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Microstructure and room-temperature mechanical properties of Si_3N_4 with various α/β phase ratios

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After polycrystalline silicon nitride samples with various α/β phase ratios were fabricated by uniaxial hot-pressing under vacuum, their microstructures, α-to-β transformations, and grain-growth mechanisms were then characterized by electron microscopy. Room-temperature fracture toughness (K_{IC}) increased with increasing β-phase content, and a value of 7.0 ± 0.5 MPa $\cdot$ $m^{1/2}$ was obtained for a sample that contained 60 vol % β phase. The increase in K_{IC} is the result of an increase in elongated-grain fractions with increasing β content, which promotes energy absorption by crack deflection, as well as by grain debonding, pullout, and bridging mechanisms.

1. Introduction

Silicon nitride (Si_3N_4) is a ceramic with high potential for structural applications. From the early studies of Lange [1], it was clear that its promising mechanical properties were the consequence of a specific microstructure [2].

Silicon nitride has two polymorphic crystal structures designated as α- and β-Si_3N_4. While the relationship between these two structures has been the subject of much controversy, there is general agreement that the α phase is trigonal while the β phase is hexagonal and that the α phase transforms irreversibly into the β phase at elevated temperatures ($>1400\,^\circ$C) through liquid-phase formation. It is well known that the presence of liquids can be controlled by modifying the type and content of additives (e.g., MgO, Al_2O_3, Y_2O_3, etc.).

The dynamics of α-to-β-phase transformation have been analyzed in several studies [3–5]. The most important consequence of the α-to-β transformation in Si_3N_4 is the morphological changes observed in the grains [6]. The α grains are equiaxed, whereas the β grains are elongated. The presence of elongated (acicular) β grains or whiskers has shown great potential for improving fracture properties through several reported mechanisms, such as crack deflection, crack bridging, grain pullout, etc. [7]. Nevertheless, the increase in fracture toughness with increasing β phase is accompanied by a reduction in hardness and elastic modulus [4]. Therefore, improved understanding and control of β-phase formation [8, 9] is critical to the tailoring of the microstructure for improved mechanical properties.

In the present study, effects of differing processing variables on α-to-β-phase transformation and the resultant microstructure were evaluated. Subsequently, the microstructure and α/β phase ratio were correlated with measured mechanical properties.

2. Experimental techniques

Dense specimens of silicon nitride with differing β-phase contents were fabricated from commercial-grade α-Si_3N_4 powder (UBE SN-E10, $\beta/(\alpha+\beta) > 95\%$). The α-Si_3N_4 powder, with 5 wt % MgO (in the form of $Mg(NO_3) \cdot 6H_2O$) as a sintering aid, was initially mixed in an ethanol suspension. Subsequently, the slurry was ball-milled for 16 h with high-density, high-purity alumina media. The resulting slurry was dried over low heat. The average particle size of this mixture was estimated by scanning electron microscopy (SEM) to be 0.6 μm.

Another batch of powder was prepared with 5 wt % β-Si_3N_4 whiskers (UBE SN-WB) added to the α-Si_3N_4–MgO powder mixture. The whiskers, in which the $\beta/(\alpha+\beta)$ ratio was $> 99\%$, were added to the slurry after the initial ball-milling, which was then continued for an additional 3 h.

Discs of monolithic powder mixtures (α-Si_3N_4–MgO), ≈ 40 mm in diameter, were hot-pressed in vacuum in a boron-nitride–coated graphite die. The thickness of the as-fabricated discs was ≈ 4 mm. Hot-pressing temperatures ranged between 1450 and 1700 °C. The holding time was 3 h at 1450 °C and 1 h

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at higher temperatures. The composite powder mixture (α-Si_3N_4–MgO with β-Si_3N_4 whiskers) was hot-pressed in vacuum for 1 h at 1450 °C and at 1600 °C. All hot-pressing runs were performed under 80 MPa pressure on the discs.

Phase contents of the hot-pressed specimens were identified by X-ray diffraction (XRD) analysis with Cu$K\alpha$ radiation at a scanning speed of 0.025° 2θ/s. The α/β ratios were then determined from the 210 reflection intensities of both phases by following the method developed by Gazzara and Messier [10]. The margin of error in this method is considered to be less than ±3%.

Density was measured by the Archimedes method, whereas microstructure was revealed by chemical etching (molten NaOH, for 4 min). Grain size was evaluated by SEM with the linear-intercept method [11] under the assumption of quasi-spherical grains. Additional microstructural features were analyzed both by SEM and by transmission electron microscopy (TEM).

Elastic moduli of the specimens (Poisson's ratio ν, Young's modulus E, and shear modulus G) were determined by measuring ultrasonic velocities with a pulse-echo technique [12]. Hardness and fracture toughness were evaluated by Vickers indentation [13, 14] with a load of 10 kg for a duration of 10 s.

3. Results and discussion

Because large β grains play a crucial role in the toughening of Si_3N_4, a better understanding of α-to-β-phase transformation and grain growth kinetics will lead to the development of Si_3N_4 ceramics with improved microstructure and enhanced toughness. In the following sections, results of studies of microstructural development and mechanical properties are presented and discussed.

3.1. Microstructure

3.1.1. Content of α and β phases

Powder preparation and hot-pressing conditions were optimized to fabricate dense polycrystalline Si_3N_4 ceramics (> 98% of theoretical density). Specimens with controlled microstructure and α/β-phase ratio were hot-pressed by appropriately selecting hot-pressing temperature and time. The β-phase content of these specimens ranged from 24 to 99%. Throughout this paper, the samples are designated by the initials SN (representing Si_3N_4), followed by a number that represents the percentage of β phase (e.g., SN24 represents Si_3N_4 with 24% β phase). Table I lists, among other features, hot-pressing time, temperatures, and β-Si_3N_4 content of each specimen. The data in the table show that the amount of β phase increases with increasing hot-pressing temperature. Similar results have been reported by several investigators. [3–5, 8]

Fig. 1 shows the variation of β-phase content in the hot-pressed Si_3N_4 with hot-pressing time and temperature. For comparison, the data from a study by Bowen *et al*. [3] for the β-phase content of Si_3N_4 have also been included. The correlation between the results of the present study and that of Bowen *et al*. [3] is remarkable, despite the difference in applied load during hot pressing. In the present study, the hot-pressing load corresponds to a stress of 80 MPa, whereas Bowen *et al*. [3] used a load corresponding to a stress of 20 MPa. Bowen *et al*. showed that the α/β ratio was independent of the applied stress up to 30 MPa. For these tests, they started with a α-Si_3N_4 powder with 5 wt % MgO, and samples were hot pressed for 1 h at 1600 °C. In a related study, Greskovich and Gazza [15] hot- pressed Si_3N_4 (5 wt % MgO) at 1600 °C under a load of 70 MPa for differing periods of time. Specimens hot-pressed at 10 and 180 min contained 15 and 100% β phase, respectively. Thus, their results are in good agreement with the results of the present study and those of Bowen *et al.* [3]. Despite differences in experimental conditions and starting materials, it appears that the sensitivity of the final β-phase content to hot-pressing load is not significant.

TABLE I Microstructure and mechanical properties of Si_3N_4 specimens hot-pressed under various processing conditions

Proc. cond. and properties[a]	SN24	SN30	SN54	SN60	SN99
T (°C)	1450	1550	1600	1630	1700
t (h)	3	1	1	1	1
ρ (% ρt)	98	99	99	98	99
β (% vol)	24	30	54	60	99
EQG d (μm)	0.85	0.60	0.65	0.81	—
ELG 1 (μm)	—	—	1.19	1.18	2.86
d (μm)	—	—	0.23	0.27	0.54
R	—	—	5.7	4.5	5.2
ν	0.250	0.256	0.279	0.276	0.269
G (GPa)	141	138	132	131	128
E (GPa)	353	347	338	335	324
H_v perp (MPa)	25070 ±3977	24424 ±4347	24742 ±4574	25081 ±3543	19755 ±2098
K_{IC} perp (MPa · $m^{1/2}$)	3.8 ±0.6	4.5 ±0.7	5.5 ±1.3	7.0 ±0.5	6.6 ±0.5

[a]d, diameter; 1, length; R, aspect ratio; perp, perpendicular to the hot-pressing direction; (ρ % ρt), percentage of the theoretical density; ν, Poisson's ratio.

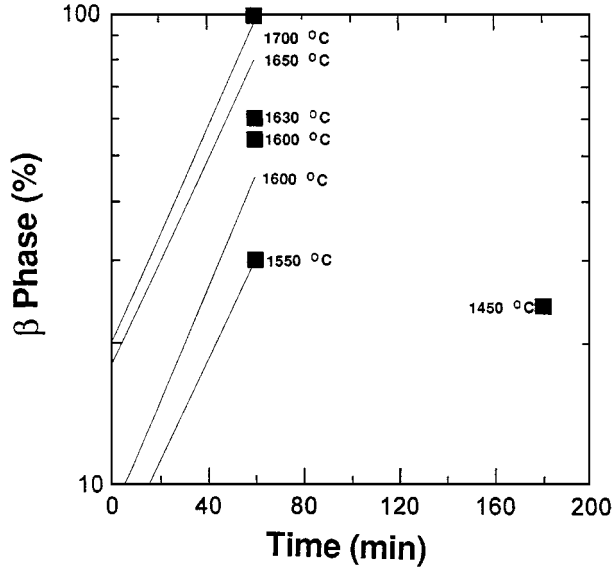


Figure 1 β-phase content of Si_3N_4 specimens hot-pressed (α-Si_3N_4 powder) at various temperatures. Solid lines represent literature values of Bowen *et al.* [3] (hot-pressing stress = 30 MPa), and squares represent data from present work (hot-pressing stress = 80 MPa).

By analyzing the diffusion kinetics of densification and α-to-β-phase transformation, Bowen *et al.* [3] concluded that a linear dependence of both processes on the applied pressure is expected during the early stages of densification (prior to full density). However, experimental results indicate that full density is rapidly achieved (3 min at ≈ 20 MPa when 5 wt % MgO has been added to the samples), after which a pressure-independent transformation rate should occur. This finding is consistent with experimental observations, as discussed in the previous paragraph.

The addition of whiskers to monolithic materials is a well-documented method of improving mechanical properties [7, 16, 17]. It has been observed that the addition of large β-Si_3N_4 particles to the starting Si_3N_4 powder influences the grain morphology of hot-pressed Si_3N_4. Hirosaki *et al.* [18] reported that the addition of large β-Si_3N_4 particles to β-Si_3N_4 powders before sintering resulted in elongated beta grains with larger diameters and smaller aspect ratios in the sintered material. Thus, for Si_3N_4 composites with β-Si_3N_4–whisker reinforcements [17], there exists a distinct possibility of enhanced α-to-β-phase transformation of the matrix phase and the consequential change in grain morphology. Therefore, we conducted a study to evaluate the effects of β-whisker addition on the conversion of α powder and the resulting grain morphology during hot-pressing.

Fig. 2 shows the effect of whisker addition on β-phase content in Si_3N_4 specimens that were hot-pressed at various temperatures. The data indicate that β-phase content increases with whisker addition and hot-pressing temperature. Similar dependence on whisker addition was also observed by Chu *et al.* [17] for β-Si_3N_4-whisker–reinforced matrix composites that were hot-pressed at 1650 °C for 2 h. In the present study, the β-phase content of the Si_3N_4–5 wt % β-Si_3N_4 whisker composites hot-pressed for 1 h at 1450 and 1600 °C was 28 and 61%, respectively (Fig. 2). For the same whisker content (5 wt % β-Si_3N_4), Chu *et al.* [17] obtained a 74% β-Si_3N_4 phase content in the composite hot-pressed at 1650 °C for 2 h. It is to be noted that if the starting β-whisker content (5 wt %) is subtracted from the final β-phase content in the composite, the net β phase formed during hot-pressing at 1450, 1600, and 1650 °C can be estimated at 23, 56, and 68%, respectively. These phase contents are similar to those obtained for the hot-pressed Si_3N_4 specimens without whisker additions.

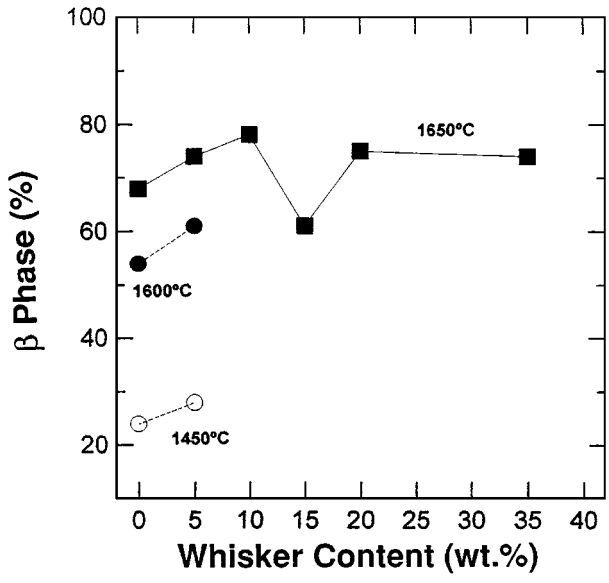


Figure 2 Effect of whisker addition on β-phase content of Si_3N_4 composites hot-pressed at various temperatures and for various lengths of time. ■ = data from [17] (hot-pressed for 2 h at 30 MPa) and ● = data from the present work.

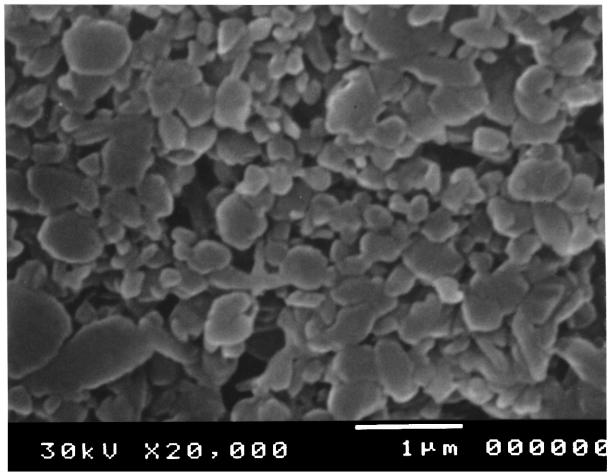
The insensitivity of β-phase content to β-whisker addition discussed above may be related to the larger aspect ratio of the β-Si_3N_4 whiskers (10–15) when compared with the smaller aspect ratio (≈ 5) of acicular β-Si_3N_4 grains (Table I) produced by α-to-β transformation, which is discussed later. Commercial β whiskers are typically obtained from vapor phase, whereas the growth of elongated β grains is controlled by liquid phase diffusion through grain boundaries [3]. According to the model of Bowen *et al.* [3] the driving force of diffusion is inversely proportional to the length of the diffusion path, which suggests that smaller β-Si_3N_4 grains are more likely to grow than larger β-Si_3N_4 whiskers. Therefore, large β-Si_3N_4 whiskers do not grow further and do not contribute to additional phase conversion.

3.1.2. Grain morphology

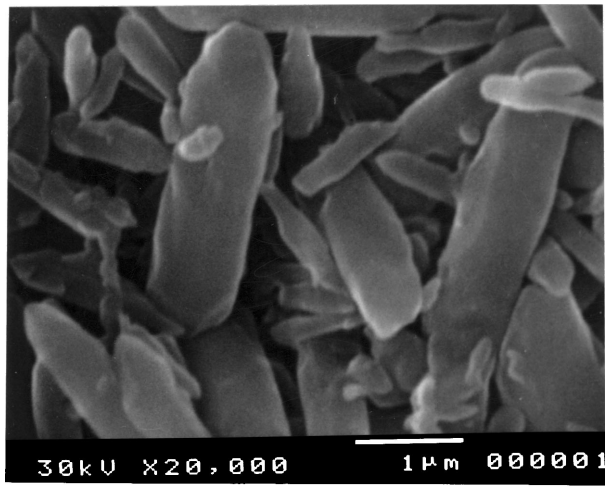
Composites polished (perpendicular to the hot-pressing direction) to a surface finish of 0.25 μm were etched to reveal the microstructure of the composite. Figs 3 and 4 show the grain microstructure of Samples SN30, SN60, and SN99 and illustrate the microstructural evolution of Si_3N_4. It can be noted that Samples SN30 (with 30% β phase, Fig. 3a) and SN99 (with 99% β phase, Fig. 3b) show primarily small equiaxed grains (EQGs) and large elongated grains (ELGs), respectively, while Sample SN60 (with 60% β phase, Fig. 4) shows bimodal grain distribution. This observation suggests that the ELG fraction increases with increasing β-phase content.

The average grain size of the equiaxed grains was estimated by the linear intercept method. The length and width of the ELGs were measured directly on the SEM micrographs, and the aspect ratio was subsequently calculated. The average values of these parameters are included in Table I. Only a few EQGs are detectable in Sample SN99, which was hot-pressed at 1700 °C for 1 h; therefore, the statistics were not significant. A similar result was observed for the ELGs in Samples SN24 and SN30. In general, higher temperatures, and especially longer hot-pressing times, produced larger EQGs.

Fig. 5, the microstructure of an etched SN60 sample, reveals the transformation of an α to a β grain. The formation of an elongated structure from an equiaxed one is clearly illustrated. The micrograph shows that the length of the ELG is $\approx 1.5\,\mu$m and its width is 0.25 μm, while the size of the EQG is 0.75 μm. These values are in good agreement with the ones in Table I. Furthermore, the wavy shape of this element suggests



(a)



(b)

Figure 3 SEM micrograph showing evolution of grain morphology with β-phase content in Samples (a) SN30 and (b) SN99.

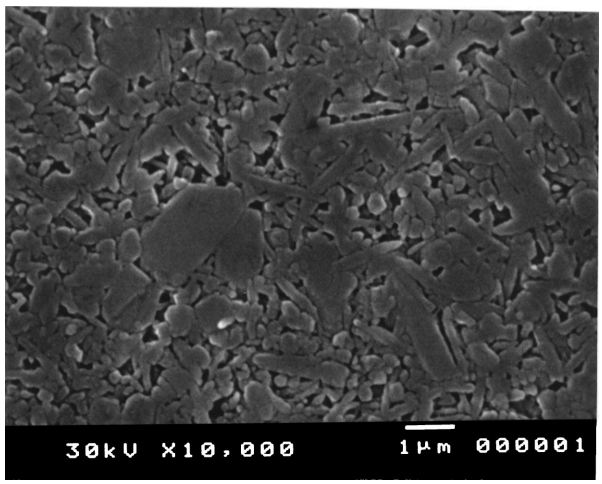


Figure 4 SEM micrograph of etched Sample SN60, showing bimodal grain distribution.

the development of β-Si_3N_4 from the liquid phase, a finding that agrees well with the morphological development model proposed by Sarin [6].

As proposed by Himsolt *et al.* [4] and Sarin [6], starting powders with higher α-phase content are expected

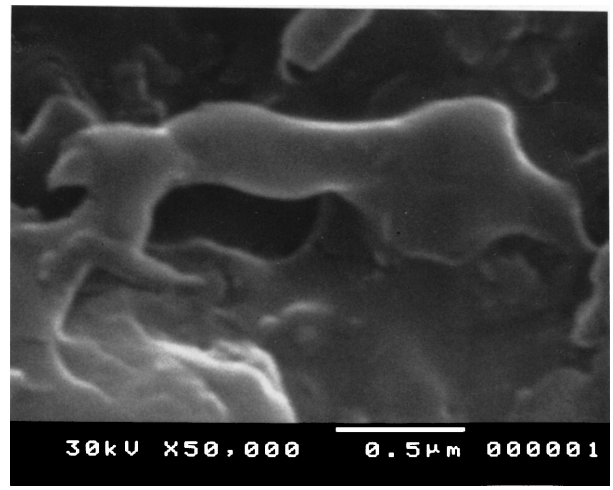


Figure 5 SEM micrograph of etched SN60 sample, showing transformation of α grain into β grain.

to produce β grains with larger aspect ratios. Lange [2] suggested that β grains grow only from the ones present in the initial powder and that the final aspect ratio was independent of the processing conditions. He proposed that the aspect ratio R of the β grains can be given by the equation

$$R = 1 + \alpha/\beta, \tag{1}$$

where α and β represent volume contents. The results of a previous study by Sarin [6] and our present work do not seem to agree with this statement, at least for powders with low and high β-phase content. Sarin [6] used starting silicon nitride powders with 10 and 100% β phase and obtained grain microstructures with aspect ratios of 6.3 ± 0.9 and 3.8 ± 0.7, respectively. The corresponding values of the aspect ratios predicted by Equation 1 is 10 and 1, respectively. In our study, with a starting powder mixture of α-Si_3N_4–5 wt% Si_3N_4 whisker ($\alpha/\beta = 19$), the average length and width of the ELGs were both observed to increase with hot-pressing temperature in aproximately the same proportion (Table I). As shown in the table, the aspect ratio of the ELGs varies from 4.5 to 5.2, which is not in agreement with the prediction of Equation 1. In a study by Hirao *et al.* [19], who used the same starting α-Si_3N_4 powder as in this study, similar values of the β-grain diameter and aspect ratio were found. Based on Lange's expression, for our study and the study by Hirao *et al.* (where the starting Si_3N_4 powder mixture had an $\alpha/\beta \approx 19$), the ELG aspect ratio should have been larger than 19. We believe that this difference may be related to the variable that controls the formation and growth of β phases, as well as to the phase purity of the starting powder.

Fig. 6 is a scanning electron micrograph of an etched SN54 specimen, and the "stairlike" pattern of growth of the ELGs is clearly evident. This observation is consistent with Sarin's [6] suggestion that the growth kinetics of the acicular β-Si_3N_4 grains are planar and controlled by the deposition rate on both the basal and prismatic faces. Such diffusion processes are possible

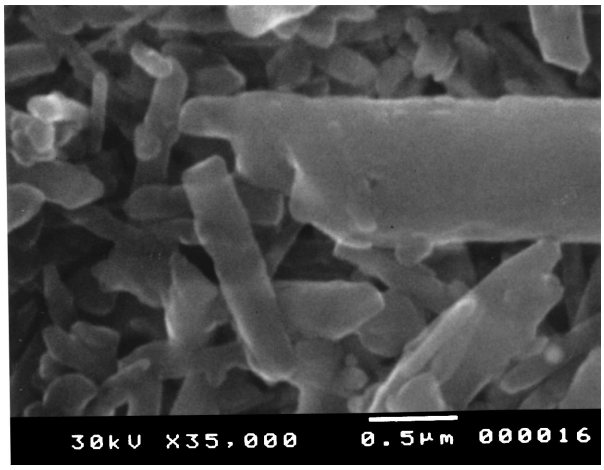


Figure 6 SEM micrograph showing "stairlike" pattern of growth of a β grain in etched SN54 sample.

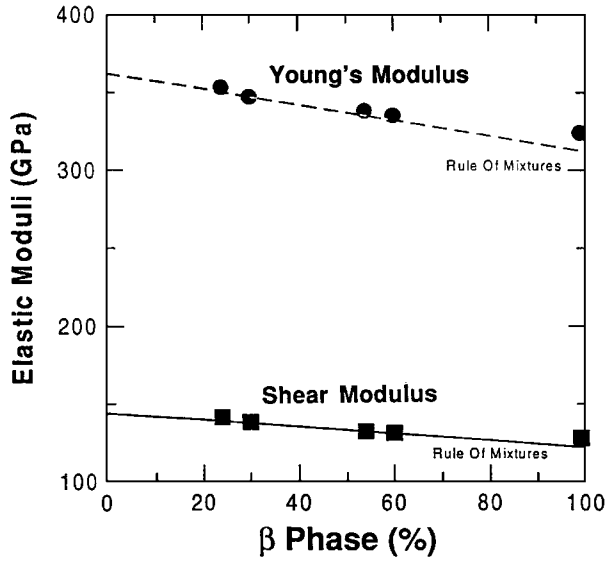


Figure 7 Experimental values of Young's modulus E and shear modulus G and values of these moduli predicted by the rule of mixtures (dashed and solid lines).

if the acicular grains are surrounded by a liquid flux throughout their growth cycle, as concluded in a previous work [17]. Thus, the presence of liquid will control not only the α-to-β transformation but also the growth of the transformed grains.

3.2. Mechanical properties

3.2.1. Elastic moduli

The values of the elastic moduli (Poisson's ratio ν, shear modulus G, and Young's modulus E) measured at room temperature are listed in Table I. The values of Poisson's ratio obtained in our study are in general agreement with literature values, as shown in Table II. The Poisson's ratio of the hot-pressed Si_3N_4 specimens increased from 0.250 to 0.279 when β-phase increased from 24 to 54%. A further increase in β-phase content resulted in a slight decrease in the value of Poisson's ratio. Similar observations were obtained by Himsolt *et al.* [4].

TABLE II Literature values of elastic moduli for Si_3N_4 with varying β-phase content

β phase (vol %)	Young's modulus E (GPa)	Shear modulus G (GPa)	Poisson's ratio ν	Reference
100	307	—		[1]
15	318	—	0.258	[5]
34	311	—	0.256	
64	302	—	0.271	
100	309	—	0.265	
0	362	144	0.250	[20]
100	312	122	0.280	
100	316	—	0.255	[16]
100	314	—	—	[17]
70	339	—	—	[8]
81	320	—	—	
81	315	—	—	
88	303	—	—	
90	320	—	—	
92	304	—	—	
92	318	—	—	
93	311	—	—	
100	325	—	—	

Both shear (G) and Young's (E) moduli decreased with increasing β-phase content. The values of G ranged between 141 and 128 GPa, and those of E ranged between 353 to 324 GPa. These values are in agreement with those in the literature for both completely dense fully α- and fully β-Si_3N_4 [8, 16, 17, 20]. Fig. 7 shows the variation of E and G with β-phase content for hot-pressed Si_3N_4 specimens. Also shown in the figure are analytically predicted straight-line variations obtained by using the rule of mixtures. For the analytical prediction, the elastic moduli for the α and β phases were taken to be $E_\alpha = 362$ GPa, $E_\beta = 312$ GPa, $G_\alpha = 144$ GPa, $G_\beta = 122$ GPa [15]. In general, the experimental values are in good agreement with the predicted variation.

The agreement between the results of this study and the analytical prediction confirms the high density of our ceramic. It suggests a strong bonding between the grains [16] and is related to the clean grain boundaries that have been observed [21].

3.2.2. Fracture properties

Table I shows the values of Vickers hardness (H_v) and fracture toughness (K_{IC}) that were measured on surfaces perpendicular to the hot-pressing direction. As shown in Table I, the measured hardness values in this study ranged from 19 755 to 25 081 MPa. These values were slightly higher than the ones reported in the literature [1, 4, 5, 8, 15, 17, 22–24] (Table III).

Hardness is a measure of plastic deformation, so for high-temperature creep, both grain size and the bonding between the grains can play an important role. It is proposed that hardness is expected to increase with grain size and decrease with β-phase content. In the present study, a combined effect of both grain size and β-phase content leads to a non-linear dependence of hardness on β-phase content. Greskovich and Yeh [22] showed that a fully β-Si_3N_4 was harder when its grain size was larger and it contained less glassy phase. In this study,

TABLE III Literature values of Vickers hardness H_v and fracture toughness K_{IC} for Si_3N_4 with varying β-phase content

β phase (vol %)	Vickers hardness H_v (MPa)	Fracture toughness K_{IC} (MPa · $m^{1/2}$)	Reference	Remarks
100	—	6.5	[1]	—
100	—	6.0	[23]	—
15	—	3.2	[4]	—
34	—	5.0		—
64	—	7.8		—
100	—	6.6		—
100	16 500	—	[22]	2% glass
100	19 500	—		no additives
100	18 400	—		no additives
15	20 900	4.5	[15]	—
80	16 400	6.0		—
100	15 850	5.7		—
100	15 000	4.5		—
100	14 670	6.8	[17]	—
<50	18 620	3.0	[5]	—
100	15 190	4.0		—
40	—	4.5	[24]	—
97	—	5.4		
70	22 300	5.0	[8]	additives up to 11 wt %
81	19 300	4.9		—
81	19 400	5.2		—
88	18 300	5.2		—
90	18 600	5.9		—
92	17 600	4.7		—
92	17 400	4.9		—
93	17 800	5.5		—
100	15 800	4.9		

the Vickers hardness H_v of β-Si_3N_4 samples with clean grain boundaries was as high as 19 500 MPa. On the other hand, in a study by Greskovich and Gazza [15], the hardness of a dense, glass-free, α-Si_3N_4 that was fabricated by chemical vapor deposition was reported to be 29 500 MPa. Thus, a relatively high hardness value (25 070 MPa) for Sample SN24 in the present study is indicative of strong bonds and clean grain boundaries for Si_3N_4 grains. The absence of significant amounts of glassy phase at grain boundaries can be confirmed by TEM, as seen in Fig. 8. We believe that higher hot-pressing load (stress) promotes stronger bonding between the grains.

Table I summarizes the results of fracture toughness (K_{IC}) as a function of β-phase content. These results have been plotted in Fig. 9, which shows a significant

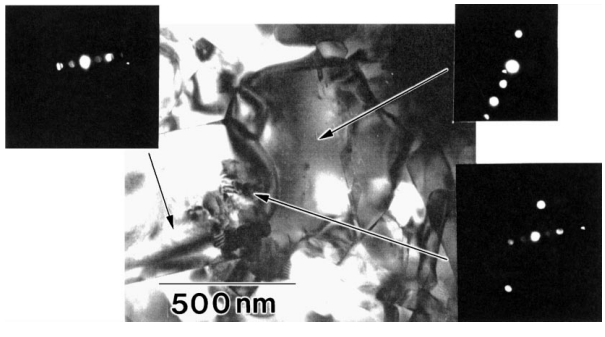


Figure 8 TEM micrograph of SN60 specimen showing clean grain boundaries. Diffraction patterns correspond to selected areas indicated by arrowheads.

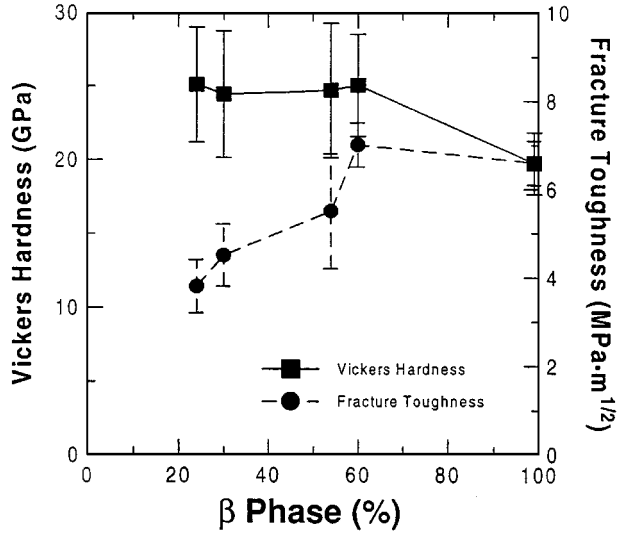


Figure 9 Variation of Vickers hardness H_v and fracture toughness K_{IC} with β-phase content.

dependence of K_{IC} on β-phase content. The value of K_{IC} increases from 3.8 ± 0.6 MPa · $m^{1/2}$ for a β-phase content of 24% to 7.0 ± 0.5 MPa · $m^{1/2}$ for a β-phase content of 60%. At higher β-phase content, the value does not change significantly. The increase in K_{IC} is related to the increase in the fraction of ELGs with increasing β-phase content. Similar increase in toughness with increasing fraction of ELGs has been observed in several studies [25–27]. The increase in toughness is related to the interaction between the crack front and the ELGs/grain boundaries, and the toughening mechanisms include crack deflection [7] as well as grain debonding, pullout, and bridging.

Fig. 10 shows SEM micrographs of a polished and indented surface of Sample SN60 with 60% β-phase content. The micrographs show the interaction of the indentation crack with the microstructure. Toughening mechanisms, such as crack deflection, grain pullout, debonding, and bridging, are clearly visible. The presence of these mechanisms has led to an increase in toughness of Si_3N_4 specimens from 3.8 ± 0.6 MPa · $m^{1/2}$ for SN24 (with 24% β content, and relatively uniform microstructure) to 7.0 ± 0.5 MPa · $m^{1/2}$ for SN60 (with 60% β content, and many ELGs embedded into a small-grained uniform matrix). This observation on the dependence of toughness on β content is in agreement with the studies by Greskovich and Gazza [15] and Himsol *et al.* [4].

4. Conclusions

Polycrystalline Si_3N_4 specimens with tailored microstructure and improved properties have been fabricated by hot-pressing α-Si_3N_4 powder at various temperatures with varying amounts of β-Si_3N_4–whisker additions. The β-phase content of the hot-pressed Si_3N_4 increased with increasing hot-pressing temperature. On the other hand, the effect of β-Si_3N_4–whisker additions on the β-phase content of the hot-pressed Si_3N_4 was minimal. The grain morphology and phase transformation mechanism were characterized by SEM, which indicated that the ELG fraction increased with increasing

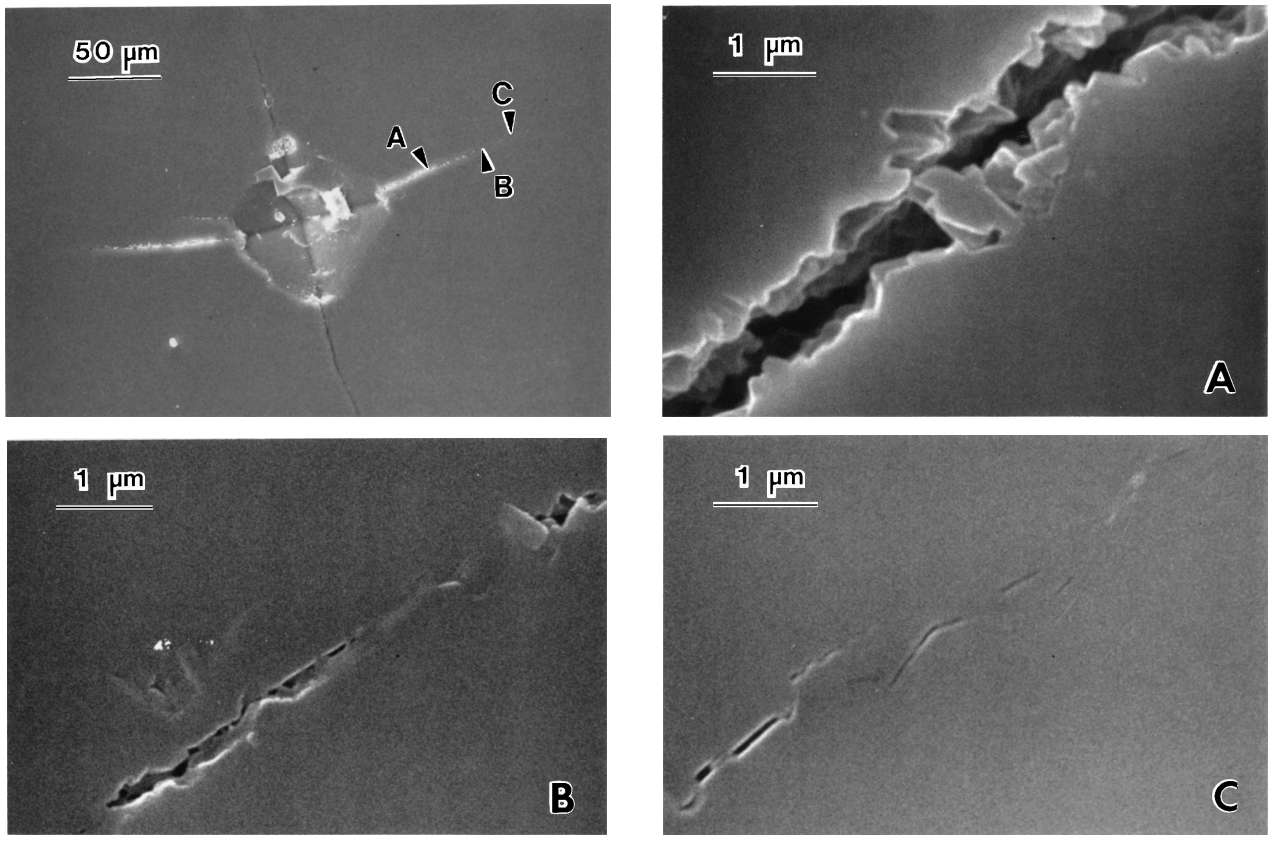


Figure 10 SEM micrograph of polished and indented surface of SN60 specimen showing presence of various toughening mechanisms such as crack deflection, grain pullout, and debonding and bridging.

β-phase content. A stairlike growth pattern of the ELGs was observed by SEM, suggesting that growth kinetics of the acicular β-Si_3N_4 grains are planar and controlled by the deposition rate on both the basal and prismatic faces.

The elastic moduli were observed to decrease with increasing β-phase content, while the dependence of hardness on β-phase content was non-linear because of a combined effect of phase content and grain morphology.

Fracture toughness (K_{IC}) increased with increasing β-phase content. A toughness value of 7.0 ± 0.5 MPa $\cdot$ $m^{1/2}$ was obtained at a β-phase content of 60% as compared to a value of 3.8 ± 0.6 MPa $\cdot$ $m^{1/2}$ at a β-phase content of 24%. At higher β-phase contents, K_{IC} does not change significantly. The increase in K_{IC} is related to the increase in ELG fractions with increasing β-phase content, which promotes energy absorption through crack deflection as well as grain debonding, pullout, and bridging.

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