

# Microstructural Control of a 70% Silicon Nitride– 30% Barium Aluminum Silicate Self-Reinforced Composite

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The processing response of a 70% silicon nitride–30% barium aluminum silicate (70%-Si<sub>3</sub>N<sub>4</sub>–30%-BAS) ceramic-matrix composite was studied using pressureless sintering, at temperatures ranging from 1740°C, which is below the melting point of BAS, to 1950°C. The relationship between the processing parameters and the microstructural constituents, such as morphology of the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker and crystallization of the BAS matrix, was evaluated. The mechanical response of this array of microstructures was characterized for flexural strength, as well as fracture behavior, at test temperatures up to 1300°C. The indentation method was used to estimate the fracture resistance, and *R*-curves were obtained from modified compact-tension samples of selected microstructures at room temperature.

### I. Introduction

THE strong interest in silicon nitride  $(Si_3N_4)$  ceramics for service temperatures through 1500°C results largely from good hightemperature strength, good thermal shock resistance, and relatively good resistance to oxidation, in comparison with other hightemperature structural materials.<sup>1-4</sup> However, Si<sub>3</sub>N<sub>4</sub> components have high manufacturing costs and poor reliability, which are major barriers to their extensive use in engineering applications. High processing pressures often are required for densification, as well as for promotion of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation. This requirement incurs a manufacturing-cost penalty, because of the need for specialized equipment, and restricts the geometric shape of the components. To fabricate complex-shaped components from dense, high-strength Si<sub>3</sub>N<sub>4</sub> with a minimum of machining, pressureless sintering has been an interesting area of study in the  $Si_3N_4$  research community.<sup>1,2,5-7</sup> To apply this technique in silicon nitride ceramics, the selection of a sintering aid becomes critical.

 $Si_3N_4$  is difficult to densify without the use of sintering additives, primarily because of the highly covalent bond character, which results in a low self-diffusion coefficient of nitrogen.<sup>8</sup> Pressureless densification typically requires a sintering-additive content of >15 vol%, compared to the ~5–10 vol% of sintering additives that is required for pressure-assisted densification.<sup>1–3</sup> In addition, eutectic liquids, which form from reactions between  $Si_3N_4$  particles and the additives during densification, typically result in residual amorphous phases after sintering. These residual amorphous phases often are the phases that adversely influence the high-temperature performance (such as creep and high-temperature strength) of the sintered body.<sup>1,2,9–11</sup> Therefore, three

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factors usually are considered when selecting a sintering aid: sinterability, refractoriness of the secondary phase, and ease of crystallization of the additives. Unfortunately, the use of morerefractory sintering additives normally precludes pressurelesssintering methods, because the associated high viscosity of the liquid phase restricts both densification and the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation. Excessive sintering temperatures also must be avoided, to minimize the decomposition of Si<sub>3</sub>N<sub>4</sub>.

Barium aluminum silicate (BAS), which is based on the composition BaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>, has been studied for decades, in both synthetic and naturally occurring forms.<sup>12-17</sup> The polymorphism of stoichiometric BAS at atmospheric pressure is represented graphically in Fig. 1. At temperatures less than the melting temperature of BAS (1760°C), BAS first undergoes a solid-state phase transformation at 1590°C, where the stable hexagonal BAS (hexacelsian) transforms to the monoclinic phase (celsian), which remains thermodynamically stable through room temperature. However, this hexagonal-to-monoclinic reconstructive transformation is extremely sluggish, which causes hexagonal BAS to persist in a metastable state at temperatures of <1590°C. When undercooled, the metastable hexacelsian will transform rapidly to an orthorhombic phase at  $\sim$ 300°C. This reversible transformation is accompanied by a volume change of  $\sim 3\%$ ; this change in volume usually is destructive.<sup>13,14</sup> Therefore, the persistence of the hexacelsian phase at temperatures of <1590°C generally is regarded as an undesirable feature of the BAS ceramic systems.

Recent work<sup>18–22</sup> has shown that  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers can be grown *in situ* from  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> in the presence of liquid BAS, which implies that the liquid phase with a composition of BaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> has adequate wettability and solubility with the Si<sub>3</sub>N<sub>4</sub> starting particles. The liquid BAS phase is essential to ensure both the progress of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>– $\beta$ -Si<sub>3</sub>N<sub>4</sub> transformation and the attainment of full densification. The unique combination of superior refractory properties (the service temperature for BAS can be as high as 1590°C and the maximum melting point of celsian BAS is 1760°C), low density, high modulus, low thermal expansion, good oxidation resistance, and low dielectric constant makes BAS–Si<sub>3</sub>N<sub>4</sub>-whisker-reinforced ceramic composites particularly interesting for high-temperature applications.

Hwang and Newman<sup>22</sup> hot-pressed Si<sub>3</sub>N<sub>4</sub> at 1750°–1925°C at a pressure of 35 MPa, using ~10 wt% of BAS as a sintering additive. The as-sintered material had an average flexural strength of 817 MPa at room temperature. Its fracture toughness ( $K_{IC}$ ), as measured from the chevron-notched bend-bar specimen, was



**Fig. 1.** Schematic representation of the possible phase transitions in the BAS system under atmospheric conditions.

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m temperature. BAS showed

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reported to be 5–6.9 MPa·m<sup>1/2</sup> at room temperature. BAS showed good crystallization capability, by crystallizing to hexacelsian during cooling, which contributed to the high-temperature strength of the as-sintered material. Ceramic-matrix composites with compositions of >20 vol% of BAS as matrix material can be processed to full density without high pressure.<sup>18,20,21</sup> Richardson *et al.*<sup>20</sup> densified Si<sub>3</sub>N<sub>4</sub> with 30 vol% BAS via pressureless sintering and observed an average flexural strength of 565 MPa and an average  $K_{IC}$  of 5.74 MPa·m<sup>1/2</sup> at room temperature.

Because of the destructive character of the phase transformation at 300°C, care should be exercised to avoid hexacelsian in these composites. However, all the above-mentioned studies of Si<sub>3</sub>N<sub>4</sub>-BAS systems reported hexacelsian as the major phase. Various methods that have been used previously in monolithic BAS, such as hot pressing and seeding with celsian particles, were ineffective in promoting the formation of celsian.<sup>17,19,21,22</sup> In addition, neither electron diffraction nor X-ray diffraction (XRD) analysis has been effective for detecting the hexacelsian-to-orthorhombic BAS transformation, because only small changes in the O-atom positions within a common framework characterize this transformation.<sup>23</sup> Using high-temperature XRD techniques, Quander et al.<sup>21</sup> monitored the phase transformation in a  $Si_3N_4$ -BAS composite in situ up to 550°C and observed no significant change in the XRD spectrum with the test temperature. However, their dilatometry studies identified the potential existence of this transformation in  $Si_3N_4$  with a high BAS content.<sup>21,24</sup> The dilatometric indication of transformation for the 30% Si<sub>3</sub>N<sub>4</sub>-70% BAS composite was significant, whereas that for the 70% Si<sub>3</sub>N<sub>4</sub>-30% BAS composite was almost negligible. The magnitude of the volume change also decreased significantly as the degree of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation increased. All these features indicated that the presence of more  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers had a tendency to preclude the hexacelsian-to-orthorhombic transformation. Richardson et al.<sup>20</sup> conducted thermal fatigue tests on both 30-vol%-Si<sub>3</sub>N<sub>4</sub>-70-vol%-BAS and 70-vol%-Si<sub>3</sub>N<sub>4</sub>-30-vol%-BAS composites, between room temperature and 600°C. They reported no decrease in strength after thermal cycling with the 70-vol%-Si<sub>3</sub>N<sub>4</sub> composite, which indicated that either this transformation was suppressed or it was not destructive anymore.

The economic incentives that are associated with the near-netshape production of pressureless-sintered components provide the basis for this study. This study intends to present our examination of the relationship between the pressureless-sintering conditions, the microstructure, and the resulting mechanical properties.

## II. Experimental Procedure

## (1) Processing

Seventy volume percent of Si<sub>3</sub>N<sub>4</sub> powder (E-10, UBE Industries, Yamaguchi, Japan) was mixed with 30 vol% of BAS constituent powders (analytical reagent grade BaCO<sub>3</sub>, from Mallinckrodt, Inc., Paris, KY; SM8 Al<sub>2</sub>O<sub>3</sub>, from Baikowski International Corp., Charlotte, NC; and 2034DI SiO<sub>2</sub>, from Nyacol Products, Inc., Ashland, WA) in isopropyl alcohol for 48 h in a ball mill, using Si<sub>3</sub>N<sub>4</sub> grinding media. The 30-vol%-BAS-70-vol%-Si<sub>3</sub>N<sub>4</sub> composition, which has been selected for the present study, corresponds to that which was developed previously,<sup>20</sup> for ease of sinterability and acceptable mechanical and electromagnetic performance. Green pellets were compacted at a pressure of 50 MPa and then packed in graphite crucibles with a Si<sub>3</sub>N<sub>4</sub>-based powder bed. Samples were sintered at temperatures of 1740°, 1770°, 1820°, 1870°, 1920°, and 1950°C, each for 30 min in a nitrogen atmosphere. Higher sintering temperatures were not attempted, because of unacceptable surface degradation. Sintering times of 5, 30, 60, 120, and 240 min also were applied to the samples that were processed at 1920°C.

#### (2) Microstructural Characterization

The density of the as-sintered samples was measured using the water-immersion method. Phase characterization via XRD was performed on the bulk material. Sintered materials were sectioned, ground, and plasma-etched, using a mixture of carbon tetrafluoride  $(CF_{4})$  and oxygen, to characterize the whisker morphology. Quantitative microstructural analysis was performed on digitized scanning electron microscopy (SEM) images that were obtained at three magnifications ( $3400\times$ ,  $6200\times$ , and  $12000\times$ ), where the diameter and length of each  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whisker were determined using commercially available image analysis software (NIH Image, National Institute of Health, Washington, DC). This method defines the grain length and diameter as the maximum and minimum grain projection, respectively. Some samples in our study contained residual  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, which was present in a primarily spherical shape; therefore, we have defined whiskers as being particles with an aspect ratio of >4. The diameter/length and the apparent aspect ratio of the whiskers were determined statistically, using the method proposed by Braue et al.25 and Mitomo and co-workers.<sup>26,27</sup> At least 1200 whiskers were measured for the samples that were processed under each condition. A transmission



Fig. 2. Weight percentage of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation ( $\beta/(\alpha+\beta)$ ) and relative density of as-sintered samples, each as a function of sintering temperature (for a constant sintering time of 30 min).

electron microscopy (TEM) system (JEM-2000FX, JEOL, Tokyo, Japan) that was fitted for energy-dispersive X-ray spectroscopy (EDS) was used to conduct microstructural observations. High-resolution transmission electron microscopy (HRTEM) images also were obtained, to explore the potential presence of amorphous phases.

## (3) Mechanical Behavior

The flexural strength of the material that was processed under each condition was obtained in three-point bending, at test temperatures up to 1300°C, in laboratory air. These specimens were cut from the as-sintered pellets in dimensions of 3 mm  $\times$  1.5 mm  $\times$  30 mm. The surfaces of the specimens were ground using a 400-grit diamond wheel. At least seven specimens were tested under each test condition.

Indentations were made on the broken flexural-strength-testing bars, in ambient air, using a universal testing machine (Instron, Danvers, MA) that was fitted with a diamond pyramid indenter. The contact loads varied over a range of 35-45 kg, and the peak-load contact time was 90 s. At least twelve valid impressions on each selected sample were used to estimate the fracture toughness, according to the approach devised by Anstis *et al.*<sup>28</sup>. A Young's modulus of 242 GPa was measured using ultrasonic methods.

The *R*-curve behavior of the samples that were processed at 1920°C for 30, 120, and 240 min was determined from modified compact-tension samples with dimensions of 17 mm  $\times$  30 mm  $\times$  3.5 mm at room temperature. Actual crack extension during loading was calculated using both boundary-element and finite-element analyses. The final *R*-curve results were the average of at least two compact-tension specimens that had been tested under the same conditions.

#### III. Results and Discussion

## (1) Density Measurement and Phase Characterization

The weight loss of the as-sintered samples remained at <2% for sintering temperatures up to 1920°C. The 1950°C/30-min samples had glassy surface layers with an average thickness of  $\sim$ 0.3 mm and experienced a weight loss of at least 4%. This surface condition seemed to be more sensitive to sintering temperature than to sintering time. In comparison, the 1920°C/240-min sample experienced a weight loss of  $\sim$ 2%, with a smooth, glassy surface layer that was  $\sim$ 0.2 mm thick.

The 1740°C/30-min sample had a measured density of  $3.14 \text{ g/cm}^3$ , which was the lowest density measured in our study. The relative density of each sample was obtained by comparison to a calculated theoretical density (TD) of  $3.25 \text{ g/cm}^3$ , as shown in Fig. 2.

The progress of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation, relative to the processing temperature, which was calculated in a manner that was described by Gazzara and Messier,<sup>29</sup> also is presented in Fig. 2. The phase transformation became detectable at temperatures less than the melting temperature of BAS. Complete transformation was detected via XRD in the samples that were processed at 1950°C for 30 min. The liquid eutectic temperature of the BaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system is in the range of  $1175^{\circ}$ –1760°C, depending on the composition.<sup>13,14</sup> In Si<sub>3</sub>N<sub>4</sub>–BAS composites, extensive BAS phase formation via solid reaction among three constituent powders is observed at temperatures as low as 1300°C.<sup>21</sup> However, the distribution of BAS constituent powders may not be stoichiometrically perfect, which can result in early local melting (<1760°C). For example, reaction between the residual silica (SiO<sub>2</sub>) layer on the surface of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> starting powders, which has been identified using both HRTEM observation and EDS methods, and the constituent powders is difficult in the low-processing-temperature range. However, at higher processing temperatures, this surface silica could result in a SiO<sub>2</sub>-rich area and form a liquid layer that surrounds the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> particles at temperatures much less than that of eutectic BAS. This phenomenon encourages early  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation. Therefore, in this material system, the use of BAS constituent powders instead of BAS exhibits an advantage of initially assisting pressureless sintering by forming a liquid phase at relatively low

temperatures, then later crystallizing to a more-refractory compound.

With the extension of sintering time at 1920°C, the density and the phase transformation exhibit behavior that is similar to that previously described. A relative density of 97% of TD, with ~68% of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> being transformed to  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, was achieved after only 5 min at 1920°C. When the sintering time was extended to 120 min, no residual  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> phase could be detected via XRD in the as-sintered material.

During the liquid-phase sintering of  $Si_3N_4$ , the material undergoes particle rearrangement, solution–diffusion–precipitation, and grain growth, assuming that the liquid phase provides good wettability and solubility for  $Si_3N_4$ . The solution–reprecipitation transformation of  $Si_3N_4$  may either help or hinder the densification, depending on whether a skeleton of whisker forms.<sup>30</sup> In the present case, a relative density of >90% of TD was attained, with only ~35%  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> transformed (Fig. 2), which illustrates its



**Fig. 3.** SEM micrographs showing the whisker morphology of the (a) 1920°C/30-min, (b) 1920°C/60-min, and (c) 1920°C/240-min samples.

minimal contribution to densification. To obtain good strength and high toughness from silicon nitride ceramics, complete densification and phase transformation should be achieved. Therefore, the sintering progress of this composite is controlled by the phasetransformation rate.

Only the hexagonal allotrope of the BAS matrix was identified via XRD. However, neither electron diffraction nor XRD can conclusively exclude the existence of orthorhombic BAS in this composite. We assume that the absence of accommodation reasonably precludes the presence of this low-temperature phase, which is consistent with the reports in the literature.<sup>18–22</sup> No microcracks, which normally accompany the hexagonal-to-orthorhombic transformation, were observed using either TEM or SEM methods.

## (2) Whisker Morphology

Figure 3 demonstrates the typical microstructures and, in particular, the development of whisker morphology, relative to sintering time. SEM observation of the as-sintered samples showed

that the material contains no pores, with  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers oriented randomly in a fine, continuous matrix of BAS. Isotropic mechanical performance is expected from this type of microstructure.

Figures 4(a) and (b) respectively illustrate the influence of sintering time and temperature on the average whisker length and average apparent aspect ratio. At 1920°C, the average whisker length increased from  $\sim 2 \,\mu$ m after 5 min to  $\sim 5 \,\mu$ m after 240 min. However, changes in the aspect ratio are much more subtle, relative to sintering time; the average apparent aspect ratio of most samples is in the range of 17–18.5. The rapid increase of both the length and aspect ratio at 1740°–1770°C most likely results from the large-scale melting of the BAS matrix and phase transformation in this temperature range.

The morphology of the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers in the present study closely resembles that of conventional hot-pressed silicon nitride ceramics, except for the absence of very large whiskers (>15 µm). Statistical analyses suggest a normal distribution of whisker width/length for all samples, with no indication of significant bimodal whisker growth, as shown in Fig. 5. Grain coarsening is evident with the extension of sintering time (Fig. 5); however, the



Fig. 4. Average whisker length and apparent aspect ratio, each as a function of (a) sintering time and (b) sintering temperature.





Fig. 5. Distribution of whisker width for the 1920°C/30-min, 1920°C/60-min, and 1920°C/210-min samples.

rate of diameter increase is small. Longer sintering times promote growth of all whiskers, which shifts and broadens the entire distribution curve. Some authors<sup>31–33</sup> reported that bimodal microstructures, which

have abnormally grown grains in a fine and uniform matrix, can be obtained in silicon nitride ceramics using a seeding method with the assistance of a high processing pressure. The presence of a certain amount of abnormally grown grains will promote combined improvements in both toughness and strength.33 Emoto and Mitomo<sup>31</sup> proposed that, after completion of the phase transformation, the driving force for  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grain growth scaled with the difference in particle size, and abnormal grain growth occurred only when the difference of particle size exceeded a critical value. In addition, the abnormal grain growth is assumed to be accelerated by the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> transformation.<sup>34-36</sup> Normally, this transformation is enhanced with increasing processing pressure, as noted by Vincenzini and Babini<sup>37</sup> in an earlier paper. In our study, the rate of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation is comparably slower, because of the high viscosity of the BAS liquid, as well as our choice of the pressureless-sintering method. Therefore, the grain-size distribution remains relatively narrow, in comparison with that of hot-pressed silicon nitride materials, which predictably suppresses abnormal grain growth in a steady state.

## (3) Crystallization of the Barium Aluminosilicate Matrix

As noted previously, the BAS glass-ceramic serves as a liquidphase-sintering aid for the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation and remains as a structural matrix. Volume fractions as high as 30% are used, in contrast to sintering-aid contents of typically <10% in conventional hot-pressed silicon nitride ceramics; therefore, a pronounced influence on the composite properties can be expected.

Compared with other silicate glasses, BAS glass is unusually refractory, with a dilatometric softening point of 925°C.<sup>15</sup> However, for high-temperature applications, crystallization to the crystalline BAS phase offers additional improvement. TEM methods identified almost-complete crystallization of the BAS matrix in all samples. Figure 6(a) is a bright-field TEM image that shows the microstructure of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> whiskers and a BAS matrix of a 1920°C/ 120-min sample. Figure 6(b) is the corresponding dark-field image, obtained using a [1101] diffracted beam from the BAS [1213] diffraction pattern, as indicated in the inset in the upper left-hand corner. The BAS regions that have the same orientation are shown in bright contrast in Fig. 6(b). Further illustrating the completeness of crystallization, BAS pockets, almost without exception, fully crystallized in the "corners" that are formed by whiskers (see Figs. 6 and 7). The TEM dark-field image in Fig. 6(b) also shows that one BAS grain may surround several whiskers. Neither cavities nor interface debonding that was associated with the crystallization, as reported for a silicon nitride ceramic with a crystallized YSiAlON matrix,<sup>7</sup> was observed via TEM.



**Fig. 6.** TEM images illustrating the crystallization of BAS in the 1920°C/120-min sample ((a) bright field and (b) dark field).



Fig. 7. HRTEM image showing the triple point of two whiskers (marked as "W") and one BAS grain (marked as "BAS") in the 1920°C/240-min sample.



Fig. 8. Vickers's hardness, as a function of sintering time.

The use of materials at higher temperatures requires a refractory matrix composition, as well as a microstructure that does not soften because of the presence of residual glassy phases. The almost-complete crystallization of the BAS matrix in this composite illustrates an important advantage for its high-temperature applications. Because the crystallization is spontaneous, no additional heat treatment (such as the extensive post-sintering annealing time required to obtain crystallized grain-boundary phases in other silicon nitride systems) is needed.<sup>1,3,5–7</sup> The excellent crystallization capability of BAS liquid also has been reported elsewhere.<sup>18–22</sup>

Using HRTEM methods, some residual glassy phase was observed, with no exception in any samples, predominantly at triple-grain junctions of whiskers and BAS grains (see Fig. 7). Also, an interlayer of glassy phase ( $\sim 1$  nm thick) persisted between the whiskers. Within the resolution capability of HRTEM, the thickness was almost constant. Also, different sintering procedures did not seem to change the characteristics of this thin film.

## (4) Mechanical Characterization

The Vickers's hardness, which was in the range of 14.9–16.2 GPa, changed with differences in the phase composition and

microstructure. This value is somewhat less than that of conventional silicon nitride materials, which usually is 17–20 GPa, probably because of the 30 vol% BAS content. We have attributed the decreasing hardness with sintering time (see Fig. 8) to the progressive replacement of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> with the softer and larger  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains.<sup>38,39</sup> After completion of the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>– $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation, the decreased softening rate is governed only by changes in grain size.

At a fixed sintering temperature of 1920°C, the roomtemperature flexural strength peaked after ~2 h of sintering (see Fig. 9). However, the fracture toughness ( $K_{IC}$ ) continued to increase as the sintering time increased. The improvements in the fraction of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>- $\beta$ -Si<sub>3</sub>N<sub>4</sub> phase transformation and the whisker morphology that result from increasing the sintering time from 5 min to 120 min were believed to contribute to the increases in both strength and toughness. The highest flexural strength of 962 ± 70 MPa, which was obtained from the 1920°C/120-min samples, corresponded to an average  $K_{IC}$  value of 5.4 MPa·m<sup>1/2</sup>. This combination of properties agrees with that of conventional hotpressed silicon nitride ceramics. The combined features of a dense, fine, and homogeneous structure, along with the *in situ* formation





Fig. 9. Flexural strength and fracture toughness ( $K_{IC}$ ), each as a function of sintering time (for a constant sintering temperature of 1920°C).



Fig. 10. Flexural strength of the 1770°C/30-min, 1870°C/30-min, 1920°C/30-min, and 1950°C/30-min samples, as a function of test temperature.

of a hexacelsian matrix, make Si<sub>3</sub>N<sub>4</sub>–BAS materials rather unique. When the coarser microstructure was obtained after sintering at 1920°C in 240 min, the  $K_{\rm IC}$  value increased to  $6.2 \pm 0.1$  MPa·m<sup>1/2</sup> but the flexural strength decreased considerably, to 852 ± 5 MPa.

An important feature that occurs in all silicon nitride ceramics at elevated temperatures is a degradation in strength, which generally has been recognized as a result of subcritical crack growth or creep. The residual glassy phase at the grain boundary and the triple junctions of grains can soften when the environmental temperature is greater than its softening temperature, which results in grain-boundary sliding, separation, void formation, and cracking. Both the amount and viscosity of the glassy phase are important to the high-temperature performance of silicon nitride ceramics.

Figure 10 shows the trend of flexural strength with test temperature for samples that have been sintered at different temperatures with a constant sintering time of 30 min. All samples

retain room-temperature strength to 600°C; the strength begins to decrease at temperatures from 600°C to 920°C. The strength decrease in this temperature range is believed to share a common origin with conventional silicon nitride materials. The inconsistency between this temperature range and the softening point of BAS glass implies that the composition of the residual glassy phase is different from that of stoichiometric BAS.

The flexural-strength-test-temperature curves of the 1870°C/ 30-min, 1920°C/30-min, and 1950°C/30-min samples all show characteristic plateaus in the temperature range of 920°–1120°C. For the 1770°C/30-min sample, this plateau occurs at a higher temperature range. Similar behavior has been reported in several silicon nitride ceramics with a crystallized matrix phase, which generally is considered to be the main contributor to this phenomenon.<sup>3,5–7,19–22,40</sup> In this case, the crystallized BAS matrix is assumed to restrict the further softening of the residual glassy phase with increases in temperature. The flexural strength of the  $1870^{\circ}C/30$ -min,  $1920^{\circ}C/30$ -min, and  $1950^{\circ}C/30$ -min samples decreases considerably at >1120^{\circ}C. At 1300^{\circ}C, no significant difference in strength is observed among these three samples.

When the test temperature is  $<900^{\circ}$ C, the load-displacement curve of each sample that is obtained from the bending test is linear, which characterizes brittle behavior. When the test temperature is  $>900^{\circ}$ C, however, some samples exhibit plastic deformation before failure. At 1120°C, the 1770°C/30-min sample still maintains brittle behavior. However, the load-displacement curves of the 1920°C/30-min and 1950°C/30-min samples exhibit both linear and nonlinear regions.

The proportional limit—i.e., the ratio between the maximum load within linear portion and the failure load—offers another

indication of the softening conditions, as illustrated in Fig. 11. Generally, a high sintering temperature results in an early decrease in the proportional limit from unity. At the same test temperature, the proportional limit normally decreases as the sintering temperature increases. This trend agrees well with the strength-test-temperature behavior that has been discussed previously. At 1300°C, the 1950°C/30-min samples have the lowest proportional limit, with an average value of ~0.38. This low value indicates that the sample underwent a significant amount of plastic deformation and also implies that more residual glassy phase that accommodates the plastic deformation may be present.

The flexural strength of samples that have been sintered at 1920°C but for various times exhibits behavior that is similar to the



Fig. 11. Proportional limit calculated from the load-displacement curve of samples sintered at different temperatures for constant time, as a function of test temperature.



Fig. 12. Flexural strength of the 1920°C/5-min, 1920°C/60-min, 1920°C/120-min, and 1920°C/240-min samples, as a function of test temperature.

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increase of test temperature (see Fig. 12). However, the starting temperature for the first significant decrease in strength varies. For the 1920°C/60-min sample, a significant decrease in strength occurs at 840°-920°C, which is close to the softening temperature of BAS glass. When sintering time was extended to 120 min, the strength decrease shifted to the temperature range of 740°-840°C. For the 1920°C/240-min sample, a large decrease in strength occurs even earlier, at 600°-740°C. In the temperature range of 920°-1120°C, all samples that have been sintered at 1920°C maintain a flexural strength of  $\sim$ 77%-80% of that at room temperature, except the 1920°C/5-min sample, which retains  $\sim$ 88% of the room-temperature flexural strength. The flexural strength of 1920°C/120-min sample, which is the strongest among all samples at room temperature, was 782  $\pm$  64 MPa in this temperature range. This value is higher than that of most silicon nitride ceramics with a crystallized matrix that have been pro-

cessed either with or without pressure. Several authors<sup>19,22</sup> indicated that the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> component in the Si<sub>3</sub>N<sub>4</sub>–BAS system was, in fact, a  $\beta$ -SiAlON. The amount of aluminum substitution in the  $\beta$ -SiAlON in this system could be in the range of 0.76–4.44 equiv.%, depending on the amount of alumina (Al<sub>2</sub>O<sub>3</sub>) that was used in the material preparation and processing conditions. Higher sintering temperatures and longer processing times can encourage the dissolution of aluminum into the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> lattice, which drives the chemistry of the remaining liquid further away from the BAS eutectic composition. Hwang and Newman<sup>22</sup> used quantitative phase analyses to compare the amount of crystallized BAS matrix after different processing conditions; they reported less hexacelsian in samples that were processed at higher temperatures or longer times. Therefore, higher sintering temperatures and longer processing times seemed to hinder complete crystallization of the BAS liquid.

Because of the limitation of the instrument, the chemistry of the glassy phase could not be obtained in our study. However, TEM observation has revealed the characteristic core structure of a  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grain, as shown in Fig. 13(a). Although the contrast of this dark core typically is weak, it could be identified in most  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains by adjusting the orientation. EDS analysis (Figs. 13(b) and (c)) illustrates the difference in aluminum content between the core and the shell. The core structure, which contains virtually no aluminum, is believed to be pre-existing  $\beta$ -Si<sub>3</sub>N<sub>4</sub> nuclei. The aluminum content within the shell structure, which may result from the formation of a SiAlON solid solution, varies with the location and size of the whiskers. Therefore, the composition of residual glass may be away from the BAS stoichiometric point and close to the BaO-SiO<sub>2</sub> side of the BaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary phase diagram. The average aluminum content of whiskers of the 1920°C/5-min sample is  $\sim$ 8% less than that of similarly sized whiskers of the 1920°C/240-min sample. The early significant decrease in strength of the 1920°C/240-min sample implies a larger departure in the chemistry of the residual glassy phase from that of BAS, when the samples are sintered under this condition. In contrast, the 1920°C/5-min samples, which have the shortest sintering time, suffered only a minimal loss of strength.

*R*-curve behavior has been characterized only on the 1920°C/30-min, 1920°C/120-min, and 1920°C/240-min samples at room temperature, as presented in Fig. 14. The 1920°C/120-min and 1920°C/240-min samples show distinct rising *R*-curves, relative to crack extension. The 1920°C/240-min sample has the largest increase in toughness ( $K_{IC} = 2.2 \text{ MPa} \text{-m}^{1/2}$ ). The  $K_{IC}$  value of the 1920°C/120-min sample increases from 4.9 MPa $\text{-m}^{1/2}$  to 5.98 MPa $\text{-m}^{1/2}$  within a crack extension of 300 µm. The *R*-curve data agree well with the  $K_{IC}$  values that have been determined using the indentation method. For the 1920°C/30-min sample, however, a large discrepancy exists between the values that have been measured using each method.

## IV. Conclusions

Composites with a composition of 70 vol% silicon nitride–30 vol% barium aluminum silicate (70 vol% Si<sub>3</sub>N<sub>4</sub>–30 vol% BAS) can be fabricated via pressureless sintering. In this composite, the BAS glass-ceramic serves as an effective liquid-phase-sintering aid, to attain full densification and complete the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>– $\beta$ -Si<sub>3</sub>N<sub>4</sub>





Fig. 13. (a) TEM micrograph of a  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grain with a core structure. Figures 13(b) and (c) respectively show EDS spectra obtained from the core and the shell.



Fig. 14. *R*-curves measured from the 1920°C/30-min, 1920°C/120-min, and 1920°C/240-min samples.

phase transformation, and remains as a structural matrix that is reinforced by the whiskers. Si<sub>3</sub>N<sub>4</sub> whiskers nucleate and grow in random directions in an almost completely crystallized matrix of hexacelsian BAS. Although small amounts of amorphous phase remain in some grains junctions, the configuration of the interface between whiskers seems to approach thermodynamic stability, which suggests little opportunity for improved crystallization of the grain-boundary glass that is present between whiskers.

High flexural strength (962  $\pm$  70 MPa) can be obtained from samples that have been sintered at 1920°C for 120 min with a fine-grained microstructure. The fracture toughness of this mate-rial is  $\sim$  5.4 MPa·m<sup>1/2</sup>. Rising *R*-curves are obtained from samples that have been processed at 1920°C for 120 and 240 min. The crystallized BAS matrix significantly benefits the hightemperature strength of this composite. The composite can maintain this high strength up to a temperature of 1120°C. At 1300°C, the composite exhibits a flexural strength of  ${\sim}500$  MPa.

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