The Korean Journal of Ceramics, **5** [2] 119 - 124 (1999)

Anisotropy of the Silicon Nitride Prepared by Tape Casting

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(Received May 13, 1998)

Silicon nitride ceramics with highly oriented microstructures were prepared by tape casting a slurry containing 5 wt% of the silicon nitride whiskers. The whiskers were aligned in the casting direction and worked as seeds for the grain growth. The anisotropy was observed from the sintering shrinkage, Vickers indentation crack lengths, and XRD patterns. The cracks were much longer on the surface normal to the aligned grains than on the tape casting surface where the lateral cracks were also observed. The effect of sintering additives and the annealing treatment on the indentation crack length was examined. The sample with higher silica content had longer cracks than the one with lower silica content. The crack length anisotropy increased after annealing at 2123K.

Key words : Silicon nitride, Whisker alignment, Anisotropy, Grain growth, Indentation crack length

I. Introduction

Ceramics often have been toughened by rod-like reinforcements. Faber and Evans reported that rod-like reinforcements of high aspect ratio were most effective for the toughening.[1] Toughening by the rod-like reinforcements was proportional to their amount, but it became harder to sinter the composite to full density as the amount increased. One way to alleviate the problem is to align the rod-like reinforcements. Wu and Messing reported that they were able to achieve dense mullite based composites with 50 vol.% SiC whiskers by using tape casting technique which aligned the whiskers and increased the percolation threshold.[2] Another way to increase the reinforcement content with less trouble with densification is using seed crystals that will grow during sintering. Since the amount of seed crystals is small, they do not interfere with densification and their growth into the elongated grains provided the same reinforcing effect as the whiskers. Wittmer *et al.* reported that the silicon nitride with seed crystals exhibited higher fracture toughness than the one without seeds.[3] However, they also reported that the strength decreased as the seeds were added.

Recently, silicon nitride ceramics with highly anisotropic microstructures were reported.[4-6] They exhibited not only high fracture toughness normal to the long axis of the reinforcements but also high flexural strength as reported by Hirao *et al.*[4] and Goto and Tsuge.[5] Even though they showed the excellent properties only in the specific direction with respect to orientation of the reinforcing grains, they provided a way to make full advantage of the reinforcements. Also, the effect of sintering additives as well as sintering temperature on interaction between crack and the reinforcing grains can be better understood by clearing up the obscurity caused by their random orientation.

II. Experimental Procedure

Sample A was prepared by tape casting of slip containing 88 wt% α-Si_3N_4 (SN-E10, Ube Industries Co., Ltd., Tokyo, Japan), 6 wt% Y_2O_3 (Fine, H.C.Starck Co. & GmbH, Berlin, Germany), 5 wt% β-Si_3N_4 whiskers (SN-WB, Ube Industries Co., Ltd.) and 1 wt% SiO_2 (S1061, Cerac Inc., Milwaukee, WI, USA). Sample B was prepared from 91.5 wt% α-Si_3N_4 (SN-E10), 3.5 wt% Y_2O_3 (Fine, H.C. Starck Co. & GmbH) and 5 wt% β-Si_3N_4 whiskers (SN-WB). Sample C was prepared from 88 wt% α-Si_3N_4 (SN-E10), 4 wt% Y_2O_3 (Fine, H.C. Starck Co. & GmbH), 5 wt% β-Si_3N_4 whiskers (SN-WB) and 3 wt% SiO_2 (S1061, Cerac Inc.). According to the manufacturer's information, α-Si_3N_4 powder and β-Si_3N_4 whisker contained 1.25 wt% and 0.61 wt% oxygen, respectively. The slip was prepared as follows. The powders except the whiskers were mixed for 4 hours by using a 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 hour mixing, polyvinyl butyral (Aldrich Chemical Co., Milwaukee, WI) and dibutyl phthalate (Aldrich Chemical Co.) were added to the jar, and milling was resumed for 3.75 hours. Then, β-Si_3N_4 whiskers were added to the jar and milling was resumed for 0.25 hours. For 120 g of the ceramic ingredients, 160 cc MIBK, 3.6 g KD1, 360 g Si_3N_4 balls, 38.4 g PVB, and 25.6 cc dibutyl phthalate were used for preparing the slip. The slip was vacuum treated for de-

airing and poured into the slurry reservoir of the tape casting equipment. The Doctor blade was lifted up by 0.45 mm from the bottom, and an array of sharpened pins 0.7 mm apart from each other was placed at the exit of the slurry reservoir in order to facilitate whisker alignment. The tape was dried overnight in open air at ambient temperature.

Sheets of 36 mm × 34 mm size were cut from the tape, and were laminated at 353 K under 30 MPa for 30 minutes. Binder removal was carried out in open air at 823 K for 10 h. The heating rate for binder removal process was 1.5 K/hr. After binder removal, the samples were cold isostatically pressed under 250 MPa. Samples A were densified by gas pressure sintering at 2148 K and at 2273 K for 4 hours under 2 MPa and 3 MPa nitrogen gas pressure, respectively. Samples were also hot pressed at 2093 K under 30 MPa for 1 h in flowing nitrogen atmosphere and annealed at 2123 K for 4h under 1.7 MPa nitrogen gas pressure.

The sintered density of the sample was measured by a water immersion method. X-ray diffraction was performed on the surfaces of sample A in order to examine how the microstructure was aligned relative to the tape casting surface (T), lamination surface (N), and surface normal to tape casting direction (P). Vickers indentation under 196 N load was carried out on surface T in two ways; the two cracks were parallel and normal to the alignment direction, or they were 45 degrees off the direction. Vickers indentation under the same load was performed on surface P in such a way that the two cracks were parallel and normal to lamination direction. Indentation crack lengths instead of fracture toughness values were used for characterizing the sample because the former is inversely related to the latter and confusion about the latter resulting from the equations can be avoided. Samples after indentation were etched by using molten (NaOH+KOH) salt at 623 K slightly and were observed by SEM.

III. Results and Discussion

Sample A was densified to higher than 99% theoretical after gas pressure sintering either at 2148 K or at 2273 K. The sintering shrinkage of sample A was highly anisotropic; shrinkage normal to whisker alignment direction in tape casting plane was about 22%, shrinkage parallel to the direction about 8.2%, and shrinkage in lamination direction 28.5%. The shrinkage anisotropy in tape casting plane was closely related to the microstructural anisotropy. The whiskers are single crystals and they do not shrink during sintering. The shrinkage parallel to long axis of the whisker should be smaller than that normal to it. Since the sample contained whiskers that were aligned in tape casting direction, the shrinkage in whisker alignment direction was smaller than that normal to the direction. A model for quantifying degree of microstructural alignment by using the shrinkage values was reported based on the above reasoning.[7] Fig. 1 shows the XRD patterns of sample A after gas pressure sintering. Patterns N and T consisted mainly of peaks from prismatic plane of β silicon nitride with hexagonal crystal structure, while pattern P was made up mainly of the peak from the basal plane. If the large elongated grains growing from the whiskers were perfectly aligned, patterns T and N should be the same. However, Fig. 1 shows that pattern N had a weak (002) peak while pattern T did not. The whiskers were laid down within the tape due to the shrinkage and high shear stress in tape thickness direction while some of them were slightly off the alignment in tape casting direction. The matrix grains should also contribute to the XRD peaks, but they were randomly oriented and their contribution to (002) peak intensity was negligible. It is interesting to note that (101) peak intensity varied in the same way as (002) peak intensity. The (101) plane is only 23° off the (002) plane in β-Si_3N_4 crystal. So, the grains represented by (101) plane were only slightly off the alignment. (002) peak intensity of pattern P increased from 76% to 81.4% as sintering temperature increased from 2148 K to 2273 K. The microstructure became more aligned as sintering temperature increased because the unidirectionally oriented large grains grew at the expense of randomly oriented fine matrix grains.

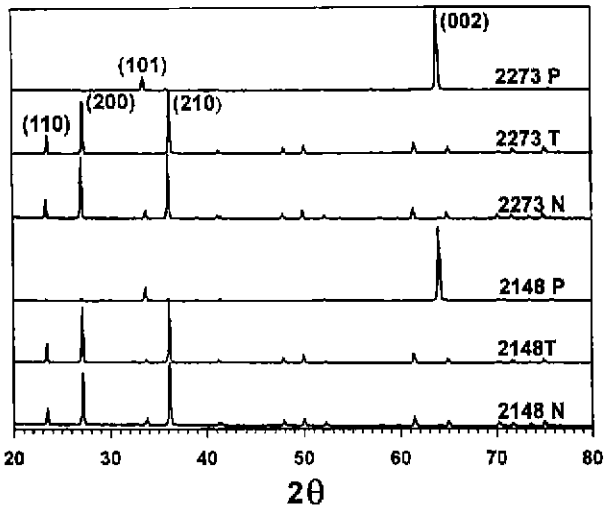

Fig. 1. XRD patterns of sample A sintered at 2148 K and 2273K; patterns are identified by sintering temperature followed by diffracting surface.

Fig. 2 shows the indentation crack lengths on surfaces T and P. The crack parallel to the whisker alignment direction on surface T was longer than that normal to the direction. It implies that the crack easily propagated along the grain boundary while its propagation normal to the large elongated grains experienced a strong resistance. According to Becher *et al.*, the debonded length that was proportional to the fracture toughness decreased as the angle between the crack and the single

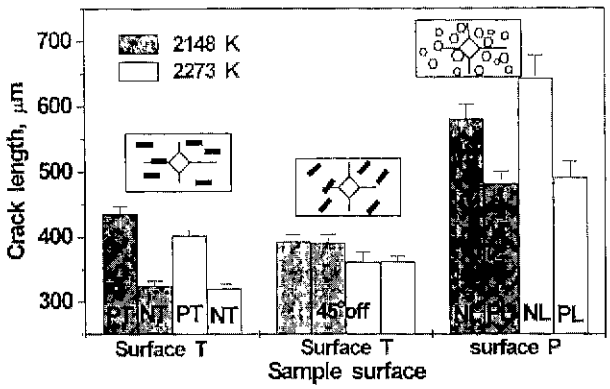

Fig. 2. Vickers indentation crack lengths on surfaces T and P; characters in the column graph represent P-parallel to, N-normal to, T-tape casting direction, L-lamination direction.

large elongated grain in the glass matrix increased.[8] Since the fracture toughness is inversely proportional to the crack length, longer crack was expected in the direction normal to the large elongated grains. However, the crack interacted with the large elongated grains more often in the normal direction than in parallel direction. The number of interacting large elongated grains is thought as one of the most important factors for determining the fracture toughness. As sintering temperature increased from 2148 K to 2273 K, length of the crack normal to the large elongated grains was not changed while that parallel to the grains seemed shortened. Also, lateral cracks were observed on surface T after etching, and they became larger as sintering temperature increased. When the indentation cracks were 45° off the alignment direction, the two cracks had the same length. This was due to the fact that the two cracks met the large elongated grains at the same angle. If the crack is semi-circular, total surface area of the two cracks that were parallel and normal to the large elongated grains is $\pi(C1^2+C2^2)/2$ where C1 and C2 are length of the long crack and the short crack, respectively For the cracks 45° off the alignment direction, total crack surface area is πC^2 where C is the crack length. Energy for generating the cracks is assumed to be the same, and then $C^2=(C1^2+C2^2)/2$. In other words, C is root mean square of C1 and C2. Measured average values of 2C1, 2C2 and 2C were 436 μm, 324 μm and 392 μm, respectively for samples sintered at 2148 K and 402 μm, 320 μm and 362 μm, respectively for samples sintered at 2273 K. So, C is close to root mean square of C1 and C2. It can be said that the crack 45° off the alignment direction was composed of the two components, parallel and normal to the direction. The lateral cracks besides the cracks 45° off the alignment direction were observed after etching and they became larger as sintering temperature increased. Crack lengths on surface P were much larger than those on surface T. It is worth mentioning that lateral cracks were not observed on surface P. The cracks on surface P longer than the ones on surface T were possibly related to the absence of the lateral cracks. In other words, all the energy for generating cracks was used for the two cracks on surface P. The crack normal to lamination direction on surface P was longer than that parallel to the direction, and it was closely related to the lateral crack on surface T. Length of the crack normal to lamination direction increased with sintering temperature, which was consistent with the fact that the lateral cracks became larger. Cracks parallel to the lamination direction were shorter than the ones normal to the direction. As described previously, the large elongated grains were laid down but some of them were off the alignment within the tape. So, while the crack normal to lamination direction met long axes of few large elongated grains, the crack propagation parallel to the direction was interfered by the grains off the alignment.

Fig. 3 shows SEM micrographs of fracture surfaces of sample A. Since fracture occurred normal to the large elongated grains, the fracture surface had many hexagons that were fracture surfaces of the grains. Sample sintered at 2148 K contained fine matrix grains and some pores. In the sample sintered at 2273 K, the large elongated grains grew and amount of fine matrix grains as well as the

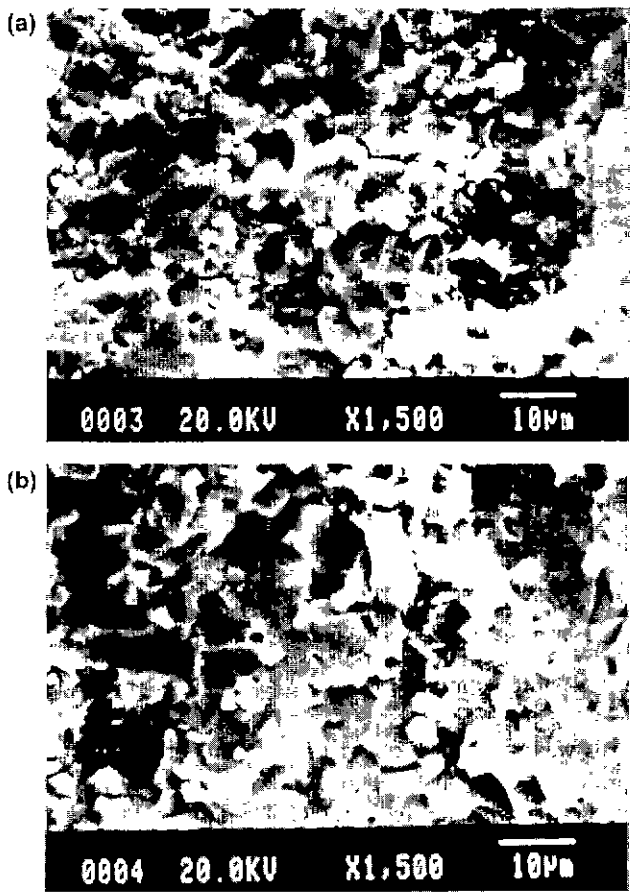

Fig. 3. SEM micrograph of sample A after flexure test; arrows indicating pores; (a) sample sintered at 2148 K and (b) sample sintered at 2273 K.

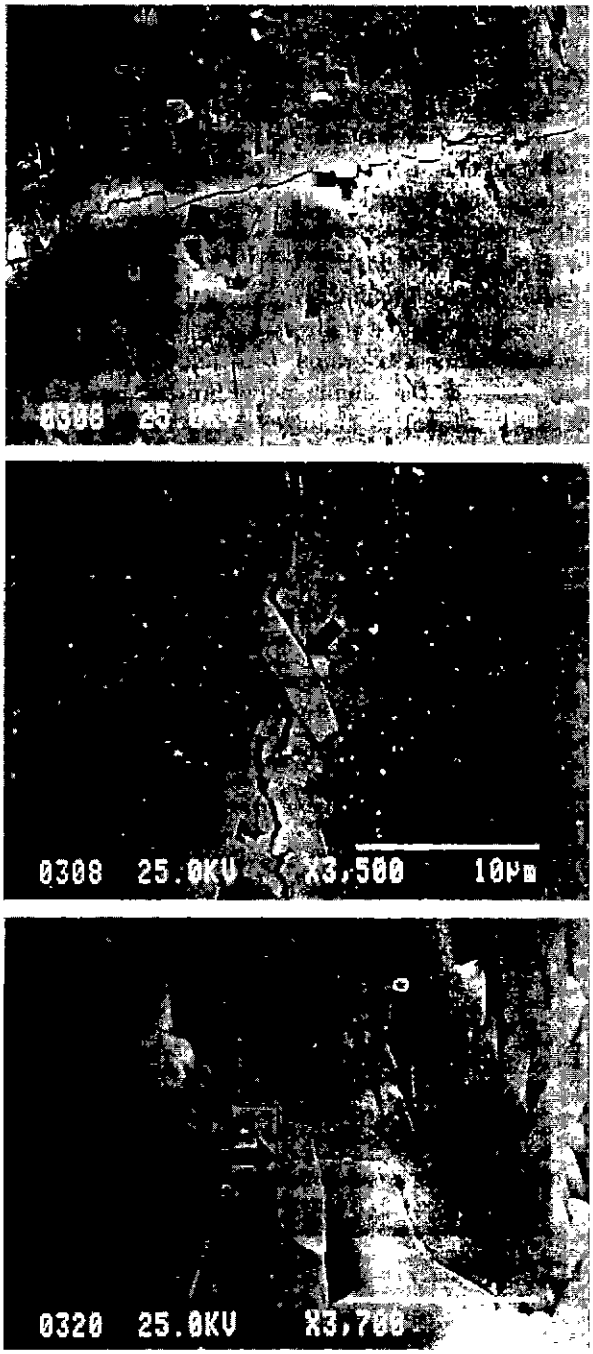

Fig. 4. SEM micrographs of the indentation cracks on surface T of sample A; (a) the crack normal to the large elongated grains, (b) the crack parallel to the grains of sample sintered at 2148 K and (c) the crack 45° off the grains of sample sintered at 2273 K.

pores was reduced. Fig. 4 shows the indentation cracks on surface T. Crack normal to the large elongated grains cut the grains with limited debonded length. This was more apparent where the larger grains were gathered as indicated by the arrow in Fig. 4(a). The crack parallel to the large elongated grains propagated preferentially along the grain boundary, but its propagation was sometimes hindered by the grains off the alignment as indicated by arrow in Fig. 4(b). It shows the bridging grain with much longer debonded length than any debonded length shown in Fig. 4(a). The angle between the crack and the large elongated grain was much smaller in Fig. 4(b) than in Fig. 4(a). So, the debonded length of individual large elongated grain was longer when the angle of incidence was smaller, which is consistent with Becher *et al.*[8]. Fig. 4(c) shows the crack 45° off the alignment. It is interesting to note that the crack often cut the large grain at 45° while it cut smaller grains at right angle as indicated by the arrows. Extensive debonding and crack bridging were observed around the smaller grain indicated by the arrow. Fig. 5 shows the indentation cracks on surface P. The crack propagated along the grain boundary. Crack deflection was very common, but some of the grains were cut through by the crack as indicated by arrow in Fig. 5(a). Fig. 5(b) shows crack branching and the large elongated grain inhibiting the crack propagation. Fig. 5 also shows that matrix grains as well as the large elongated grains grew in the sample sintered at higher temperature.

In order to examine effect of the sintering additives on the crack lengths, three kinds of samples were prepared and subjected to the indentation. After hot pressing, densities of samples were only 97-97.3% theoretical. After annealing at 2123 K, the densities increased to 97.3-98.6% theoretical. One of the most influential factors on the crack propagation behavior in the silicon nitride is thought to be the thermal residual stress developed from the thermal expansion mismatch between silicon nitride grain and the grain boundary glassy phase as reported by Peterson and Tien.[9] They also reported that thermal expansion coefficient of β-Si_3N_4 was 3.0×10^{-6}/K. Koga reported that thermal expansion coefficient of the Y-oxynitride glass decreased as silica content increased.[10] If only yttria and silica were considered, molar ratios of the two oxides in the samples A, B and C were 34/66, 30/70 and 17/83, respectively. So, glass in sample A and B was thought to have bigger thermal expansion coefficient than the silicon nitride grain while thermal expansion coefficient of glass in sample C might be smaller than that of the grain. According to Koga and Peterson and Tien, higher thermal expansion coefficient of the grain boundary than the silicon nitride grain and, therefore, the compressive residual stress in the grains were beneficial for the fracture toughness. However, it has been often observed that the crack cut through the large silicon nitride grains while it detoured around small elongated grains. If the compressive stress of the grain improved the fracture toughness by strengthening the grain, the crack should detour around the large grains more often than around the small ones. Davidge and Green reported that higher thermal expansion coefficient of the matrix glass than the dispersed spherical ceramic particle caused the crack cut through the particle while it detoured around the particle when the thermal expansion coefficient was lower.[11] So, it was expected

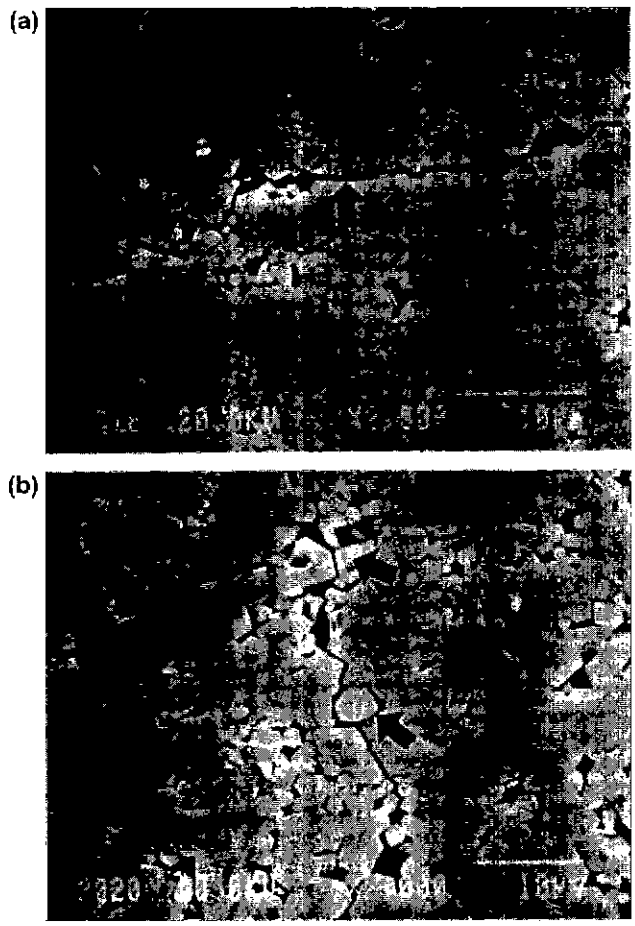

Fig. 5. SEM micrographs of the indentation cracks on surface P; (a) the crack normal to lamination direction of sample sintered at 2148 K, (b) the crack parallel to lamination direction of sample sintered at 2273 K.

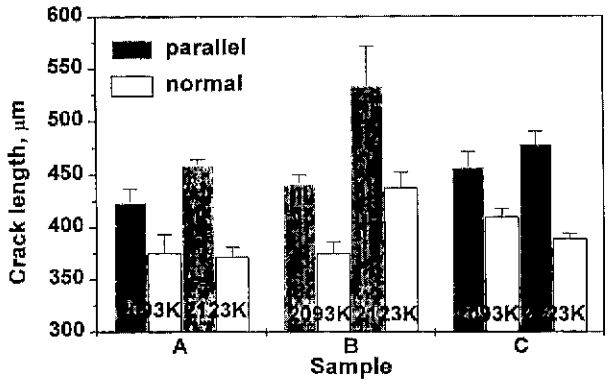

Fig. 6. Indentation crack lengths of samples A, B and C after hot pressing at 2093 K and after aging at 2123 K; "parallel" and "normal" represent the orientation of the cracks with respect to the alignment direction.

that the crack showed more zigzags and that the crack length was shorter in sample C than in the other two samples. However, Fig. 6 shows that crack lengths of sample C were longer than sample A. Silicon oxynitride (Si_2N_2O) was detected by XRD analysis on sample C, which implied that a significant amount of the silicon nitride reacted with silica to form the oxynitride. During the annealing treatment, some of the oxide constituents evaporated and the silicon nitride precipitated. However, silicon oxynitride was still detected by XRD analysis from the annealed sample. Even though the crack length of sample C was longer than what was expected from the thermal residual stress considerations, it was possibly due to the reaction between the silicon nitride grain and the glass. Effect of the thermal residual stress on the crack propagation behavior is yet to be clarified.

IV. Conclusions

Silicon nitrides with the aligned whisker seeds were prepared by tape casting followed by gas pressure sintering or hot pressing and annealing. The silicon nitride showed a strong anisotropy of the sintering shrinkage, the microstructure, and the indentation crack length. The crack length anisotropy was explained by difference in number of the large elongated grains interacting with the crack. The lateral cracks were observed on tape casting surface, but they were not present on the surface normal to the aligned grains. The lateral crack was thought to explain in part the difference in the crack lengths on the two surfaces. Silicon oxynitride was formed in sample C hot pressed at 2093 K, and the crack lengths on the sample were longer than the other samples hot pressed at the same temperature. Effect of thermal residual stress on the crack propagation behavior still needs to be clarified.

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