Crystallizing the grain-boundary glass of a liquid-phase-sintered Si₃N₄ ceramic for 2 h or less at 1500°C led to formation of δ-Y₂Si₂O₆. After 5 h at 1500°C, the δ-Y₂Si₂O₆ had transformed to β-Y₂Si₂O₆ with a concurrent dramatic increase in dislocation density within β-Si₃N₄ grains. Reasons for the increased dislocation density are discussed. Annealing for 20 h at 1500°C reduced dislocation densities to the levels found in as-sintered material. [Key words: silicon nitride, microstructure, grain boundaries, grains, glass.]

I. Introduction

The predominantly covalent nature of the atomic bonds in Si₃N₄ hinders atom migration so that the solid-state sintering below the decomposition temperature (1878°C at atmospheric pressure in air) is limited. Fabrication of structural components may therefore be facilitated by adding one or more oxides to the Si₃N₄ powder (e.g., Refs. 2 and 3), which combine with surface and (occasionally) added SiO₂ to form a low-melting-point silicate liquid. Liquid-phase sintering (LPS) occurs by a solution-reprecipitation mechanism as originally proposed by Drew and Lewis. In this process the α-Si₃N₄ starting powder dissolves in the silicate liquid and is precipitated out as β-Si₃N₄, with the silicate liquid solidifying as a glass at the grain boundaries of the final product. Unfortunately, the low melting point of the silicate phase used to advantage during sintering is detrimental to the mechanical properties of the monolithic material at high temperatures, since the glass typically begins to soften at relatively low temperatures (about 1000°C).

One method of improving the high-temperature mechanical strength is to alter the glass composition to increase its softening point (e.g., Ref. 5). Another technique is to use a post-sinter heat treatment to crystallize the glass to a more refractory phase. In a recent study⁶ we employed the latter technique for Si₃N₄ fabricated with a Y₂O₃ sintering aid and crystallized Y₂Si₂O₆ at the grain boundaries. We present here observations of the effect of this crystallizing treatment on the microstructure of the β-Si₃N₄ grains.

Fig. 1. Bright-field (BF) TEM image of the general microstructure of as-sintered Si₃N₄, with (inset) EDS spectrum from glassy phase.

Fig. 2. BF TEM image of a group of b = (0001) dislocations in a β-Si₃N₄ grain of as-sintered material.
II. Experimental Procedure

The starting powders were Si₃N₄, Y₂O₃, and SiO₂. The powders were mixed in the ratio 90:6:4:3:6 wt%, respectively, and milled as 100-g charges in 1-L Si₃N₄ mills using high-purity Si₃N₄ milling media and ethanol. After oven drying under vacuum, the powders were die-pressed into bars at 21 MPa followed by cold isostatic pressing at 414 MPa. These bars were then sintered at 2140°C for 4 h and ethanol. After oven drying under vacuum, the powders were charges in 1-L Si₃N₄ mills using high-purity Si₃N₄ milling media and an edge component where the contrast at the g-b = 0 but pure screw dislocations, it is commonly applied to those containing an edge component where the contrast at the g·b = 0 but g·b × a = 0 condition is minimal. Residual contrast can arise from the g·b × a term and/or from elastic anisotropy and in some cases requires image-contrast calculations to determine b. Image-matching calculations were not attempted here. Weak-beam dark-field (WBDF) imaging was necessary when examining dislocations in Si₃N₄. This technique images only the dislocation core and enables high densities of dislocations to be studied. In conventional bright-field (BF) and dark-field (DF) images, the overlapping strain fields of the dislocations make analysis of them impossible. Diffraction patterns for Si₃N₄ were solved with the assistance of Ref. 10.

Dislocation densities for 100 adjacent grains were determined in each sample, using the method of counting intersections of dislocations with drawn circles as described in Ref. 7. Convergent beam electron diffraction was used to measure the thickness of representative grains and an average value of 200 nm used in all density calculations. This will introduce some error in the dislocation density measurements. Further error is introduced because the technique of Hirsch et al. leads to an underestimate of dislocation density, since at all orientations some dislocations will be out of contrast. This error was minimized by using g = 0002 at the [1210] zone axis whenever possible in images used for density determinations. At this orientation the majority of dislocations with b = (0001) or with c and a components in their b are in contrast but not those with b = [1210]. The maximum total error associated with this procedure for dislocation densities is expected to be on the order of 25%.

III. Results

(1) As-Sintered Microstructure

A BF TEM image of the general microstructure is shown in Fig. 1. Hexagonal β-Si₃N₄ grains are contained in a glue of yttrium silicate glass. Other minor phases occasionally observed in the microstructure include α-Si₃N₄, α-SiC, and up to 5 vol% Si₃N₂O. An EDS spectrum from the glass is shown inset in Fig. 1. More detailed BF examination of the silicon nitride grains shows that some of them contain dislocations (Fig. 2) which we assume are simply “grown in” during the reprecipitation process. The distribution of dislocation densities in β-Si₃N₄ grains (Fig. 3(a)) reveals that about 60% of the grains do not contain dislocations and the maximum dislocation density observed in any grain is 31 x 10⁹/cm². Burgers vector b analysis on
selected dislocations indicates that the vast majority of the dislocations have \( b = (0001) \). However, dislocations having other \( b \)'s were occasionally observed; for example, some dislocations had \( b = \frac{1}{3}(1210) \).

(2) Microstructure After Heating 0.5 h at 1500°C

After crystallization for only 0.5 h at 1500°C, the microstructure was significantly altered. At the resolution utilized (about 1 nm) the glass had completely crystallized. Electron diffraction patterns matched \( \beta-Y_2Si_2O_7 \) which had a "mottled" morphology in BF, described as "blocky" by Ref. 12, shown in Fig. 4. The dislocation density was slightly higher than in the as-sintered microstructure (Fig. 3(b)), with about 52% of the grains being dislocation-free.

(3) Microstructure After Heating 2 h at 1500°C

The microstructure after 2 h at 1500°C was essentially unchanged from that observed after the 0.5-h crystallizing heat treatment. The dislocation density is given in Fig. 3(c).

(4) Microstructure After Heating 5 h at 1500°C

After a crystallizing heat treatment of 5 h at 1500°C, a highly stressed microstructure is observed (Fig. 5), with large numbers of bend and strain contours visible in the silicon nitride grains. As discussed in Ref. 6, the glassy grain-boundary phase has recrystallized to \( \beta-Y_2Si_2O_7 \) after this anneal, with no \( \delta-Y_2Si_2O_7 \) remaining. The inset diffraction pattern in Fig. 5 is the [001] zone for \( \beta-Y_2Si_2O_7 \). WBDF imaging reveals that the strain contours arise from complicated and dense dislocation networks and tangles within the \( \beta-Si_3N_4 \) grains (Fig. 6). The distribution of dislocation densities (Fig. 3(d)) shows that now only about 20% of grains are dislocation-free, while the maximum density is \( 86 \times 10^7/cm^2 \). Again the predominant \( b \) is (0001), as indicated by the Burgers vector analysis of Fig. 7 (see the \( g \cdot b \), Table 1), in which all dislocations are in contrast for \( g = 0002 \) and 0111 but invisible for 3630 and 1320. The heterogeneous nature of the dislocation distribution should be emphasized here in that a dislocation-free grain is often found next to a highly dislocated grain, with no gradual change apparent. Preparation of TEM specimens from material after this treatment was more difficult than for material given any other treatment; samples invariably cracked on ion thinning.

(5) Microstructure After Heating 20 h at 1500°C

Long heat treatment times at 1500°C led to reduced dislocation densities (Fig. 3(e)), presumably due to the dislocations annealing out. However, the dislocations remaining had undergone extensive rearrangement during the longer heat treatment, giving
rise to morphologies such as those of Fig. 8. The Burgers vector analysis illustrated in Fig. 8 suggests that a large number of the dislocations still have \( \mathbf{b} = (0001) \), i.e., those in contrast for \( g = 0002 \) and \( 0\bar{1}1\bar{1} \) but out for \( g = 3630 \) and \( 0220 \), e.g., A. However, dislocations having other \( \mathbf{b} \)'s are present. If we consider only the perfect dislocation listed for hexagonal structures in Table I, other possible \( \mathbf{b} \)'s are \( \{211\overline{3}\} \), e.g., B (in contrast for \( 0002, 0\bar{1}1\bar{1}, \) and \( 3630 \) but out for \( 0220 \)), and \( \{2110\} \), e.g., C (in contrast for \( g = 3630 \) but out for \( 0\bar{1}1\bar{1}, 0002, \) and \( 0220 \)).

(6) Sub-Grain Boundaries and Polygonized Networks

All samples contained occasional examples of dislocation networks and sub-grain boundaries, e.g., Fig. 9. Initial attempts at \( \mathbf{b} \) analysis suggest that many of these boundaries are complicated and may require comparison to calculated images for complete interpretation. This is beyond the scope of the present study but will be pursued in the future.

IV. Discussion

Crystallization of the grain-boundary glass to increase the re-fractoriness of Si₃N₄ ceramics has been intensively studied since the initial work of Tsuge et al., and also on the Y₂O₃–Si₃N₄ system. However, this is the first observation that crystallization of the grain-boundary phase may have an effect on the Si₃N₄ grains. While some caution must be heeded with these data in that, because of the complexity of the experiments, only 100 grains were examined in each sample, the trends observed were reproducible. Several explanations can be proffered for the appearance of the dislocations, including a volume change on crystallizing the glass, a volume change upon transformation of one polymorphic form of the crystalline phase to another, or a difference between the thermal expansion coefficient of the phases present.

While the densities of the Y₂Si₂O₇ polymorphs are available (see Ref. 14 and Table II), the density of Y₂Si₂O₇ glass is not, and experiments to fabricate it and measure its density have been unsuccessful. Crystallization of a glass, however, usually leads to a reduction in volume due to the closer packing of atoms in a crystalline structure, and it seems likely that a volume decrease will occur. Any volume change (increase or decrease) in the grain-boundary phase will impose a strain on the Si₃N₄ grains, deforming them and creating dislocations. The slight increase in dislocation density in the sample crystallized for 0.5 h compared to the as-sintered sample (Figs. 3(a) and (b)) may be attributed to this.

However, the biggest increase in dislocation density occurs between 2 and 5 h at 1500°C (Figs. 3(c) and (d)), during which time, as revealed by electron diffraction analysis, the grain-
boundary phase transforms from δ- to β-$\text{Y}_2\text{Si}_3\text{O}_5$. This strongly suggests that a volume change associated with this transformation is responsible for the observed stress and dislocation formation after 5 h at 1500°C. The volume changes between the polymorphs in $\text{Y}_2\text{Si}_3\text{O}_5$ are given in Table III, calculated from data in Ref. 14. As can be seen, the largest volume change on any transformation is for $\alpha = \beta$. However, the nearly 2% volume change associated with the δ-to-β transition could well generate the stresses necessary to deform the Si$_3$N$_4$ grains at 1500°C. Any shear associated with the δ-to-β transition, which is from orthorhombic to monoclinic symmetry (see Table II), could also contribute to dislocation formation. The dislocation microstructures formed in the crystallized material are typical of those induced in ceramics by high-temperature deformation. The reduced dislocation density after 20 h at 1500°C is due to annealing out of the dislocations by the prolonged heat treatment (Fig. 3(e)).

According to Liddel and Thompson, $\alpha$-$\text{Y}_2\text{Si}_3\text{O}_5$, the low-temperature form, transforms to $\beta$ at 1225°C, which should trans-

<table>
<thead>
<tr>
<th>Table I. Values of $g \cdot b$ for Relevant Reflections in the Hexagonal Crystal Structure for Perfect Dislocations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h\cdot l$</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>$\pm [1120]$</td>
</tr>
<tr>
<td>$\pm [1210]$</td>
</tr>
<tr>
<td>$\pm [2110]$</td>
</tr>
<tr>
<td>$\pm [0013]$</td>
</tr>
<tr>
<td>$\pm [1132]$</td>
</tr>
<tr>
<td>$\pm [123]  $</td>
</tr>
<tr>
<td>$\pm [213]  $</td>
</tr>
<tr>
<td>$\pm [1123]$</td>
</tr>
<tr>
<td>$\pm [1213]$</td>
</tr>
<tr>
<td>$\pm [2113]$</td>
</tr>
</tbody>
</table>
form to γ at 1445°C. Possible reasons for the observation that γ was never detected in the room-temperature microstructure after heat treatment at 1500°C are discussed at length by Lee et al. The thermal expansion coefficient of YSi2O5 is not available while that of β-Si3N4 is known to be low but highly anisotropic. For the temperature range 0°C to 1000°C, the thermal expansion coefficient is 3.23 × 10^-6/°C along the a axis and 3.72 × 10^-6/°C along the c axis. This anisotropy is expected to remain at temperatures up to the crystallization temperature used in this study (1500°C) and may cause a significant amount of stress on a local scale, especially if the thermal expansion coefficient of YSi2O5 is also anisotropic. Thermal expansion mismatch, however, would be expected to lead to similar stress and consequent dislocation formation in all samples regardless of hold time at temperatures, since the stress arises only during the heating and cooling cycle. This cannot, therefore, be invoked to explain the much higher dislocation densities observed after a 5-h crystallization treatment as compared to material receiving other treatments.

Fig. 9. WBDF image of a sub-grain boundary and a polygonized network (arrowed) in a β-Si3N4 grain imaged using g = 220 at the [0001] orientation. The edges of the hexagon are the projections of (1010) planes.

Table II. Space Groups, Specific Volumes, and Densities for the YSi2O5 Polymorphs

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>Space group</th>
<th>Specific vol (m³)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>Monoclinic P21/m</td>
<td>0.1407</td>
<td>4.083</td>
</tr>
<tr>
<td>α</td>
<td>Triclinic P1</td>
<td>0.1336</td>
<td>4.300</td>
</tr>
<tr>
<td>β</td>
<td>Monoclinic C2/m</td>
<td>0.1425</td>
<td>4.032</td>
</tr>
<tr>
<td>γ</td>
<td>Monoclinic P21/n</td>
<td>0.1422</td>
<td>4.040</td>
</tr>
<tr>
<td>δ</td>
<td>Orthorhombic Pna21</td>
<td>0.1398</td>
<td>4.110</td>
</tr>
</tbody>
</table>

V. Summary and Conclusions

Crystallizing the grain-boundary glass in a Si3N4 ceramic containing 6 wt% Y2O3 led to the formation of δ-YSi2O5 after 0.5- or 2-h anneals at 1500°C. A slight increase in dislocation density in the β-Si3N4 grains was noted after crystallization. However, after a 5-h anneal at 1500°C the δ-YSi2O5 had transformed to β-YSi2O5, and associated with the transition was a dramatic increase in dislocation density in the β-Si3N4 grains. The most likely origin for the deformation of the silicon nitride grains is the volume change accompanying the 5- to β-YSi2O5 transition. Longer anneals at 1500°C for times up to 20 h reduced the dislocation density to the levels observed in as-sintered materials, suggesting that any affect on the mechanical properties of the silicon nitride may be removed.
Table III. Volume Changes Associated with Transformations between Y$_3$Si$_2$O$_5$ Polyomorphs on Heating

<table>
<thead>
<tr>
<th>Polyomorphs</th>
<th>Vol change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \rightarrow \beta$</td>
<td>+0.233</td>
</tr>
<tr>
<td>$\beta \rightarrow \gamma$</td>
<td>-0.198</td>
</tr>
<tr>
<td>$\gamma \rightarrow \delta$</td>
<td>-1.733</td>
</tr>
<tr>
<td>$\beta \rightarrow \delta$</td>
<td>-1.984</td>
</tr>
</tbody>
</table>

References

7. M. Long; private communication.
15. D. R. Clarke, private communication.
Microstructural Evolution in Near-Eutectic Yttrium Silicate Compositions Fabricated from a Bulk Melt and as an Intergranular Phase in Silicon Nitride

William E. Lee,** Charles H. Drummond III,* Gregory E. Hilmas,** and Suresh Kumar***

Department of Materials Science and Engineering, The Ohio State University, Columbus, Ohio 43210

Near-eutectic composition $Y_2O_3-SiO_2$ melts were formed as bulk samples or as an intergranular phase in $Si_3N_4$. Upon cooling to room temperature the bulk material partially crystallized to $\delta Y_2Si_3O_5$ whereas the intergranular phase was glass. On heat-treating at 1500°C the bulk material transformed to $\gamma Y_2Si_3O_5$ whereas the intergranular glass crystallized first to $\delta Y_2Si_3O_5$ and then to $\beta Y_2Si_3O_5$. Possible reasons for the different behavior are discussed. [Key words: crystallization, glass, yttria, silica, silicon nitride.]

I. Introduction

To facilitate liquid-phase sintering (LPS) a metal oxide, or a mixture of oxides, is added to $Si_3N_4$ powder. The ubiquitous silica film present on the nitride particles (occasionally with added silica powder) combines with the oxide to form a low melting temperature liquid phase which is the host for the solution–reprecipitation sintering mechanism known to occur in this material. The liquid composition influences its viscosity and hence the kinetics of sintering.1,2 Sintering is carried out at high temperatures ($>1700^\circ C$) in nitrogen atmospheres to retard decomposition of silicon nitride. Upon cooling to room temperature the silicate liquid has usually solidified to a glass and the $Si_3N_4$ powder has converted to $\beta Si_3N_4$ during the solution–reprecipitation process. Unfortunately, the low melting temperature of the silicate phase, used to advantage during sintering, is detrimental to the mechanical properties of the monolithic material at elevated use temperatures since the glass begins to soften. This softening can promote grain-boundary sliding, cavitation creep, and subcritical crack growth at relatively low temperatures (about 1000°C).

The compositions of intergranular silicate glasses formed with various oxide additions have been examined using a range of analytical techniques such as analytical electron microscopy,1-3 electron probe microanalysis,1-3 and Auger electron spectroscopy.1-3 Several authors8-11 have even attempted to examine the properties of bulk glass fabricated with the approximate composition of the intergranular glass. These studies indicate that the presence of nitrogen not only increases the viscosity of the melt but also increases the glass transition temperature, hardness, density, and fracture toughness of the bulk glass at room temperature. Consequently, nitrogen incorporation in the intergranular silicate phase is envisaged as a route to improved high-temperature properties in silicon nitride based ceramics. Crystallization of the intergranular glass by pre- or post-sinter12-14 heat treatments can also lead to improved high-temperature behavior by formation of a more refractory phase at the grain boundaries. No studies, however, have been made of the crystallization behavior of intergranular glass and bulk glass of the same composition. Microstructural characterizations of the crystallization of large volumes of bulk glass are more straightforward since the very high resolution analytical techniques (such as convergent beam electron diffraction, structure imaging, and field emission energy dispersive spectroscopy) needed to study small intergranular phases may be avoided. If the microstructural evolution of intergranular and bulk material can be shown to be equivalent, then the effect of latter on phase stability studies is envisaged. This communication reports an attempt to compare the crystallization of an yttrium silicate melt in bulk form and as an intergranular phase in LPS silicon nitride.

II. Experimental Procedure

Bulk melts were prepared from 50-g batches of $Y_2O_3$ and $SiO_2$ powder which were wet ball-milled in silicon nitride mills for 4 h using high-purity $Si_3N_4$ milling media and ethanol. After drying and dry milling for 2 h the batch was passed into pellets at 10.3 MPa and melted in W crucibles at 2100°C for 4 h under 50 atm (about 5 MPa) of nitrogen. The heating rate was 45°C/min and the cooling rate was 520°C/min for the first minute after switching off the furnace and 170°C/min averaged over the next 10 min. The melt composition was chosen to be at the eutectic in the $Y_2O_3-SiO_2$ phase diagram. NASA 6Y composition silicon nitride samples15 were prepared from $Si_3N_4$, 8% $Y_2O_3$ and $SiO_2$ powders mixed in the weight ratio 96:4:3:6, respectively, and 100-g batches were milled for 300 h in 1-L silicon nitride ball mills again using high-purity $Si_3N_4$ milling media and ethanol. This milling process is known to increase $SiO_2$ content by about 1 to 2 wt% because of the oxidation of silicon nitride.15 After drying, the powders were die-pressed into $3 cm \times 0.56 cm \times 0.28 cm$ bars at 21 MPa, cold isostatically pressed at 414 MPa, and sintered at 2140°C for 4 h under 50 atm (about 5 MPa) of nitrogen. Heating and cooling rates were the same as for the bulk material. Crystallizing anneals at 1500°C were in air for the bulk material (heating rate 10°C/min, cooling rate 20°C/min) but 50 atm of $N_2$ for the silicon nitride (heating and cooling rates as for sintering).

The elemental content of the bulk material (Table I) was determined by X-ray fluorescence (XRF) for all elements except N, which was determined by inert gas fusion (IGF). The composition of the intergranular glass was calculated from...
the starting powders (Table I). Allowing for SiO impurity and oxidation of Si₃N₄ during milling, the final composition is expected to be close to the eutectic. Intergranular glass composition was also determined using energy dispersive X-ray spectroscopy (EDS) assuming oxides and ignoring the presence of N, which cannot be detected with a Be-window EDS detector. Microstructural and crystallographic analysis was performed using a transmission electron microscope (TEM) equipped with a Be-window EDS detector and an X-ray powder diffractometer using CuKα radiation. Electron energy loss spectroscopy (ELS) was carried out at NASA Lewis Research Center.

### III. Results and Discussion

#### (1) Bulk and Intergranular Melts on Cooling

After bulk powders were melted (at 2100°C) and Si₃N₄ bars were sintered (at 2140°C), furnace-cooled samples were examined using XRD. The bulk powders partially crystallized to δ-Y₂Si₂O₇ (Fig. 1(a)), the highest-temperature polymorph according to Refs. 16 and 17 (Table II). Some remnant silica glass is expected since this eutectic composition is richer in silica than pure Y₂Si₂O₇. Dinger et al. found crystals of δ- or β-Y₂Si₂O₇ in as-melted bulk material of similar composition near the Y₂O₃-SiO₂ binary in their study of Y₂O₃-SiO₂-AIN glasses. The as-melted bulk sample contained about 0.73 wt% W (presumably present as WO₃) and a small amount (0.12 wt%) of nitrogen (Table I), attributed to contamination by container and nitrogen atmosphere, respectively. The 6Y composition Si₃N₄, however, only contained XRD peaks from β-Si₃N₄. Electron diffraction and EDS analysis in the TEM confirmed that the intergranular phase was amorphous with a Si/Y ratio similar to that obtained by XRF for the eutectic composition bulk material (Table I). ELS analysis of nitrogen in the intergranular glass was inconclusive since the nitrogen edge could not be clearly distinguished from the background. This suggests that nitrogen is not present in large (i.e., >10 atom%) quantities upon cooling the melt to room temperature. Nitrogen will, however, be present in the silicate liquid at high temperatures from solution of α-Si₃N₄ powder and it is not surprising that many (determined at about 2 vol% from TEM images) lath-shaped Si₃N₄ crystals were also detected in the as-sintered Si₃N₄ (Fig. 2). Si₃N₄-O crystals, distinguishable by characteristic stacking faults along (100) planes, reprecipitate along with β-Si₃N₄ grains. No evidence of any other devitrification was observed in the intergranular phase.

Assuming that the nitrogen content of the bulk material is low in the melt (otherwise Si₃N₄-O would also have formed on cooling or high nitrogen contents would be present) the major chemical differences between the two melts are nitrogen content (higher in the intergranular melt) and the W/WO₃ impurity in the bulk melt. Oxynitride silicate melts are more viscous than the corresponding oxide melts. This is thought to be due to the incorporation of nitrogen capable of bridging three network tetrahedral groups forming oxygen which is only capable of bridging two. The higher viscosity of the intergranular melt may kinetically hinder crystallization of Y₂Si₂O₇ whereas the greater fluidity and presence of W/WO₃ in the bulk melt sample may tend to increase crystallization rates upon cooling. Neither the Si₃N₄ crystals nor any impurities scavenged by the silicate liquid below the detection limit of EDS appear to facilitate crystallization of the intergranular glass on cooling.

The nitrogen contents are low in both bulk material (Table I) and intergranular glass (indicated by ELS analysis). Consequently, in the following discussion we will consider only the binary system Y₂O₃-SiO₂. In contrast to the yttrium SiAlONs, very little work has been published on the Y-Si-O-N system because of the difficulty of forming glasses. Drew et al. obtained bloating and high weight loss due to nitrogen evolution when attempting to form glasses in this system, suggesting nitrogen incorporation in the glass, as opposed to the melt, is difficult.

#### (2) Heat Treatment at 1500°C

After 5 h at 1500°C δ-Y₂Si₂O₇ in the partially crystallized bulk sample had transformed to γ-Y₂Si₂O₇ (Fig. 1(b)) consistent with the polymorphism of Y₂Si₂O₇ given in Table II. The 6Y-Si₃N₄ behaved very differently. After 2 h at 1500°C it had completely crystallized to δ-Y₂Si₂O₇ (Fig. 3), which is expected since crystallization of glasses often begins with metastable formation of the highest-temperature polymorph even at temperatures below its equilibrium field of stability. Additional Si₃N₄-O was also detected in the 6Y-Si₃N₄ after crystallization but with a different morphology than in as-sintered material (Fig. 4). In this case the Si₃N₄-O is not present as lath-shaped grains but crystallized around Si₃N₄ grains although still with the characteristic (100) stacking faults and streaks in electron diffraction patterns. This crystallization and the observed morphodexy may result from formation of Y₂Si₂O₇, leaving a nitrogen-containing silica-rich glass which itself crystallized as Si₃N₄-O. This result indicates that some nitrogen remained in the intergranular glass after cooling from the sintering temperature and was only incorporated

### Table I. Chemical Composition of the Bulk and Intergranular Glass

<table>
<thead>
<tr>
<th>Composition (wt%)</th>
<th>Y₂O₃</th>
<th>SiO₂</th>
<th>WO₃/W</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-mixed powder (bulk glass)</td>
<td>59.4</td>
<td>40.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>As-melted bulk glass by XRF and IGF</td>
<td>60.96</td>
<td>39.94</td>
<td>0.92/0.73</td>
<td>0.12</td>
</tr>
<tr>
<td>As-mixed powder (intergranular)</td>
<td>64.0</td>
<td>36.0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Values total 101.75%, indicating a small error associated with the analytical techniques. **Not including oxide impurity and oxidation of Si₃N₄ powder during milling.

![Fig. 1](image-url) XRD spectra for (a) as-melted bulk sample, (b) bulk melt after 5 h at 1500°C in air, (c) intergranular glass after 5 h at 1500°C in 50 atm of nitrogen.
and interracial free energies are not available. However, the ions on the polymorphism of Y2Si2O7 has not been clarified the results is not available. For example, the effect of impurity conjecture since the information required to fully interpret crystals of 5-Y2Si2O7. Admittedly much of what follows is morphic transitions, and the presence or absence of quench tors can be considered, such as impurity content, atmosphere, glass during postmelt heat treatments, several significant fac-

After 5 h at 1500°C the δ-Y2Si2O7 had transformed to β-Y2Si2O7 (Figs. 1(c) and 5), which remained even after 20 h at 1500°C. The 1.931% positive volume change associated with this transformation is thought to be responsible for the generation of large numbers of dislocations in the Si3N4 grains. Transformation to β is unexpected since, according to the data in Table II, 1500°C is outside the field of stability of the β polymorph; instead δ would be expected to transform to γ at this temperature. As well as the differing initial phase assemblages, empirical differences between the crystallizing heat treatments for bulk and intergranular material include atmosphere (air and 50 atm of nitrogen, respectively) and quench rate (20°C/min and 170°C/min, respectively) contained similar amounts (110° and 170°C/min, respectively). To test that these variables were not significant, bars of 6-Y2Si2O7 were crystallized at 1500°C in the same furnace as the bulk glass, i.e., in air and with 20°C/min cooling rate. The Y2Si2O7 polymorphs formed were the same as with the nitrogen atmosphere and the rapid quench rate. While it may not be possible to state explicitly the reasons for the difference in behavior of the bulk and intergranular glass during postmelt heat treatments, several significant factors can be considered, such as impurity content, atmosphere, quench rate, crystal nucleation, the characteristics of the polymorphic transitions, and the presence or absence of quench crystals of δ-Y2Si2O7. Admittedly much of what follows is conjecture since the information required to fully interpret the results is not available. For example, the effect of impurity ions on the polymorphism of Y2Si2O7 has not been clarified and interfacial free energies are not available. However, the following factors are expected to influence the crystallization behavior.

Intergranular glass in Si3N4 is known to scavenge impurity cations from the starting powders. These impurities outdiffuse along the grain boundaries during elevated-temperature treatments. Falk detected β-Y2Si2O7 in grain boundaries at the near surface regions of Si3N4 bars but α in grain boundaries at depths near the bar center after 7 h at 1400°C in air. She attributes this result to stabilization of β by impurity cations outdiffusing during the heat treatment but also suggests that the annealing atmosphere may play a role in determining the particular polymorph which forms during crystallization. However, unpublished work by Kumar and Drummond found that the quench rate of melts was a more significant variable than nitrogen pressure. Melts in 1- or 50-atm nitrogen overpressures and quenched at different rates (110° and 170°C/min, respectively) contained similar amounts of nitrogen (about 0.1 wt%) but crystallized to the γ and δ polymorphs of Y2Si2O7, respectively. As discussed above, the atmosphere and quench rate have less effect once crystals have formed. Incorporation of impurity cations is known to stabilize the Y form of Y2Si2O7, which forms on oxidation of Y2O3-SiO2 glasses and β may be similarly stabilized. The observation that δ forms before β suggests that it too may be impurity stabilized.

Dinger et al. found that Y2Si2O7 nucleated on Fe-Si impurity particles in bulk glass and then transformed to δ-Y2Si2O7 although they found two closely related but different polymorphs by HREM designated δ1 and δ2. Their results are also inconsistent with the stability fields of Ref. 17. This may
be due to the formation of metastable phases. The nucleation of crystals on impurities such as Fe-Si or W/WO$_3$ depends upon many factors, such as contact angle between nucleus and impurity substrate; impurity surface area, shape, and dispersion in the glass; lattice mismatch and interfacial free energy between the impurity and the nucleating crystal. However, we observed no such microcrystals which might act as nucleants in the bulk melt glass of this study. In the intergranular glass the polymorph with the lowest interfacial free energy difference with respect to $\beta$-Si$_3$N$_4$ will crystallize as a transient or metastable phase if $\gamma$-Si$_2$N$_2$O nucleus on Si$_3$N$_4$ grains. Support for the suggestion that $\beta$-Si$_3$N$_4$ favors the nucleation of $\beta$-$\gamma$-Si$_2$N$_2$O$_5$ was obtained by melting the eutectic glass composition at 2100°C for 4 h in 50 at% of nitrogen with a 6Y-Si$_3$N$_4$ bar and quenching. The resulting melt contained dissolved silicon nitride and only $\beta$-Y$_2$Si$_2$O$_5$.

The volume change on cooling associated with the $\delta$-to-$\beta$ transformation is 1.931% whereas it is 1.733% for the $\delta$-to-$\gamma$ transition so that it is unlikely that the volumetric constraint imposed by the Si$_3$N$_4$ grains would restrict one transformation in favor of the other. It is also unlikely that $\beta$ is forming as a metastable phase en route to forming $\gamma$ after sufficient time at temperature since $\beta$ is a lower temperature polymorph and therefore less stable than $\gamma$ at this temperature (Table II).

Some information on polymorphic transitions in other grain-boundary phases may also be gained from this study. The first polymorph to form upon crystallization, $\delta$, has a characteristic mottled morphology and a small grain size, about 1 $\mu$m (Fig. 3), suggesting many nucleation sites are available (similar to cordierite crystallized in SiAlON grain boundaries). However, after continued annealing at 1500°C the $\delta$ transforms to $\beta$ with concurrent grain growth so that single grains of $\beta$-$\gamma$-Si$_2$N$_2$O$_5$ (about 10-$\mu$m diameter) extend over large volumes around many Si$_3$N$_4$ grains (Fig. 5). The greater grain size of $\beta$ compared to $\delta$ suggests few $\beta$ nuclei and/or rapid growth rates of the $\beta$ nuclei present. If, as seems likely, the $\beta$ grains nucleate on the $\delta$ grain boundaries, then rapid grain growth must be occurring. The large grains of garnet in SiAlON grain boundaries may have formed in a similar manner.

IV. Summary and Conclusions

Attempts to form glass of identical composition from bulk melts and as an intergranular phase in Si$_3$N$_4$ were unsuccessful. While the intergranular material was amorphous, the bulk material contained crystals of $\delta$-$\gamma$-Si$_2$N$_2$O$_5$ and a silicate glass at room temperature. On heat-treating at 1500°C the bulk material transformed to $\gamma$-$\gamma$-Si$_2$N$_2$O$_5$, whereas the intergranular glass crystallized first to $\delta$-$\gamma$-Si$_2$N$_2$O$_5$ and then to $\beta$-$\gamma$-Si$_2$N$_2$O$_5$. Variables discussed which may explain different behavior include impurity ions, impurity phases, and crystallographic factors. Quench rate and nitrogen content in the crystallization atmosphere were less significant variables. Si$_3$N$_4$O forms in Si$_3$N$_4$ with two morphologies: as lath-shaped grains arising from nitrogen solution in as-sintered material (Fig. 2) and also crystallized around Si$_3$N$_4$ grains (Fig. 4) after a post-sinter heat treatment. The latter morphology may arise since crystallization of Si$_3$N$_2$O$_5$ leaves a N-containing silica-rich glass which itself crystallizes as Si$_3$N$_4$O.

References

Microstructural Evolution in Near-Eutectic Yttrium Silicate Compositions

