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Self-reinforced silicon nitride of controlled microstructural orientation

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Silicon nitride ceramics with 0–5 wt % silicon nitride whiskers were prepared by tape casting and gas pressure sintering at 2148 K for 4 hours. The whiskers worked as seed crystals and grew into the large elongated grains. The whiskers were aligned during tape casting. Orientations of the large elongated grains in sintered samples were controlled by stacking sequence of sheets cut from the tape. Samples of each composition had three structures; unidirectional, cross-plied, and 45° rotated. Samples with the uni-directionally oriented grains exhibited anisotropy that became stronger as the whisker content increased, while samples of the other two structures did not show the anisotropy.

1. Introduction

Silicon nitride has been considered as candidate for the structural applications including automotive parts, wear resistant parts, gas turbine parts and others. It is known to have good and balanced properties such as fracture toughness, hardness, flexural strength at room temperature and at high temperature, and low density among ceramics. However, it needs to have higher reliability for wider applications. In other words, brittle and catastrophic failure, which is actually common to the ceramics, should be suppressed as much as possible. One way for increasing reliability of the ceramics is to increase the fracture toughness. Whiskers have been incorporated into the ceramic matrix composites for toughening. Becher indicated that the toughness of the composite increased as the whisker content increased [1]. However, it becomes difficult to sinter the composite with high content of the whiskers to the full density by pressureless sintering as reported by Lee and Sacks [2]. In case of the self-reinforced silicon nitride, the large elongated grains were reported to develop during sintering at high temperature [3] and to work as reinforcements like the whiskers. It does not require hot pressing for the full density.

Kawashima *et al*. [4] and Mitomo and Uenosono [5] reported that fracture toughness of the silicon nitride increased as width of the large elongated grains increased. According to Becher, fracture toughness of the silicon nitride was proportional to square root of average width of the large elongated grains. So, it is thought desirable for higher fracture toughness to have larger elongated grains. Wittmer *et al*. developed the self-reinforced silicon nitride by using the seed crystals, and obtained high fracture toughness compared with the one sintered without using the seed [6]. Grain growth behavior of the silicon nitride has attracted a lot of attention because it has been thought important for improving the fracture toughness. Petzow and Hoffmann indicated that the silicon nitride grain in the oxynitride glass liquid grew faster in length direction than in width direction until α to β phase transformation of the silicon nitride was complete [7]. Growth of the grain in length direction was hindered by the neighboring grains in polycrystalline silicon nitride. Upon impingement of the grains, small grains were to dissolve and large ones to grow. The seed crystals were bigger than the particle size of the starting powder and they were able to grow into the large elongated grains at the expense of small matrix grains. Alignment of the seed crystals is thought to reduce the chance of impingement among the large elongated grains during sintering, and to allow them to have higher aspect ratio than randomly oriented ones.

Not only size but also alignment of the large elongated grains is important for toughening silicon nitride because the number of reinforcing grains that interact with a crack is increased by aligning them normal to the crack. It is important especially for improving fracture toughness and strength of the silicon nitride at the same time because increasing the grain size by simply dispersing the seed crystals accompanied decrease in the strength as indicated by Becher [1]. Hirao *et al*. reported that they were able to increase fracture toughness and flexural strength of the silicon nitride by tape casting the slurry with the seed crystals of their own [8].

2. Experimental

87–92 wt % α silicon nitride powder (SN-E10, Ube Industries Ltd., Tokyo, Japan), 6 wt % yttria (Fine,

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H.C.Strack Co. & GmbH, Berlin, Germany), and 2 wt % alumina (AKP-30, Sumitomo Chemical Co., Osaka, Japan) were mixed by planetary ball milling. Methyl-isobutyl-ketone (MIBK), dispersant (KD1, ICI Chemical Co., Barcelona, Spain), silicon nitride balls of 5 mm in diameter (SUN11, Nikkato Corp., Tokyo, Japan) and plastic jar were used for milling. Milling stopped after 4 hours for addition of binder (polyvinyl butyral from Aldrich Chemical Co., Milwaukee, Wisconsin, USA) and plasticizer (dibutyl phthalate from Aldrich Chemical Co.). Then, milling was resumed for 3.75 hours and stopped for the whisker addition. 1–5 wt % of β silicon nitride whiskers (SN-WB, Ube Industries Ltd.) were added to the jar and then milling was resumed for 0.25 hours. For a reference sample, slurry without the whisker addition was prepared in the same way as the others. For 120 g of the ceramic ingredients, MIBK 160 cc, KD1 3.6 g, silicon nitride balls 360 g, PVB 38.4 g, and dibutyl phthalate 25.6 cc were used for preparing the slurry. The mixed slurry was vacuum treated for de-airing, and poured into the reservoir of tape casting equipment. The doctor blade was lifted up by 0.5 mm from top surface of the carrier film that was moving at 10 mm/s. Tape casting was modified by placing an array of the sharpened pins (tip diameter: 0.08 mm, stem diameter: 0.7 mm) 0.7 mm apart from each other next to the doctor blade in order to facilitate the whisker alignment parallel to tape casting direction. Tape was dried overnight in open air at room temperature. Sheets of 34 mm $\times$ 36 mm size were cut from the tape. Samples were prepared by stacking up the sheets in three ways; unidirectional, cross-plied (0°/90°), every 45° (0°/45°/90°). 50 to 55 sheets were stacked for one sample with 8 mm thickness. Lamination was carried out by lever press at 353 K under 50 MPa for 0.5 hour. Binder burn-out was performed by heating at 823 K for 10 hours in air. Heating rate was 1.5 K/hr. After binder burn-out, the samples were vacuum sealed in latex tubing and cold isostatically pressed under 250 MPa. Dimensions of the cold isostatically pressed body were measured, and then samples were sintered by gas pressure sintering under 1.7 MPa nitrogen gas pressure at 2148 K for 4 hours. Powder bed consisting of 40 wt % boron nitride (A01, H.C.Starck Co. & GmbH) and 60 wt % silicon nitride was used for the sintering.

Sintered density of sample was measured by water immersion method. Dimensions of the sample were measured in three directions, i.e. parallel to and normal to tape casting direction in tape casting plane and in lamination direction, by micrometer (accuracy: 0.01 mm) in order to obtain the shrinkage. Samples were ground and polished to 1 μm diamond slurry. The three point flexural strength of sample was measured by using 3 mm $\times$ 4 mm $\times$ 20 mm dimensions. Lengths of cracks generated by Vickers indentation under 196 N were measured in the two directions (parallel and normal to the casting direction), and were used for obtaining the fracture toughness according to Evans and Charles' equation [9]. Microvickers hardness under 9.8 N was also measured. Fracture surface of sample after the three point flexure test was examined by scanning electron microscopy (SEM).

3. Results and discussion

Samples exhibited densities higher than 98.5% theoretical after the gas pressure sintering. There was no noticeable effect of the whisker content or the sample structure (unidirectional, cross-plied and 45° rotated) on the sintered density. Fig. 1 shows the shrinkage values of samples with 0% and 5 wt % whiskers. Sample without the whisker did not exhibit the shrinkage anisotropy in tape casting plane while the shrinkage was bigger in lamination direction than in the other two directions. Samples with the whiskers also exhibited the biggest shrinkage in lamination direction than in any of the other two directions. Sample with unidirectionally oriented whiskers exhibited the shrinkage anisotropy in tape casting plane; the shrinkage normal to tape casting direction was bigger than that parallel to the direction. It implies that the whisker inhibited the shrinkage parallel to its long axis. For cross-plied samples and 45° rotation samples, the whisker orientation was changed as it went from bottom to top of the sample, and the shrinkage anisotropy observed from the unidirectional sample disappeared. It is interesting to note that cross-plied samples and 45° rotation samples were sintered to the full density without any trouble in spite of big difference in the shrinkage behaviors of neighboring sheets. Fig. 2 shows the three point flexural strength values of samples. Sample without the whisker was considered as the reference sample. The strength of reference

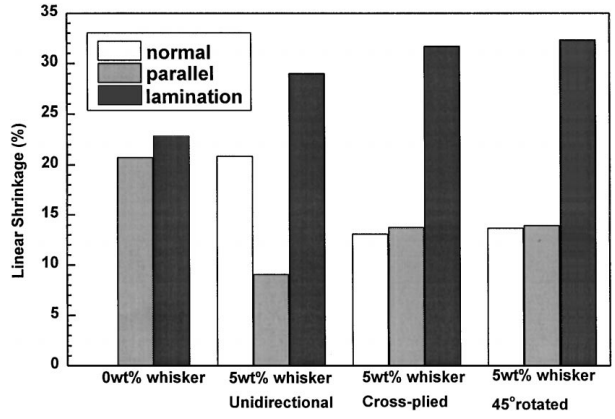

Figure 1 Linear shrinkage of samples after gas pressure sintering at 2148 K for 4 hours; normal-normal to the casting direction, parallel-parallel to the casting direction, and lamination-lamination force direction.

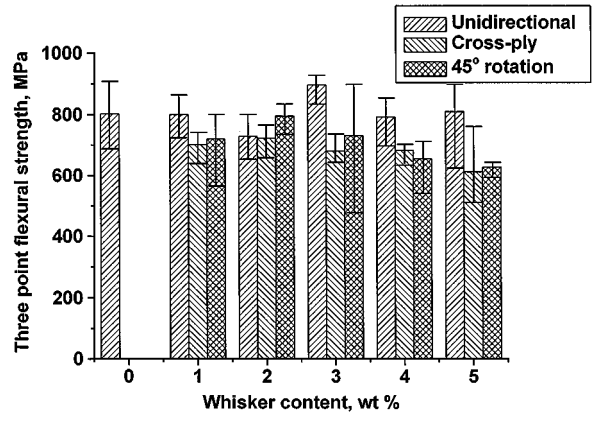

Figure 2 The three point flexural strength values of samples; error bar represents maximum and minimum of data.

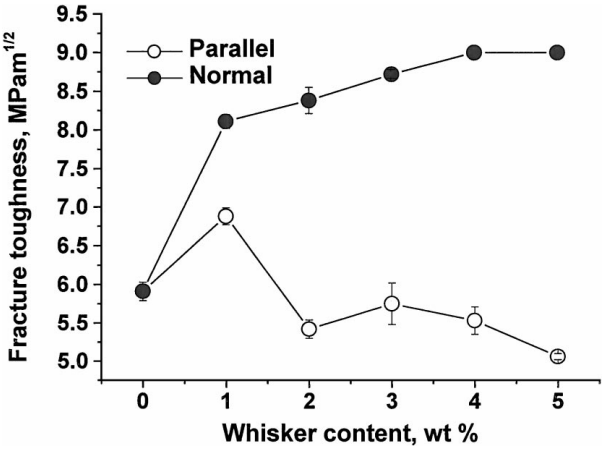

Figure 3 Variation of the fracture toughness of samples with the unidirectionally oriented whiskers; parallel and normal represent parallel to and normal to tape casting direction, respectively.

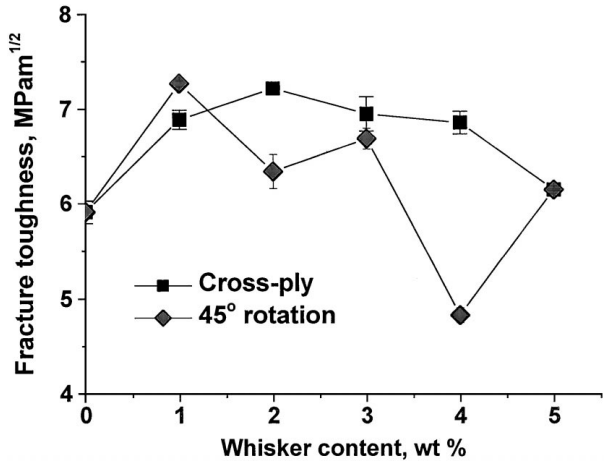

Figure 4 Variation of the fracture toughness of the cross-plied samples and the 45° rotation samples according to the whisker content.

sample was 803 MPa. Samples with the unidirectionally oriented whiskers exhibited the flexural strength comparable to that of the reference sample. Samples of the other two structures showed lower strength than the reference sample, and their strength slightly decreased as the whisker content increased. According to Bhatt's report on the silicon nitride composites reinforced with silicon carbide fibers, the strength of cross-plied composite was lower than that of unidirectional sample [10]. So, lower strength of the cross-plied and 45° rotation samples originated from the structure. Fig. 3 shows variation of the fracture toughness in the two directions on tape casting plane of sample with the unidirectionally oriented whiskers. Microhardness values were 13.77 ± 0.25, 14.83 ± 0.25, 14.60 ± 0.23, 14.6 ± 0.28, 15.17 ± 0.28, and 14.16 ± 0.26 GPa for samples without the whisker addition, with 1, 2, 3, 4 and 5 wt % whisker addition, respectively. The fracture toughness values in tape casting direction were lower than those normal to the direction. As the whisker content increased, the difference between the fracture toughness values parallel to and normal to the casting direction increased. The fracture toughness of sample with 1 wt % whiskers parallel to the casting direction was higher than that of the reference sample. It was suspected to result from the fact that the sample did not have as well aligned microstructure as the others with higher whisker content. Fig. 3 strongly suggests that the crack propagated along grain boundary of the large elongated grains while it experienced difficulty in advancing against the reinforcements. When the crack met the grain at high angle, it was reported to have very limited debonded length [11]. According to Becher [1], the fracture toughness increased with the debonded length. Based on the above two reports, it was expected that the fracture toughness normal to the casting direction was low. However, Fig. 3 reveals that the fracture toughness normal to the casting direction of samples with the whisker addition was much higher than that of the reference sample. Therefore, the high fracture toughness normal to the casting direction can not be explained by individual deonded length generated by interaction between the crack and grain. There was a big difference in the numbers of reinforcing grains that interacted with the two cracks. The crack normal to the long axis of the grain met approximately its aspect ratio times as many grains as the crack parallel to the axis, which might explain why the former resulted in higher fracture toughness than the latter as shown in Fig. 3. It is readily recognized from Fig. 3 that the average of the two fracture toughness values of each composition was higher than that of the reference sample and varied little from 7.1 MPam$^{1/2}$ when the whisker content was more than 2 wt %. Fig. 4 shows the fracture toughness values on the casting plane of the cross-plied samples and the 45° rotation samples. The fracture toughness anisotropy observed from the unidirectional samples was absent from the samples shown in Fig. 4. The fracture toughness of samples shown in Fig. 4 varied between 6.15 and 7.26 MPam$^{1/2}$ except for the value obtained from sample of 45° rotation structure with 4 wt % whiskers. The reason for the low fracture toughness value of 45° rotation structure with 4 wt % whiskers was not clear at this point. Since the crack is actually two dimensional object, it interacted not only with surface layer of one orientation but also with subsurface layers that were oriented 45° or 90° off the surface layer orientation. Fig. 5 schematically shows the situation. The crack

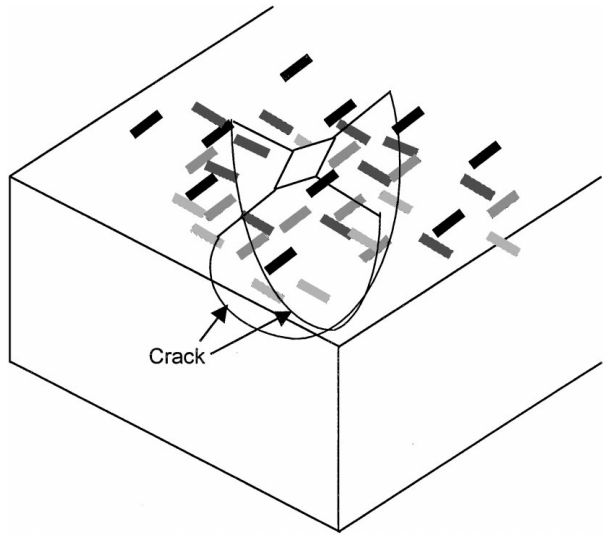

Figure 5 Schematic diagram for the indentation cracks on sample of cross-plied structure; whiskers of lighter contrast were present at deeper layer from the surface.

easily propagated along the grain boundary in one layer and experienced a strong resistance from the large elongated grains in the neighboring layers at the same time, or vice versa. So, difference in the two crack lengths was no longer present. Each layer was about 70 μm thick and the crack length measured was about 170 μm.

Fig. 6 shows SEM micrographs of fracture surface of the samples. The reference sample consisted of fine needle-like grains and a few large grains of 3–4 μm in width and more than 30 μm in length as indicated by the arrow near the top of Fig. 6a–c showed fracture surfaces of unidirectional sample and cross-plied sample with 3 wt % whiskers, respectively. Since the large elongated silicon nitride grains were actually hexagonal prisms and fracture occurred normal to their c-axis, their fracture surfaces appeared as hexagons as shown in Fig. 6b. The large elongated grains were larger in Fig. 6b and c than those shown in Fig. 6a. Whiskers initially 0.6 μm wide and 10.5 μm long [12] grew into the large elongated grains shown in Fig. 6b and c. Fig. 6b shows that the large elongated grains were aligned normal to the plane of view, which implies that the whiskers were aligned during tape casting. Fig. 6c shows that the large elongated grains in left half of the micrograph were aligned normal to the plane of view and those in the right half lay in the plane of view. Lamination direction was indicated by the arrow in the figure. Orientations of the large elongated grains in the two neighboring layers were normal to each other. Fig. 7 shows the fracture surface of 45° rotation sample with 5 wt % whiskers. As indicated by the diagrams in the left, orientation of the large elongated grains varied from 0° to 180° in 5 layers. There was no noticeable defects at the interface between the layers, and fully dense silicon nitride with the large elongated grains of controlled orientation was successfully fabricated by the tape casting method and gas pressure sintering.

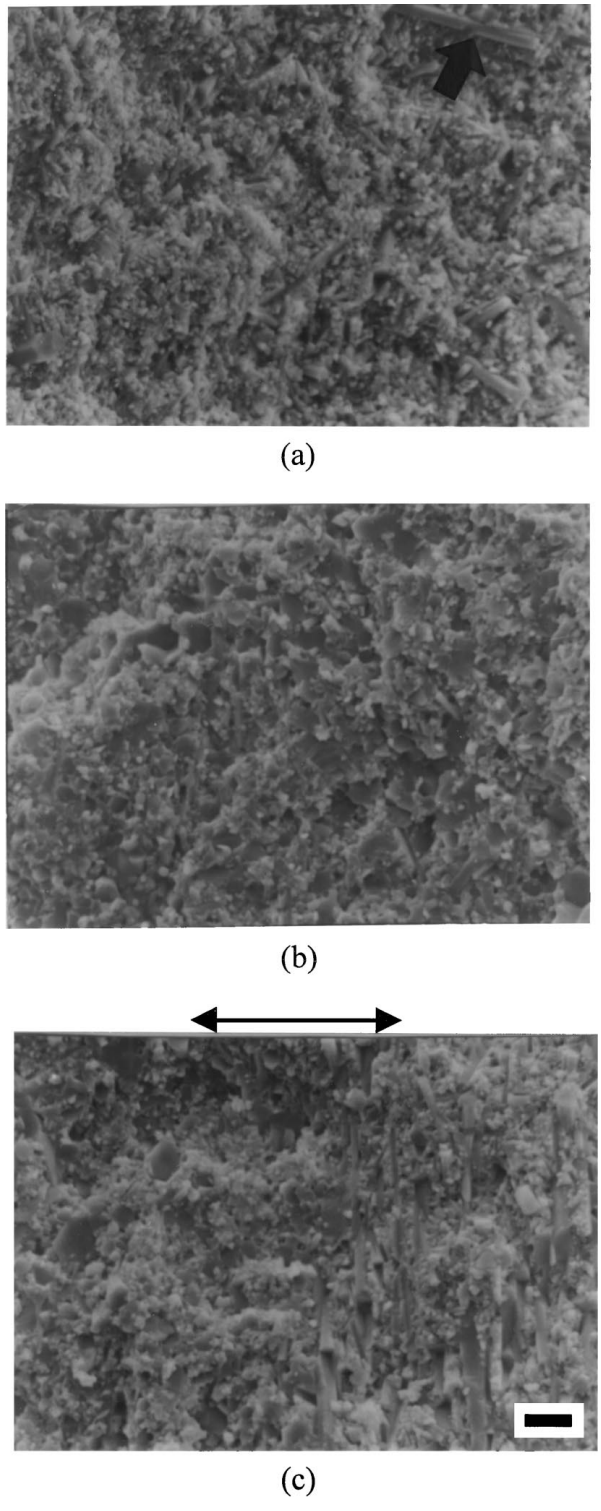

Figure 6 SEM micrographs of the fracture surfaces of (a) the reference sample, (b) unidirectional sample with 3 wt % whiskers and (c) cross-plied sample with 3 wt % whiskers; bar represents 10 μm.

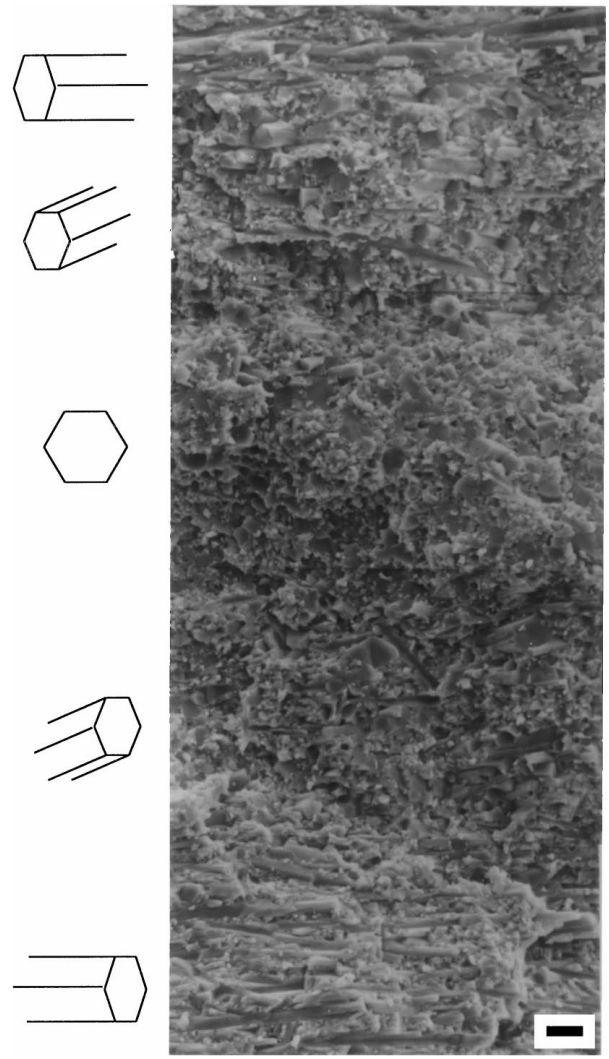

Figure 7 SEM micrograph of the fracture surface of 45° rotation sample with 5 wt % whiskers; bar represents 10 μm.

4. Conclusions

Silicon nitride with the large elongated grains of controlled orientation was prepared by tape casting of the slurry containing the silicon nitride whiskers and gas pressure sintering. The silicon nitride whiskers worked as seed crystals, and alignment of the large elongated grains was accomplished by aligning the whiskers. According to stacking sequence of the sheets cut from the tape, three kinds of samples were prepared; unidirectional, cross-plied, and 45° rotation. Unidirectional sample exhibited anisotropy of the shrinkage and the indentation crack length, which increased as the whisker content increased. The anisotropy disappeared from cross-plied samples and 45° rotation samples. Microstructural observations through SEM as well as the sintered density showed that there was no difficulty in densification of the cross-plied samples and the 45° rotation samples in spite of large difference in the shrinkage behaviors of the two neighboring layers.

Acknowledgement

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