A modification of tape casting for aligning the whiskers

DONG-SOO PARK, CHANG-WON KIM*
Ceramic Materials Group, Korea Institute of Machinery and Materials
66 Sang-Nam-Dong, Chang-Won City, Kyong-Nam, South Korea
E-mail: pds1590@kmail.kimm.re.kr

Tape casting was modified in order to align the silicon nitride whiskers in the silicon nitride slurry. Based on a simplified fluid dynamics model, it was understood that torque for aligning the whisker was increased by n^2 times by dividing the flow into n narrow ones. Samples with 3 wt % silicon nitride whiskers of a hexagonal crystal structure were prepared by using three different tape casting methods; conventional tape casting, tape casting modified by using an array of razor blades, and tape casting modified by using an array of sharpened pins. The razor blades of 13 mm in length were 5 mm apart from each other in the array, and the sharpened pins of 0.08 mm in diameter 0.7 mm apart from each other in the array. Samples were fully densified by gas pressure sintering. Both the sintering shrinkage anisotropy and X-ray diffraction analysis showed that the sample prepared by employing the pins had the best whisker alignment among the three samples.

1. Introduction

Whiskers have been used as reinforcements for ceramic matrix composites. They increased the fracture toughness through interaction with the crack. Faber and Evans suggested a crack deflection mechanism for the toughening [1], and Becher *et al.* a crack bridging mechanism [2]. According to Faber and Evans [1], as the aspect ratio of the rod-like reinforcement increased, the crack deflection angle increased. Increase in the deflection angle resulted in an increase of the fracture toughness. Becher *et al.* reported that the debonded length of the reinforcing grain decreased as angle of incidence of the crack increased [2]. Decrease of the debonded length resulted in decrease of the fracture toughness. However, aligning the rod-like grains normal to crack propagation direction can maximize the number of those grains that interact with the crack, and both the crack deflection model and the crack bridging model indicate that the fracture toughness increases as the amount of the reinforcing phase increases. So, the fracture toughness can be maximized by aligning the rod-like grains.

Kragness *et al.* prepared alumina composites reinforced with aligned silicon carbide whiskers by using the tape casting technique [3]. They noticed that the properties of the composite became highly anisotropic as the whisker content increased. Wu and Messing also fabricated mullite composites reinforced with silicon carbide whiskers by using tape casting [4]. They quantified the degree of whisker orientation by using the parameter based on relative intensity of X-ray peak diffracted from the basal plane of the whiskers with respect to sum of all the peak intensities. They noticed that whiskers exhibited a higher degree of orientation as the tape casting speed increased. They ascribed orientation of the whiskers to the shear stress that increased as the tape casting speed increased. Farkash and Brandon employed the slip extrusion technique for aligning silicon carbide whiskers in silicon nitride or alumina matrix by using a syringe fitted with the needle [5]. They mentioned that optimum whisker alignment was accomplished when the length-to-diameter ratio of the needle was large, viscosity of the slip low and extrusion speed high. Goto and Tsuge measured mechanical properties of silicon nitride ceramics reinforced with unidirectionally oriented silicon carbide whiskers that were prepared by extrusion and hot pressing method [6]. They observed that the flexural strength and the fracture toughness of the composites with the aligned whiskers were higher than those of hot pressed samples with the randomly oriented whiskers. Muscat *et al.* extruded silicon nitride slurry containing silicon nitride whiskers [7]. They noticed that the whiskers were aligned by extrusion and preferentially grew into the large elongated grains during sintering. Hirao *et al.* reported anisotropic thermal conductivity of the silicon nitride with the aligned large elongated grains that grew from the seed crystals [8]. According to them, the thermal conductivity increased rapidly in the beginning, but it became saturated after a long annealing treatment. It is interesting to note that the ratio of the thermal conductivity values in the two directions (parallel and

* Graduate student, Dept. Material Science and Engineering Pukyong Nat'l Univ.

normal to the large elongated grains) increased very slowly compared with the thermal conductivity itself as the annealing treatment went on.

In this study, a simple model for fluid dynamics of tape casting is constructed, and silicon nitride samples with 3 wt % silicon nitride whiskers were prepared by three different tape casting methods in order to find a way based on the model to obtain better aligned microstructure. Also, the effect of sintering temperature on the degree of microstructural alignment was examined.

2. Model

Assume that the slurry containing the whiskers shows a fully developed flow and behaves like a Newtonian fluid. Fig. 1 shows schematic diagrams for the flows. It is widely recognized that a steep velocity profile develops under the doctor blade due to the narrow opening through which the slurry is carried by the film. The velocity distribution is much smoother in the tape width direction than under the doctor blade due to the much larger opening as shown in Fig. 1a. The situation is similar to the flow between two parallel plates that was described by Geiger and Poirier [9]. For the wide flow,

$$V_x = C\left[y^2 - \left(\frac{W}{2}\right)^2\right], \tag{1}$$

where $V_x =$ velocity in tape casting direction, $C =$ shape constant, $y =$ position in width direction measured from the center and $W =$ width of tape. The flux of the slurry under the doctor blade can be expressed as

$$J_x = \frac{1}{W}\int_{-W/2}^{W/2} V_x \, dy, \tag{2}$$

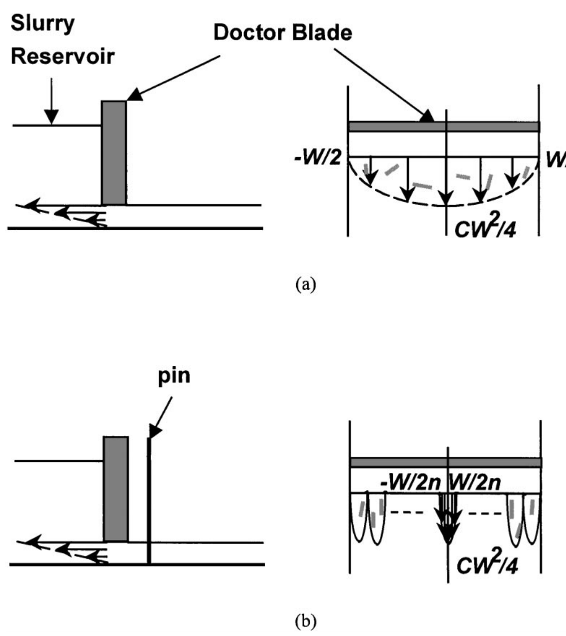

Figure 1 Schematic diagrams for slurry flow during tape casting: (a) Conventional tape casting; (b) tape casting modified by dividing the flow into *n* narrow ones.

where $J_x =$ the flux in the tape casting direction. When the flow is divided into n narrow ones as shown in Fig. 1b, the velocity distribution in each narrow flow is expressed as

$$V'_x = C'\left[y'^2 - \left(\frac{W}{2n}\right)^2\right], \tag{3}$$

where $V'_x =$ velocity in the tape casting direction, $C' =$ shape constant, $y' =$ position in width direction within one narrow flow and $W =$ width of tape. The flux of the slurry under the doctor blade can be expressed as

$$J'_x = \frac{n}{W}\int_{-W/2n}^{W/2n} V'_x \, dy', \tag{4}$$

where $J'_x =$ the flux in the tape casting direction. The two fluxes should be equal.

$$J_x = J'_x \tag{5}$$

So,

$$C' = n^2 C, \tag{6}$$

And

$$V'_x = n^2 C\left[y'^2 - \left(\frac{W}{2n}\right)^2\right] \tag{7}$$

In other words, the slope of the velocity distribution curve is increased by n^2 times by dividing the flow into n narrow ones, and the maximum velocity is the same for the two flows. The shear stress can be expressed as

$$\tau_{yx} = \eta\left(\frac{dV_x}{dy}\right), \tag{8}$$

where $\tau_{yx} =$ shear stress and $\eta =$ viscosity of the slurry. The torque that rotates the whisker is generated by the difference in the shear stresses at the two end points, and can be expressed as

$$M = \eta\left[\left(\frac{dV_x}{dy}\right)_{y+\delta y} - \left(\frac{dV_x}{dy}\right)_y\right]\delta y, \tag{9}$$

where $M =$ torque and $\delta y =$ projection length of the whisker on the line normal to the tape casting direction.

From Equations 3, 7 and 9, it is understood that the torque in the narrow flow is n^2 times as high as that in the wide flow.

3. Experimental procedures

Samples were prepared by tape casting of slurry containing 90 wt % α-Si_3N_4 powder (SN-E10, Ube Industries Co., Ltd., Tokyo, Japan), 5 wt % Y_2O_3 powder (Fine, H.C.Starck Co. & GmbH, Berlin, Germany), 3 wt % β-Si_3N_4 whiskers (SN-WB, Ube Industries Co., Ltd.) and 2 wt % Al_2O_3 powder (AKP30, Sumitomo Chemical Co., Osaka, Japan). The slurry was prepared as follows. The powders except the whiskers were mixed for 4 h by using planetary ball mill. Methyl isobutyl ketone (MIBK), silicon nitride balls of 5 mm in diameter (SUN11, Nikkato Corp., Tokyo, Japan), plastic jar and dispersant (KD1, ICI Chemical Co, Barcelona, Spain) were used for mixing. After 4 h mixing, poly(vinyl butyral) (Aldrich Chemical Co., Milwaukee, WI, USA) and dibutyl phthalate (Aldrich Chemical Co.) were added to the jar, and milling was resumed for 3.75 h. Then, β-Si_3N_4 whiskers were added to the jar and milling was resumed for 0.25 h. For 120 g of the ceramic ingredients, MIBK 160×10^{-6} m^3, KD1 13.6 g, Si_3N_4 balls 360 g, PVB 38.4 g, and dibutyl phthalate 25.6×10^{-6} m^3 were used for preparing the slurry. The slurry was vacuum treated for de-airing and then poured into the slurry reservoir of the tape casting equipment. The Doctor blade was lifted up by 0.45 mm from the bottom and tape casting speed was 10 mm/s. The tape was 150 mm wide. Sample A was prepared by conventional tape casting. Sample B was prepared by placing an array of blades 5 mm apart from each other at the exit of the reservoir and the tape casting the slurry. Sample C was prepared by using an array of sharpened pins 0.7 mm apart from each other at the exit of the slurry reservoir in order to facilitate whisker alignment. Schematic diagrams for the shape of the pin and the blade were shown in Fig. 2. The tape was dried overnight in open air at ambient temperature.

Sheets of 36×34 mm size were cut from the tape, and were laminated at 353 K under 50 MPa for 30 min. Lamination of samples A, B and C was carried out in such a way that the sheets were parallel to each other. Sample D was prepared by stacking up the same sheets as for sample C in cross-ply fashion. Binder removal was accomplished in open air at 823 K for 10 h. The heating rate for the binder removal process was 1.5 K/h. After binder removal, the samples were cold isostatically pressed under 250 MPa. Samples were densified by gas pressure sintering at 2148 K and at 2273 K for 4 h under 2 and 3 MPa nitrogen gas pressure, respectively. Sintering shrinkage was obtained by measuring the dimensions of the sample before and after gas pressure sintering. The sintered density of sample was measured by the water immersion method. X-ray diffraction (XRD) was performed on the surfaces of the sample in order to examine how microstructure was aligned; tape casting surface (T), surface normal to tape casting direction (P), and lamination surface (N). Sintered samples were etched by molten (NaOH + KOH) salt at 623 K and examined by scanning electron microscope (SEM).

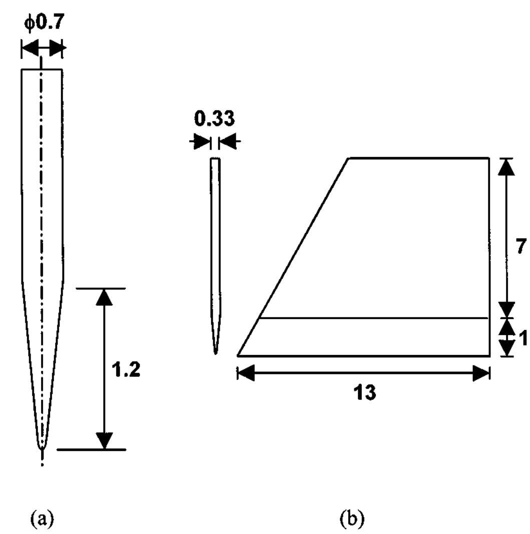

Figure 2 Schematic diagrams for (a) the sharpened pin and (b) the blade: tip diameter of the pin was 0.08 mm and edge width of the blade was 0.03 mm; unit: mm.

4. Results and discussions

All the samples exhibited higher than 99% of theoretical density after gas pressure sintering. Fig. 3 shows that the shrinkage of the sample varied according to the direction of measurement. All the samples exhibited the highest shrinkage in the thickness direction. The shrinkage of samples A, B and C normal to the tape casting direction was bigger than that parallel to the direction, while sample D exhibited almost the same shrinkage in the two directions. Among samples A, B and C, the shrinkage anisotropy increased in the order A < B < C. As the sintering temperature increased, the shrinkage anisotropy of samples A, B and C increased slightly and the two shrinkage values of sample D became very close to each other in the tape casting plane. Shrinkage in the thickness direction increased as the temperature increased.

Fig. 4 shows XRD patterns from the surfaces of sample C. It is readily recognized that the microstructure

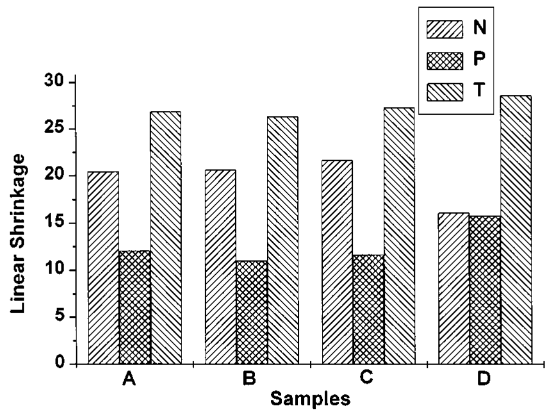

Figure 3 Linear sintering shrinkage of samples sintered at 2148 K; N-normal to the casting direction, P-parallel to the direction and T-Stacking direction.

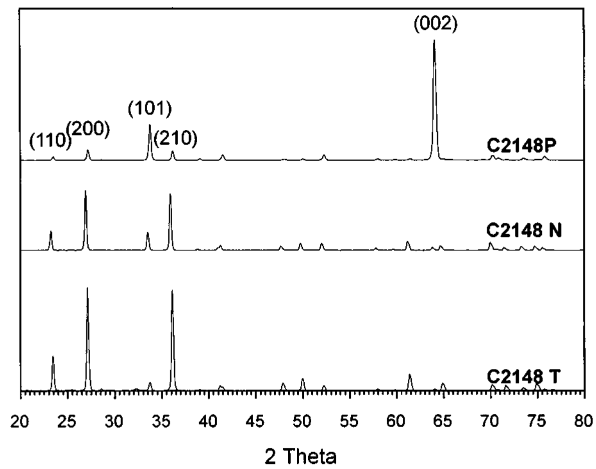

Figure 4 XRD patterns of sample C sintered at 2148 K; C2148T, C2148N and C2148P represent the patterns from surfaces T, N and P, respectively.

was highly anisotropic. Patterns from the three surfaces showed that the tape surface had the strongest (2 0 0) and (2 1 0) peaks while the surface normal to the tape casting direction had the strongest (0 0 2) peak. The (2 0 0) and (0 0 2) peaks represent the prismatic plane and the basal plane of the hexagonal prism of the silicon nitride grain, respectively. It is interesting to note in Fig. 4 that the intensity of the (1 0 1) peak increased when that of the (0 0 2) peak increased. The (1 0 1) plane makes about 23° with the basal plane, and the peak represents the grains slightly off the alignment. Comparison of patterns C1875T and C1875N revealed that almost all the large elongated grains were lying in the tape while a small fraction of them were off the alignment within the tape. Since the large elongated grains grew from the whiskers, their alignment in the sintered sample represented alignment of the whiskers during tape casting. Because both the XRD patterns in Fig. 4 and the sintering shrinkage shown in Fig. 3 were closely related to the microstructure of the sample, they should be related to each other. When the whiskers were well aligned, the shrinkage normal to the alignment direction (N or T direction) should be large and that parallel to the direction (P direction) small. Meanwhile, if the large elongated grains were well aligned, the intensity of the (0 0 2) peak of the XRD patterns from surface N and surface T should be weak and that from surface P strong. For sample C sintered at 2148 K, the shrinkage values were 21.67%, 11.66% and 27.3% for N, P and T directions, respectively. The relative intensity values from surfaces N, P and T that were obtained by dividing the intensity of the (0 0 2) peak by the sum of the intensities of 11 major peaks of the pattern were 1.2%, 57.8% and 0.5%, respectively. So, the two sets of data proved that the shrinkage and the XRD peak intensity were closely related.

Fig. 5 shows XRD patterns from the surface normal to the tape casting direction of different samples. Since the patterns were adjusted to have the same intensity for the (1 0 1) peaks, comparison of (0 0 2) peaks revealed which sample had better aligned microstructure.

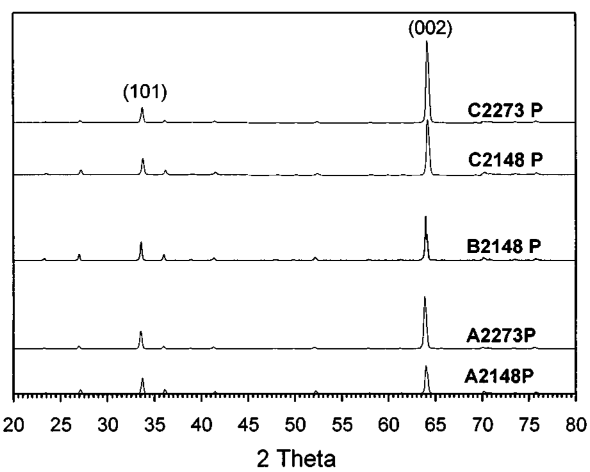

Figure 5 XRD patterns from surface P of samples; A2148P—sample A sintered at 2148 K, A2273P—sample A sintered at 2273 K, B2148P—sample B sintered at 2148 K, C2148P—sample sintered at 2148 K, C2273P—sample sintered at 2273 K.

Among samples sintered at 2148 K, sample C had the strongest (0 0 2) peak and sample A the weakest. The relative intensity values were 44.6%, 47.7% and 57.8% for samples A, B and C, respectively. Variation of the relative intensity values was consistent with that of the shrinkage shown in Fig. 3. As the sintering temperature increased to 2273 K, the relative intensities of the (0 0 2) peaks of samples A and C increased to 61.7% and 75.8%, respectively.

In order to rotate and align the whiskers parallel to the tape casting direction, torque was needed. Shrinkage anisotropy shown in Fig. 3 and the XRD patterns from the three surfaces of sample A revealed that the conventional tape casting produced a torque big enough to align a significant portion of the whiskers in the sample. Wu and Messing reported that the shear stress was increased by increasing tape casting speed which was one way to increase the velocity gradient in the slurry flow. Another way to increase the gradient was decreasing the width while the maximum velocity was kept the same. According to the model shown in Section 2, dividing the flow into n narrow ones increased the torque by n^2 times. In this study, the flow during tape casting was divided into 214 narrow ones by employing the row of pins for sample C, and the torque was increased by more than 45,000 times according to the model. In case of sample B for which the row of blades was used, the torque was increased by 900 times. Another variable to consider for aligning the whiskers was the time for which the torque was applied. In order to examine the effect of the time on the whisker alignment, sample B was prepared by employing the blades that were 13 mm long in the tape casting direction. Sample C was prepared by using sharpened pins with tip diameter 0.08 mm. Since it was suspected that the whiskers close to the carrier film were difficult to rotate and those near to the top surface of the tape were readily rotated, the time for which the whiskers close to the film were under the torque was considered. The whiskers in sample B was under the torque as much as 162 times longer than those in sample C. However, the results showed that the whisker alignment in sample C was the best among the samples although the whiskers in sample B were under the torque much longer. It implied that the torque exerted stronger influence on the whisker alignment than the time. During tape casting, the whiskers close to the carrier film were hard to move due to the constraint imposed by the film. Even though the torque was big enough to rotate the whiskers away from the film, it needed to be much bigger for rotating those close to the film. Little difference was found in the two sets of data on the sintering shrinkage and the XRD patterns of sample A and sample B revealed that the degrees of the whisker alignment in the two samples were close to each other in spite of the 900 times difference of the torque. So, it can be concluded that the torque required for rotating the whisker increased very rapidly within a layer close to the film and that fine division of the flow during tape casting as in sample C was needed for noticeable improvement in the whisker alignment.

Fig. 6 shows SEM micrographs of the fracture surfaces of samples. The fracture surface was normal to

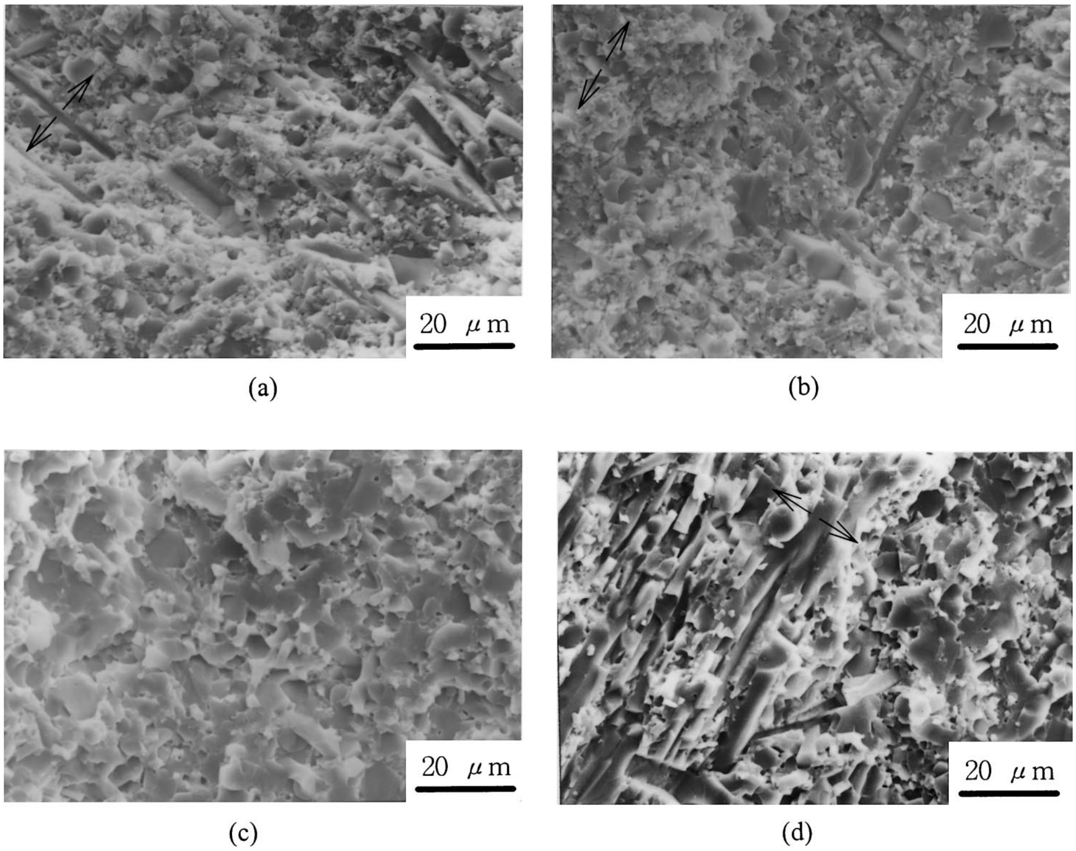

Figure 6 SEM micrographs of the fracture surface of samples: (a) Sample A sintered at 2148 K; (b) sample C sintered at 2148 K; (c) sample C sintered at 2273 K; (d) sample D sintered at 2273 K; arrow indicates direction of lamination.

the tape casting direction, and the micrograph was supposed to show the basal planes of the aligned large elongated grains. Most of the grains were aligned and the fracture surface showed many hexagons. Alignment of the grains in sample A was not as good as that in sample C as shown in Fig. 6a and b. It was noticeable that the region of misalignment in sample A shown in Fig. 6a formed a layer which was suspected to be the one close to the film. As the sintering temperature increased, fine matrix grains disappeared and the size of the large elongated grains increased as shown in Fig. 6b and c, which explains the increase of the (0 0 2) peak intensity with increase in sintering temperature as shown in Fig. 5. Fig. 6d shows the fracture surface of sample D that had cross-ply structure. The large elongated grains growing from the whiskers in the two adjacent sheets were oriented normal to each other. Since the shrinkage anisotropy resulted from the fact that the shrinkage parallel to the whisker was much smaller than that normal to it, it averaged out in sample D as shown in Fig. 3. Fig. 7 shows etched surfaces of sample A which were parallel to the tape casting plane. Even though the two micrographs were taken from the same sample, they look very different. Each sheet had a thin layer in which the whiskers were randomly oriented close to the carrier film, and the sheets were stacked to make the sample. After sintering, the sample was ground and regions of different depth within the sheet were exposed due to the uneven surface. Part of the ground surface exhibited the aligned microstructure while randomly oriented grains were exposed in the other part of it.

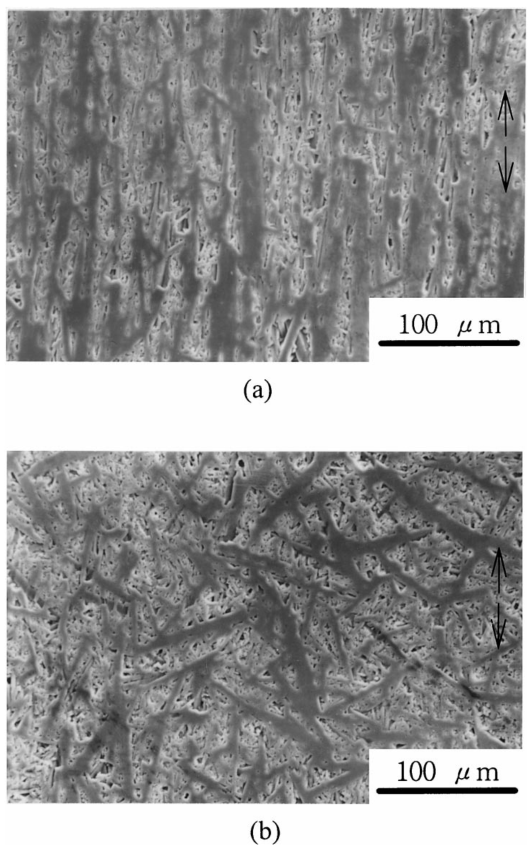

Figure 7 SEM micrographs of etched surface of sample A sintered at 2273 K: (a) Area with the aligned grains and; (b) area with randomly oriented grains; arrow indicates tape casting direction.

5. Conclusions

A simple model was constructed for the flow dynamics during tape casting. The model indicated that the torque for rotating the whiskers was increased by dividing the flow during tape casting. Silicon nitride ceramics with large aligned elongated grains were prepared by tape casting the slurry with silicon nitride whiskers in three different ways. Both the sintering shrinkage anisotropy and the XRD patterns from the three surfaces of sintered samples showed that the sample prepared by dividing the flow into more narrow ones exhibited a higher degree of alignment. The time during which the torque was applied to the whiskers did not exert as strong an influence on aligning them as the torque itself. The sintering shrinkage and the XRD patterns were closely related to the microstructure, and the sample with cross-ply structure did not show shrinkage anisotropy on the surface normal to the lamination direction.

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