mainly based on particles rearrangement with some accommodation of the particles shape. At early stage of the densification, the elongated fibrous Si₃N₄ particles were difficult to move due to intertwining, which restrained the rearrangement of the particles and decreased the shrinkage of the ceramics. The decreased particle length and aspect ratio of the fibrous Si₃N₄ particles through ball milling contributed to their rearrangement, which improved the densification of the ceramics consequently. With the decreased porosity of green body and increased shrinkage, the porosities of porous Si₃N₄ ceramics with same sintering additive and sintering temperature could be tailored from 55.6% to 19.3% by changing the ball milling time of the fibrous α -Si₃N₄ powder.

XRD patterns of the original fibrous α -Si₃N₄ powder and the porous β -Si₃N₄ ceramics are shown in Fig. 4. It can be seen that the original powder was consisted of α -Si₃N₄ phase with a trace of β -Si₃N₄ phase. The main phase in the sintered sample was β -Si₃N₄, and the Y₂Si₂O₃N₄ was formed by the reaction among Si₃N₄, Y₂O₃ and SiO₂ existed on the surface of the Si₃N₄ particles. The XRD patterns indicated that complete phase transformation from α -Si₃N₄ to β -Si₃N₄ could be achieved at 1750 °C for all specimens.

Microstructure and mechanical properties

Fig. 5 shows the fracture surface microstructures of



Fig. 5. SEM micrograph of porous Si_3N_4 ceramics with different ball milling time: (a) 0 hr, (b) 4 hrs, (c) 12 hrs, (d) 24 hrs.



Fig. 6. Grain size distribution of the porous Si_3N_4 ceramic obtained from fibrous α - Si_3N_4 with different ball milling time.

porous Si₃N₄ ceramics after sintering at 1750 °C for 2 hrs. A significant influence of the ball milling time of the fibrous α -Si₃N₄ powders on the mean length and aspect ratio of β -Si₃N₄ grains after sintering was demonstrated. Evidently, the porous Si₃N₄ ceramics prepared by the original fibrous α -Si₃N₄ powder consisted of elongated rod-like β -Si₃N₄ grains with high aspect ratio only. However, a distinct bimodal microstructure was obtained by increasing the ball milling time to $4 \sim 12$ hrs, in which elongated rod-like β -Si₃N₄ grains embedded in short β -Si₃N₄ grains. As the ball milling time was prorogated to 24 hrs, dense microstructure with a number of fine, equiaxed β -Si₃N₄ grains was achieved. Image analysis of the β -Si₃N₄ grains also was carried out to quantitatively evaluate the microstructure. Fig. 6 demonstrates the grain width and length distribution of the $\beta\mbox{-}Si_3N_4$ grain in the porous Si_3N_4 ceramics. As can be seen in the Fig. 6(a), the sample prepared by the original Si₃N₄ powder demonstrated a large scatter of dimension and aspect ratio of the β -Si₃N₄ grain in comparison with other samples. With increasing the ball milling time,



Fig. 7. Flexural strength as a function of porosity of the porous ${\rm Si}_3{\rm N}_4$ ceramics.

relatively uniform size and shape were obtained for the β -Si₃N₄ grains, and the mean grain size and aspect ratio for the sample obtained from the powder after 24 hrs milling were the smallest .The ball milling treatment of the raw fibrous α -Si₃N₄ powder contributed to a general refinement of the β -Si₃N₄ grain size.

During liquid phase sintering, the transformation of α -Si₃N₄ to β phase is caused by dissolution of α -Si₃N₄ into Y-Si-O-N liquid phase and reprecipitation on β -Si₃N₄ grains. [25, 26] The grain growth of β -Si₃N₄, which is predominantly one-dimensional, is dependent on driving force, nuclei amount and vacant space. In this study, as the fibrous α -Si₃N₄ particles were refinement through ball milling treatment, higher driving force and numerous β -nuclei could be obtained, resulting in a more uniform β -Si₃N₄ grain size with a low aspect ratio, due to the limited space for the grain growth of the β -Si₃N₄ grains. In a word, the β -Si₃N₄ morphology and fraction of elongated grains could be tailored over a very wide range by controlling the ball milling treatment of the fibrous α -Si₃N₄ particles.

Fig. 7 shows the flexural strength of porous Si₃N₄ ceramics as a function of porosity in a semi-log scale after sintering at 1750 °C for 2 hrs. As shown in Fig. 7, as the porosity decreased from 55.6% to 19.3%, the flexure strength of porous Si₃N₄ ceramics increased from 62 MPa to 205 MPa. The high density was primarily favorable for the improvement of the mechanical properties and it was nearly linear relation between the descending strength of porous ceramics and increasing of porosity, which was consistent with Rice's model [27]. On the other hand, the strength increased considerably from 62 MPa to 151 MPa as the porosity of porous Si₃N₄ ceramics decreased from 55.6% to 46.8%, however, when the porosity further reduced to 19.3%, the strength of the porous ceramics increased modestly to 205 MPa. This may be related to the morphology and grain shape of the obtained β -Si₃N₄ microstructure, as shown in the Fig. 5. As the fibrous α -Si₃N₄ particles

were ball milled with short time, the growth of rod-like β -Si₃N₄ grains was sufficient with the high aspect ratio in an interlocking structure, so the strength could be enhanced by the crack deflection, bridge and pull-out performance of the rod-like β -Si₃N₄ grains. When the fibrous α -Si₃N₄ particles were ball milled further, the growth of rod-like β -Si₃N₄ grains was restrained and the aspect ratio of the obtained β -Si₃N₄ grains was low, resulting in a modestly increase of the flexural strength by the improved densification.

Conclusions

Porous Si₃N₄ ceramics with tailored porosity were fabricated by fibrous α-Si₃N₄ powder through ball milling treatment with different time. With increasing the ball milling time form 0h to 24 hrs, the mean particle length of the fibrous α -Si₃N₄ decreased from 5.5 µm to 1.0 µm, which contributed to prohibited grain growth of β -Si₃N₄ and decreased porosity of porous Si₃N₄ ceramics from 55.6% to 19.3% due to the increased nuclei number of β-Si₃N₄ grains. With the change of porosity and β -Si₃N₄ grain size, the flexural strength of the porous β -Si₃N₄ ceramics can be ranged from 62 MPa to 205 MPa. These results suggested that porous β-Si₃N₄ ceramics with controlled porosity and mechanical properties could be obtained from fibrous α -Si₃N₄ particles with appropriate particle size through ball milling treatment.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 51302208), and by the Fundamental Research Funds for the Central Universities (Grant No. xjj2013110).

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