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Microstructural modification to improve mechanical properties of a 70%Si_3N_4-30%BAS self-reinforced ceramic composite

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Different microstructures of the 70%Si_3N_4-30%BAS self-reinforced composite, fine, coarse and bimodal, are obtained by pressureless sintering at 1920°C. Flexural strength, fracture toughness and crack-growth resistance (*R*-Curve) behavior of each microstructure are characterized by three-point bending, indentation and modified compact tension methods respectively, at room temperature. The crack deflection, whisker bridging and pullout are considered as major toughening mechanisms in the composite. It is found that coarsening β-Si_3N_4 whiskers of this composite can improve the toughness/fracture resistance but deteriorate the strength. When limited large abnormally grown whiskers are introduced into the microstructure, the composite shows an improved toughness/fracture resistance behavior and concurrently sustains a high strength.

1. Introduction

Despite some desirable properties of Si_3N_4-based materials, such as high strength at elevated temperatures, good thermal shock resistance and chemical stability, a wide range of application is still not realized. It is not only inhibited by the high manufacturing costs, but also delayed by their brittleness. To overcome this problem, the research community has expended much effort toward the microstructure design to develop more damage tolerant Si_3N_4-based ceramics.

Early work by Lange [1, 2] showed that a fibrous grain morphology, which was beneficial to the strength and the fracture toughness, could be fabricated from a α rich Si_3N_4 powder. Himsolt *et al.* [3] reported that both strength and fracture toughness of Si_3N_4 ceramics increased significantly with the increasing amount of β-Si_3N_4 but the strength decreased as the further grain growth occurs. Basing on a better understanding of the processing-microstructure-property relationship of Si_3N_4 ceramics [4–12], some major progresses have been made in recent years on the fracture toughness and strength. Flexural strength as high as 1.5 GPa could be achieved in Si_3N_4-Al_2O_3-Y_2O_3 system with fine whisker morphology (<2 μm in length) by HIP [13]. Some Si_3N_4 ceramics with coarse microstructure (several microns in width and >10 μm in length) exhibited high toughness and strong R-Curve behavior [8, 9, 14–16]. According to Becher [17], whisker bridging and pullout are the major toughening mechanisms of silicon nitride and the increase of whisker diameter can promote these toughening effects. Kawashima *et al.* experimental result [18] indicated that the toughness increase is proportional to the square root of whisker diameter that agrees well with the theoretical approach. Also, both empirical results and theoretical calculation have shown that increasing the whisker diameter can result in a stronger *R*-Curve effect, steeper rising region and high plateau level in the whisker-reinforced ceramic composites, such as Si_3N_4 [8, 9] and SiC whisker reinforced Al_2O_3 [19]. However, it has been realized that there is a trade-off in improving the strength and fracture toughness/resistance. Generally, the existence of larger elongated grain causes a drop in flexural strength because large grains may act as crack initiation sites [8, 9, 12, 18, 20, 21].

The bimodal/duplex microstructure, which has abnormally grown elongated Si_3N_4 grains surrounded by the matrix of fine Si_3N_4 whisker or equiaxed grain, was proposed recently to compromise the conflicting between strength and fracture toughness of Si_3N_4 materials [4, 5, 8, 9, 21–26]. Some work [8, 9, 17, 21, 23, 24, 27] showed that even small amount of large β-Si_3N_4 whiskers could significantly improve the fracture resistance without sacrificing the high strength.

This novel idea could be combined with our recent work [28–32]. It has been shown that barium aluminum silicate (BAS) with the composition of $BaO \cdot Al_2O_3 \cdot 2SiO_2$ is a promising matrix material reinforced by the β-Si_3N_4 whiskers. With 30vol.% BAS, silicon nitride can be processed to full density using pressureless sintering. An assintered material with fine whisker morphology showed an attractive high strength about 963 MPa at room temperature along with a critical fracture toughness of 5.4 $MPa \cdot m^{1/2}$ [30, 31]. Showing an excellent crystallization capability, BAS crystallized into hexacelsian almost completely upon cooling,

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contributing to good high-temperature strength. These properties make the BAS-Si_3N_4 ceramic matrix composite particular interesting for both room and high temperature applications. However, appropriate improvements in the fracture toughness and damage tolerance must be obtained to fully realize the engineering benefits of this material. This work describes our preliminary attempt to obtain a Si_3N_4-BAS composite with high strength and toughness by whisker morphology modification and clarify the possible contributions from both the coarse and bimodal microstructure.

2. Experimental procedure

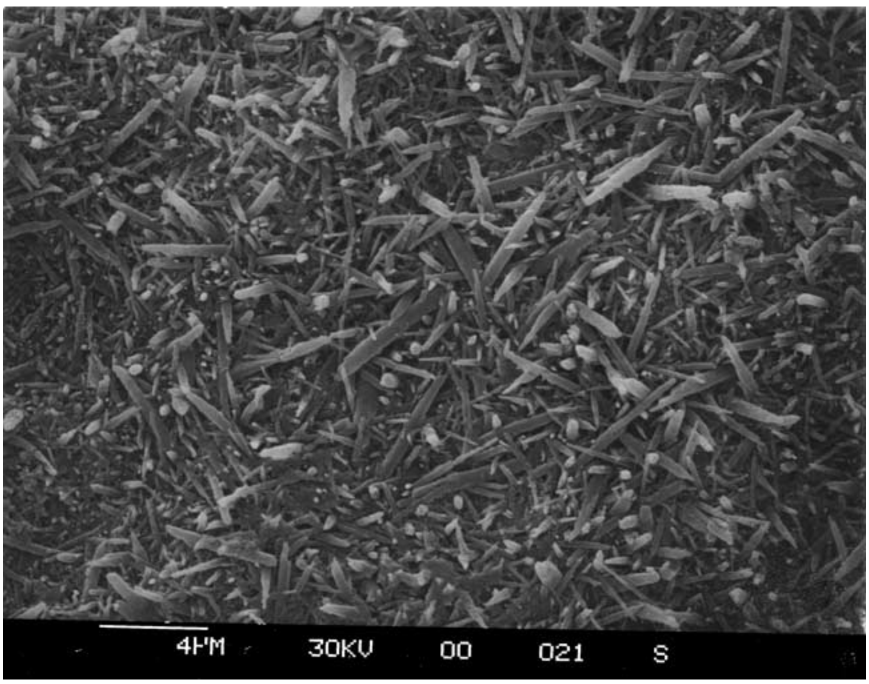
Our previous work [32] indicated that the addition of some coarse silicon nitride powder (UBE-ESP) to the starting powders (UBE-E10) encourages the abnormal growth of β grains in the 70vol%Si_3N_4-30vol%BAS system by changing the initial size distribution and β content in the starting Si_3N_4 powder. 30 vol% BAS constituent powders ($BaCO_3$, AR Grade, Mallinckrodt Inc., Paris, KY; SM8 Al_2O_3, Baikowski International Corp., Charlotte, NC; 2034DI SiO_2, Nyacol Products Inc., Ashland, WA) were mixed with 70vol% Si_3N_4 powders, which were prepared by mixing E10 and ESP in ratios of 100 : 0 and 50 : 50 respectively. Powder batches were homogenized by ball milling in isopropyl alcohol for 48 h. Green pellets were compacted at a pressure of 50 MPa and then packed in graphite crucibles with a silicon nitride based powder bed. Samples were sintered at 1920°C in different time, as presented in Table I, in 1 atm nitrogen.

The bulk density of as-sintered samples was measured by Archimedes method. X-ray diffraction analysis was conducted to estimate the phase transformation. Assintered samples were polished and etched for microstructure observation. To characterize quantitatively the microstructure of samples, diameter (d) and apparent length (L) of two-dimensionally exposed grains on SEM micrographs were measured for about 1000 grains in each sample by commercially available image analysis software (NIH Image, National Institute of Health, USA). The diameter and length of each grain were determined from the shortest and longest diagonal, respectively. The grain size distribution was evaluated by plotting area frequency against grain diameter as proposed by Hirosaki *et al.* [33, 34].

The flexural strength of the material processed under each condition was obtained in three-point bending. Specimens were cut from the as-sintered pellets in dimensions of 3 mm × 1.5 mm × 30 mm. The surfaces of the specimens were ground using a 400-grit diamond wheel. At least 5 specimens were tested under each test condition. Indentations were made on the spent flexural strength testing bars, using an Instron Universal Testing machine fitted with a diamond pyramid indentor. The contact peak load was hold at 90 sec and 12 valid indents were performed on each sample. The fracture toughness was calculated according to the Anstis approach [35]. Young's modulus of 242 GPa, measured by an ultrasonic technique, was applied in the calculation. Modified compact tension specimens were tested at a crosshead speed 5.08×10^{-4} mm/min. The fracture resistance behavior was calculated by compliance method. The detailed description of this test was addressed in our previous paper [31]. All the tests were conducted at room temperature.

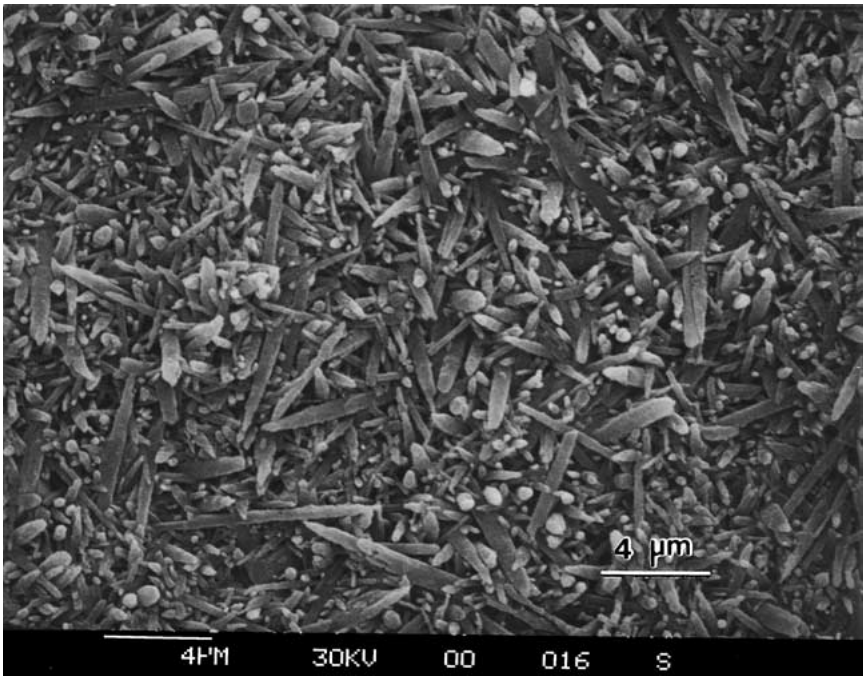
TABLE I Si_3N_4 specimen powder constituent, sintering procedure and mechanical properties.

Sample	Ratio of Si_3N_4 powder (E-10 : ESP)	Sintering time (min)	K_{IC} ($MPa \cdot m^{1/2}$)	Flexural strength (MPa)
A	100 : 0	120	5.4 ± 0.1	963 ± 71
B	100 : 0	240	6.3 ± 0.1	853 ± 47
C	50 : 50	240	6.6 ± 0.2	916 ± 49

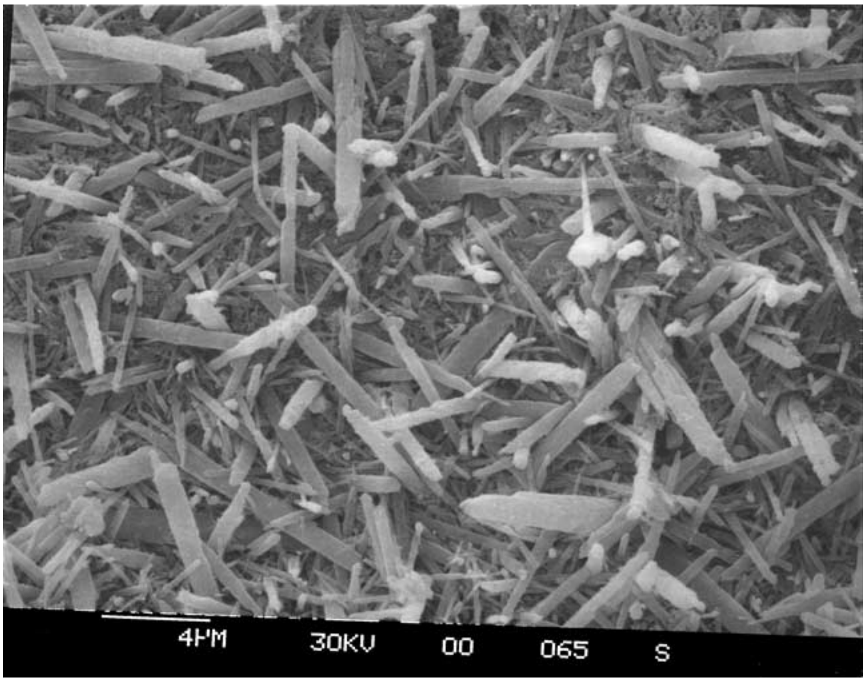


(a)

Figure 1 specimen A shows a fine whisker morphology(a), specimen B shows a coarsening microstructure comparing with A (b) and specimen C shows bimodal microstructure with large abnormal grown whiskers well disperse in the comparatively fine whiskers(C). (*Continued*.)



(b)



(c)

Figure 1 (*Continued*).

3. Results and discussion
3.1. Microstructural characterization
Fully densification was achieved in all samples after sintering. No residual α Si_3N_4 phase can be detected in all as-sintered materials by XRD methods. Fig. 1a–c show the typical microstructure of samples A, B and C, respectively. SEM observations showed that sample A has a fine β-Si_3N_4 whiskers morphology in which whiskers are oriented randomly in a continuous matrix of BAS. Most whiskers of this material have width less than 0.4 μm. Grain coarsening is evident from the micrograph of sample B due to the longer sintering time. Similar to our previous study [32], sample C exhibits a strong indication of abnormal grain growth, as shown in Fig. 1c. The abnormally grown β-Si_3N_4 whiskers have diameters larger than 1 μm. Isotropic mechanical performance is expected from all these three microstructures.

According to Becher *et al.* [17, 19], the volume fraction of large elongated grains/whiskers is one of the critical factors controlling the final properties of materials. Correspondingly, the area fraction of grains on the two-dimensional cross-section, which represents the volume fraction more accurately than grain population, was used in order to address the importance of coarse grains [33, 34].

Fig. 2 shows the statistical evaluation of whisker-diameter distribution of each sample. It suggests that Sample A has a microstructure with normal grain size distributions. The peak of distribution curve is at

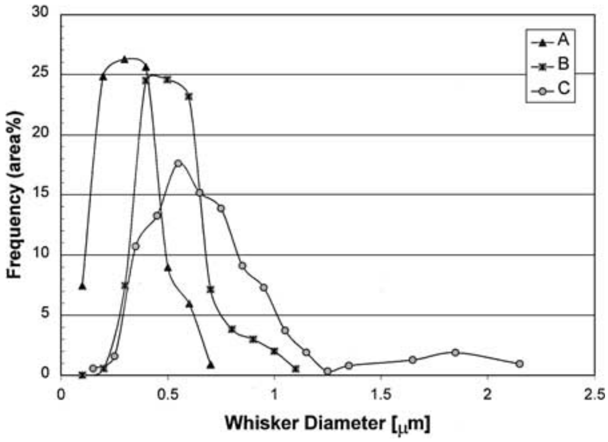


Figure 2 The whisker size distribution of specimen A, B and C.

$\sim$0.3 μm. With the extension of sintering time, the distribution curve shifts to larger sizes with a little broader normal distribution range. Most whiskers of Sample B have width falling into a range between 0.2 and 0.7 μm. The pronounced abnormal grain growth in Specimen C can be identified although the majority of grains show the similar growth behavior as Sample B. Our previous work [32] has identified that the heterogeneous nucleation is the predominant nucleation mechanism for β grains in the BAS liquid. The addition of some coarse silicon nitride powder to the starting powders encourages the abnormal grain growth. It appears that the first peak represents the normal grain grown from fine β nuclei in the E-10 while the second peak stands for the abnormal grain growth of the coarse β nuclei in the ESP powder. The abnormal grain grown seems to have little influence on the grown of majority of grains, which is consistent with the experimental result on Si_3N_4 abnormal grain growth by seeding [26].

3.2. Mechanical properties

The K_{IC} values measured by indentation test at room temperature are presented in Table I. The fracture toughness increase in the order of specimen A, B and C. All three specimens exhibit the rising fracture resistance behavior (R-Curve behavior) in same order, as shown in Fig. 3. The specimen A with the lowest toughness of 5.36 $MPa \cdot m^{1/2}$ shows the low starting of R-Curve and low plateau level. Specimen C has

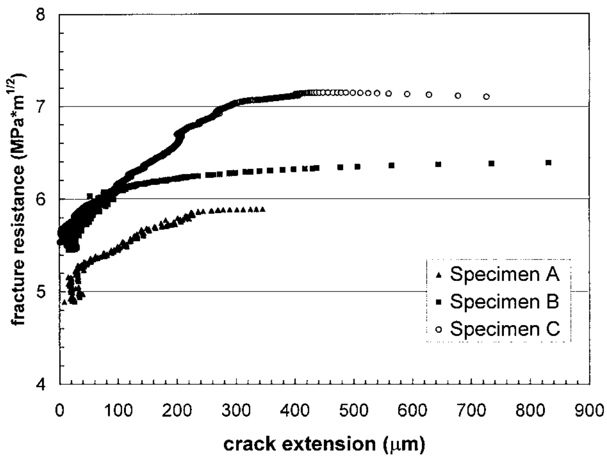


Figure 3 Fracture resistance behavior of specimen A, B and C.

a higher starting and the highest steady state about 7.15 $MPa \cdot m^{1/2}$. The flexural strength and K_{IC} value of BAS, which are $\sim$100 MPa and <2 $MPa \cdot m^{1/2}$ respectively [36, 37], are much lower than those of silicon nitride. In addition, the BAS matrix has grain size of submicron [29, 30]. The difference in whisker morphology rather than in BAS matrix is believed to attribute to the discrepancy of mechanical behaviors of different specimens.

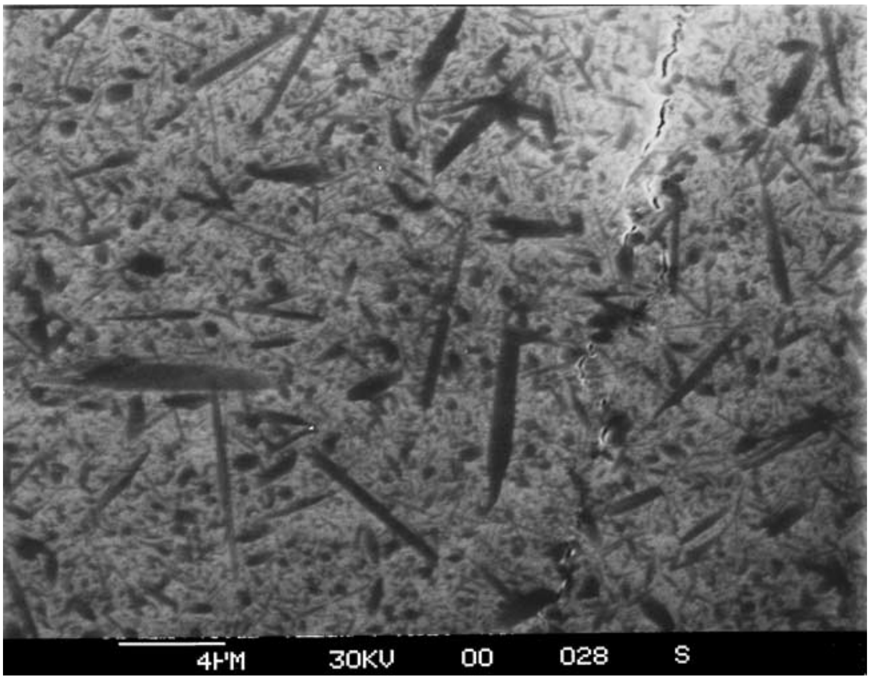
In our study, K_{IC} increases with the coarsening of whisker morphology (specimen A and B), that agrees well with theoretical approach [17] and experimental results [8, 9, 18, 19]. Also, crack in specimen B starts to propagate at higher toughness and R-Curve ends at higher plateau level (Fig. 3). When some large abnormally grown grains are introduced (specimen C), K_{IC} value of the material further improves to 6.6 $MPa \cdot m^{1/2}$. In addition, the R-curve of sample C exhibits a longer wake zone, which is close to 500 μm in length, and a much higher steady state. It appears that the existence of even a small amount of large elongated grains/whiskers benefit to not only the higher fracture resistance but also better damage tolerance (larger wake zone size).

Similar behavior was also reported by Hirao *et al.* [24] in Si_3N_4-Y_2O_3-SiO_2 system when applying rod-like β particles as seeds during powder preparation. When adding only 2 vol% β seeds, K_{IC} values of as-sintered samples could be improved more than 30%. With further increase in seed content to 6 vol%, the value of K_{IC} increased only several percent. It seems that small amount of larger whiskers would more effectively improve the fracture toughness. The further addition of larger whiskers may increase the possibility of whisker tangling which in turn decreases the whisker bridging and pullout effect. Further study to identify the optimum amount of larger whiskers for best toughening effect is necessary.

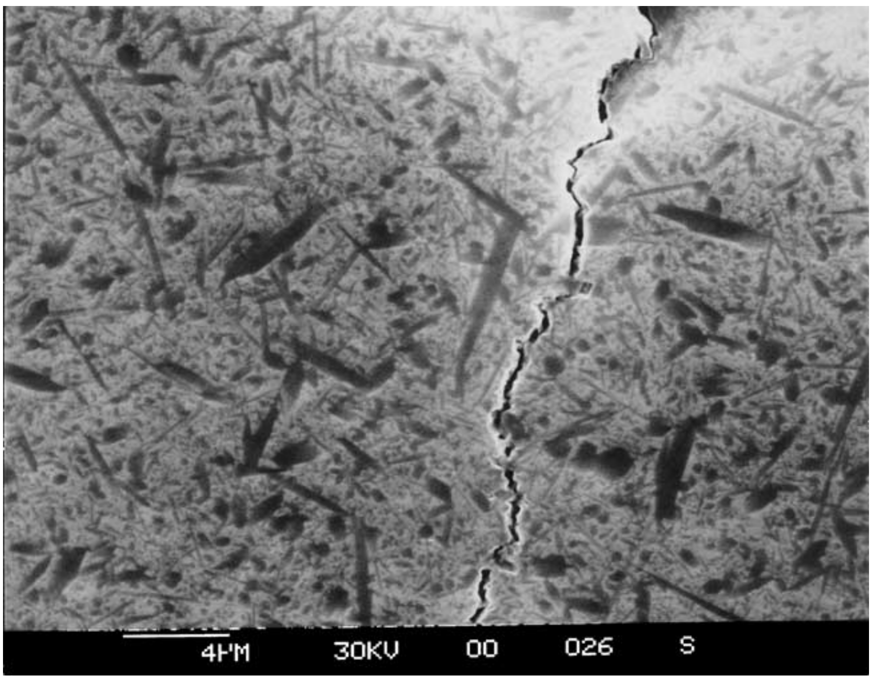
As reported, the toughening response in silicon nitrides with elongated grains can be described in terms of crack wake mechanims, as grain bridging and pullout [7–9, 17–19, 22]. However, the presence of larger elongated grains is not sufficient to ensure a toughening effect. A weak interface between matrix and Si_3N_4 grain is necessary to assure the occurrence of crack wake mechanisms because all these mechanisms require that the crack tip should bypass the whiskers rather than cutting through them.

Extensive crack deflection, grain-bridging sites are observed from SEM observations of the indentation crack path on the specimen C. Fig. 4a–c shows the position close to crack tip, in the middle of the crack and the site close to the indentation site, respectively. A discontinuous crack path can be seen in Fig. 4a. When crack approaches the whiskers, it seems to either deflect out of the crack plane when the incidence angle between crack plane and whisker is small, or the crack tip looks arrest as it encounters the interface, then goes around the whisker and reappears in the matrix ahead of the whisker, leaving the whisker intact and functioning as a bridging ligament. At the location far behind the crack tip, extensive whisker pullout could be observed from the interior fracture surface. These SEM observations (Fig. 4) indicate that the grain boundary is the preferred crack path. The interface properties of this composite, therefore, favor the occurrence of crack deflection, whisker bridging and pullout. Obviously, whisker morphology under this circumstance, becomes an important issue in the design of microstructure with high toughness, high strength and better damage tolerance.

The flexural strength of all three specimens are shown in the Table I. The specimen A has the highest strength, which is averaging about 962 MPa. It was reported [3, 8, 9, 12, 13, 21] that silicon nitride suffers a very substantial loss in strength with increase in grain size because the boundaries of larger whiskers may act as initiation sites of larger flaws. Therefore, it is quite straightforward that the average strength of specimen B is about 100 MPa lower than that of specimen A. However, the difference in microstructure of sample C does not result in a further drop in strength as expected. Sample C has an average flexural strength around 916 MPa that is higher than strength of specimen B. This indicated that the achievement of both high fracture toughness and strength in this composite is made possible by encouraging the abnormal grain growth, where both the size and quantity of large whiskers are controlled within a certain range. Hirosaki *et al.* [21] also reported that seeded silicon nitride retained a high strength level of about 1 GPa in spite of the existence of larger grains. They proposed that the cluster of numbers of large whiskers instead of the large whisker itself undermined the strength of the material. When the large elongated grains are relatively small in number, uniformly

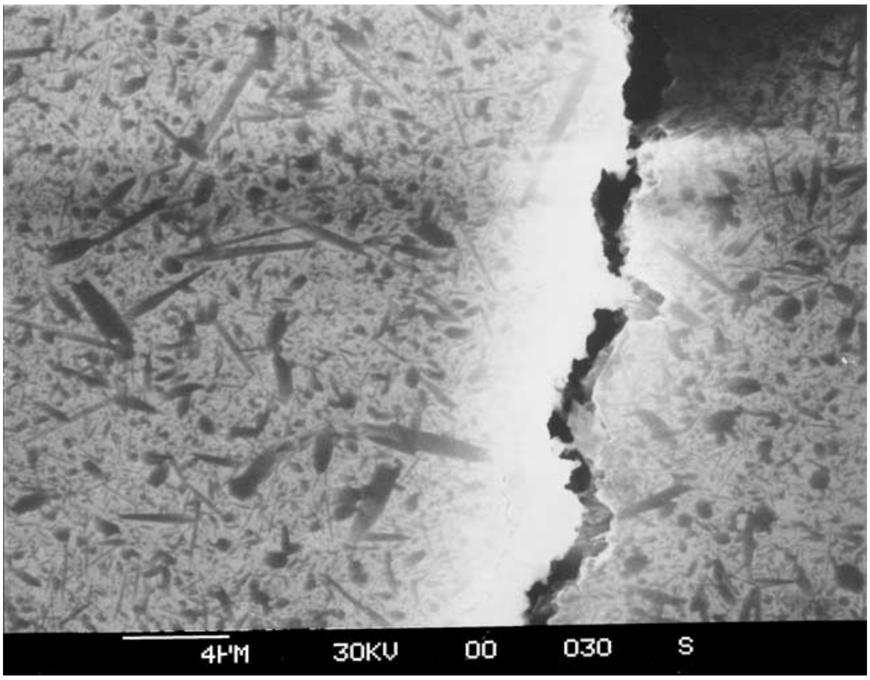


(a)



(b)

Figure 4 Indentation crack on the specimen C at position close to crack tip(a), in the middle of crack(b) and far behind the crack tip(c). (*Continued*.)



(c)

Figure 4 (*Continued*).

dispersed and do not come in contact, high strength still could be retained because not all the large whisker will result in a large flaw. As shown in Fig. 4, the large whiskers in specimen C are well dispersed without much clustering.

In addition, according to Griffith law, the increase in the toughness will result in higher strength while keeping the flaw size constant. The toughening effect contributed mostly from the large whiskers can minimize the strength variation. The fine-grained silicon nitride without the toughening contribution from those larger whiskers will exhibit larger scatter in strength.

4. Conclusions

The coarsening of whisker morphology in 70vol% Si_3N_4-30vol% BAS improves the toughness and crack resistance behavior. But simply increasing the size of the elongated grains without controlling the volume fraction and the distribution of the largest elongated grains could be detrimental to the mechanical performance. The presence of small amount of larger elongated grains in this composite can improve the fracture toughness significantly without compromising too much in strength. Through optimizing the final whisker size distribution, a Si_3N_4-BAS composite with higher strength and improved toughness can be achieved using pressureless sintering.

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