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Synthesis and evaluation of anisotropic porous silicon nitride

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Abstract

Anisotropic porous silicon nitride (Si_3N_4) was synthesized by using whiskers or seed crystals via tape casting. Evaluation of mechanical properties was performed in both directions parallel to and perpendicular to the grain alignment of anisotropic porous silicon nitride. In the parallel direction to the grain alignment, the fracture energy ranged from 300 to 500 J/m^2 in the porosity range below 20%. High fracture toughness above 17 MPa m$^{1/2}$ as well as high strength above 1.5 GPa was attained in the porosity range below 5%. The existence of pores around the aligned fibrous grains causes crack deflection. Crack deflection resulted in promoting debonding between the interlocking fibrous grains and increase of total numbers of the grains contributing to the toughening. Bridging the crack and /or pullout of aligned grains drawn apart without breaking caused increase of sliding resistance contributing large fracture energy. In the perpendicular direction to the grain alignment, tilted fibrous grains give rise to almost the same mechanisms of toughening.

Keywords: Mechanical properties; Porosity; Seeds; Si_3N_4; Tape casting

1. Introduction

A number of studies have been conducted to improve the fracture toughness of silicon nitride (Si_3N_4).[1–7] Based on the incorporation of secondary phase with anisotropic shape, Hirao et al.[8] developed highly anisotropic Si_3N_4 with aligned fibrous grains, which had high fracture toughness, ~11 Mpa m$^{1/2}$ as well as high fracture strength, ~1100 MPa when a stress was applied parallel to, or a crack extended normal to, the grain alignment. Shigegaki et al.[9] developed a porous Si_3N_4 with a porosity of 14.4% where the fibrous silicon nitride grains were uniaxially aligned; this material has a high fracture strength, ~1080 MPa, as well as a low elastic modulus, 246 GPa. Moreover, fracture energy of this porous Si_3N_4 was ~500 J/m^2, which is ~7 times larger than that of dense Si_3N_4 where fibrous grains were randomly oriented.[10] Introduction of anisotropic grains and pores caused crack deflections and enhanced debonding between interlocking fibrous grains, which lead to increase of drawn-out grains being unbroken.

The purpose of this study is to investigate the relationship between porosity and mechanical properties of anisotoropic porous silicon nitride in both directions parallel to and perpendicular to the grain alignment as well as the effects of pores to the mechanical properties.

2. Experimental procedures

2.1. Materials

Porous silicon nitride was fabricated by almost the same method as reported elsewhere,[9] except for using different starting material, seed crystals.[10] Briefly describing the procedure, seed crystals were mixed with additives of 5 wt.% Y_2O_3 and 2 wt.% Al_2O_3. Whiskers were also used as starting material for comparison. The green sheets formed by tape casting were stacked and bonded under pressure at 120 °C. Sintering was performed at 1850 °C for 6 h under nitrogen pressure of 0.9 MPa.

2.2. Fracture testing

Three-point flexural strength measurements were performed at room temperature (RT), according to JIS R1601 (Japanese Industrial Standards). Flexural test specimens for fracture energy measurement, whose

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nominal dimensions are 4.0 mm in height, 3.0 mm in width, and 35 mm in length, were cut from the sintered billets so that the tensile axis and tensile surface were parallel / perpendicular to the casting direction and the stacking plane, respectively. Details of the employed testing procedures were the same as those that had been used for a previous study.[11] The shape of the ligament was a regular triangle with an edge length of 3 mm, and the initial crack length, a_0, was 1.4 mm. The width of the chevron-notch was 0.1 mm, and the fracture testing was carried out at room temperature when three-point bending with a lower span of 30 mm at a cross-head speed of 0.01 mm/min. A bending fixture of silicon carbide was used to realize high rigidity of the testing system, which is needed for stable crack growth. The true load–displacement (*L–D*) curve was determined by subtracting the compliance of the testing machine and the fixture, which was obtained in advance by an independent calibration, from the experimentally observed curve.

2.3. Fracture energy and fracture toughness

The effective fracture energy, γ_{eff}, is defined as follows:

$$\gamma_{eff} = W_{WOF}/2A \quad (1)$$

where W_{WOF} is the energy under *L–D* curve, and *A* is the area of the specimen web portion.

The fracture toughness is defined as follows:

$$K = (2E'\gamma_{eff})^{1/2} \quad (2)$$

where E' is the Young's modulus for plane strain condition, which is given by $E' = E / (1 - n^2)$ with *n* being the Poisson's ratio.

3. Results and discussion

Fig. 1 shows the schematic of the casting and laminating directions. The textures of porous Si_3N_4 with almost same porosity ~30% made of seed crystals and whisker via tape casting were shown in Fig. 2 and 3 respectively. Seen from Fig. 2, the fibrous grains were well aligned in the X–Y casting plane. Comparing Fig. 2 with Fig. 3, the textures of specimen originated with seed crystals were very similar to those of porous Si_3N_4 made of whisker. Therefore, seed crystals could be a substitute of whisker and the similar texture to that of porous Si_3N_4 made of whisker was successfully fabricated by using seed crystals.

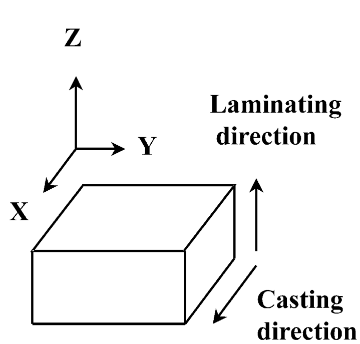

Fig. 1. Schematic of the casting and laminating direction.

Fig. 4 shows the dependencies of fracture strength and fracture energy on porosity in the parallel direction to the grain alignment of the porous silicon nitride. The fracture strength became larger as the porosity decreased as reported.[12] In the porosity range below 5%, the strength attained above 1.5 GPa. This value was almost comparable to that of anisotropic dense silicon nitride prepared by superplastically forging technique.[13] When fibrous grains were aligned, pores around the grains promoted debonding between interlocking fibrous grains without broken. Therefore, even small amount of pores enhanced the grain bridging improving the strength when fibrous grains were aligned.

On the other hand, fracture energy of porous silicon nitride ranged from 300 to 500 J/m^2 in the porosity range below 20%. These values were considerably high compared with other studies.[13,14] Large fracture energy was mainly due to the effect of bridging crack by aligned fibrous grains and/or pullout of the grains. Promoted debonding by the existence of pores, aligned grains bridging the crack or interlocking each other were drawn apart without broken, which resulted in increase of sliding resistance. Fig. 5 shows the SEM image of the ligament area of fractured surface where fibrous grains have been pulled out, supporting this speculation. As porosity increased near to 15%, fracture energy became larger, however, fracture energy decreased monotonously in the porosity range over 15% with increase of the porosity. This drop of fracture energy is presumably due to the reduction of substantial bridging and/or pullout area.

Fig. 6 shows the dependencies of fracture strength and fracture toughness on the porosity for porous silicon nitride with aligned fibrous grains, produced via tape casting from whiskers and seeds. Fracture toughness, *K* was calculated by substituting Young's moduli of each porous silicon nitride specimen and 0.25 as the Poisson's ratio into Eq. (2). As seen from Fig. 5, high fracture toughness above 17 MPa m$^{1/2}$ as well as high strength above 1.5 GPa was attained in the porosity range below 5%. Especially, fracture toughness of a specimen with a very small porosity less than 5% exceeded that of a fully dense specimen. In general, there has been a contradictory relation between fracture toughness and fracture strength as to silicon nitride.[15,16] On the contrary, present study succeeded high fracture toughness and high strength simultaneously.

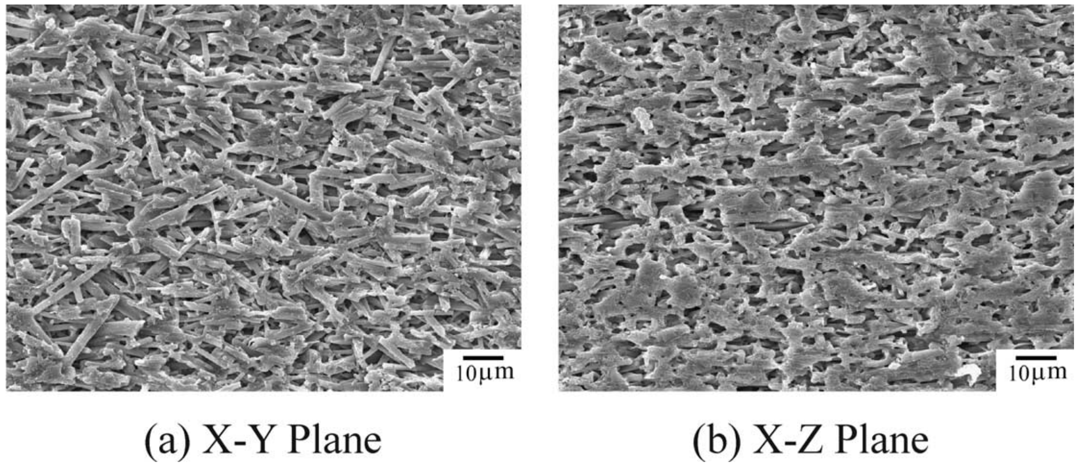

Fig. 2. SEM micrographs of polished and plasma-etched surface of porous Si_3N_4 made of seed crystals.

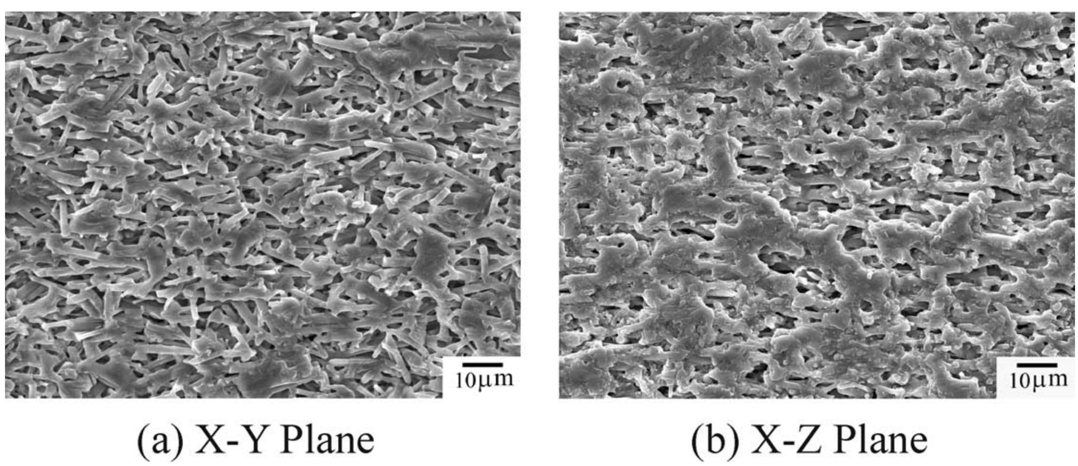

Fig. 3. SEM micrographs of polished and plasma-etched surface of porous Si_3N_4 made of whisker.

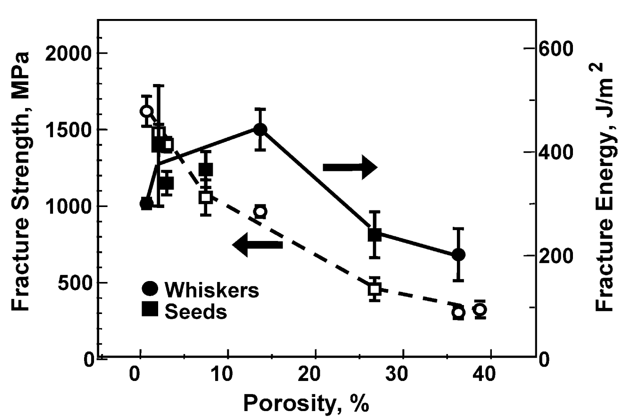

Fig. 4. Porosity dependence of fracture strength and fracture energy of PSN in parallel direction to the casting direction.

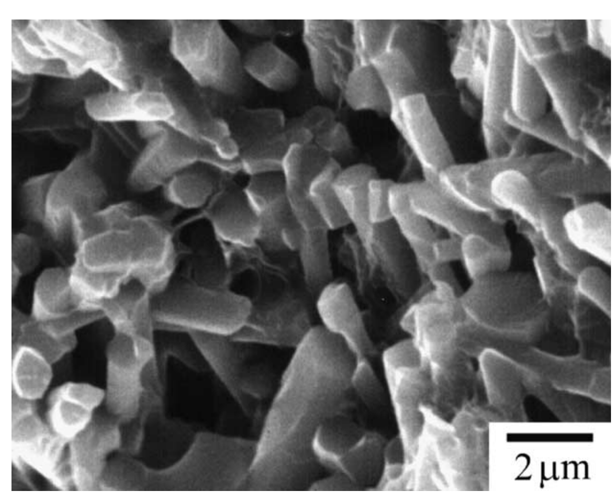

Fig. 5. SEM micrograph of fractured surface for the PSN.

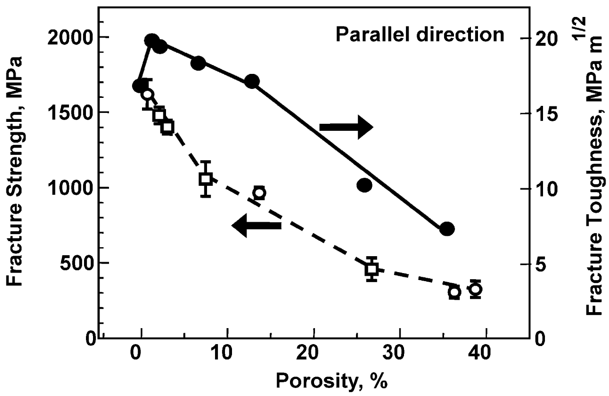

Fig. 6. Porosity dependence of fracture strength and fracture toughness of PSN in parallel to the casting direction.

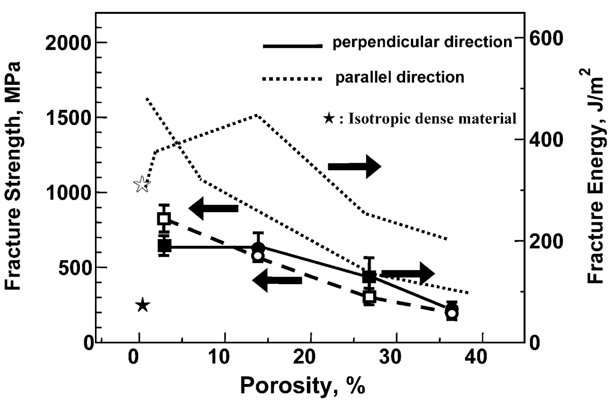

Fig. 7. Porosity dependence of fracture strength and fracture energy of PSN in parallel direction to the casting direction.

Fig. 7 shows the dependencies of fracture strength and fracture energy on porosity in the perpendicular direction to the grain alignment of the porous silicon nitride. The values of fracture strength and fracture energy in the porosity range from 0 to 35% indicate lower than that in the parallel direction, however, fracture energy was relatively high compared with that of isotropic dense material (70 J/m^2).[11] Therefore, owing to the existence of tilted fibrous grains, a wedge effect was also caused in the perpendicular direction to the grain alignment.

4. Summary

Anisotropic porous silicon nitrides were prepared by using whiskers and seed crystals. The textures of porous Si_3N_4 made of seed crystals were almost the same as those of a specimen fabricated from whisker via tape casting. Mechanical properties in both directions parallel to and perpendicular to the grain alignment of anisotropic porous silicon nitride were evaluated. In the parallel direction, high fracture toughness and high strength were simultaneously achieved by grain alignment and introducing pores. Pores around the aligned fibrous grains cause crack deflections tilting or twisting perpendicular to the alignment. Crack deflections result in promoting debonding between the interlocking fibrous grains and in increase of numbers of the grains contributing to the toughening. Bridging by aligned fibrous grains/pullout of the grains without being broken bring an increase of the sliding resistance which results in large fracture energy. Wedge effect improving properties, both in the parallel to and perpendicular to grain alignment is due to tilted grains to the casting direction.

Acknowledgements

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