Morphology, composition, and growth defects of α'-SiAlON have been studied in a fine-grained material with an overall composition \( Y_{0.33}Si_{1.5}Al_2O_3N _{1.5} \), prepared from \( \alpha-Si_N_4, AlN, Al_2O_3 \), and \( Y_2O_3 \) powders. TEM analysis has shown that fully grown α'-SiAlON grains always contain an \( \alpha-Si_N_4 \) core, implicating heterogeneous nucleation operating in the present system. The growth mode is epitaxial, despite the composition and lattice parameter difference between \( \alpha-Si_N_4 \) and α'-SiAlON. The inversion boundary that separates two domains in the seed crystal is seen to continue in the grown α'-SiAlON. Lacking a special growth habit, the different growth fronts impinge on each other to give an equiaxed appearance of α'-SiAlON. Misfit dislocations on the α'/α interface are identified, as interface dislocations between \( \alpha-Si_N_4 \) and α'-SiAlON with a Burgers vector along either \( a \) or \( c \)-axis have also been identified. (While dislocations in \( \beta-Si_N_4 \) are fairly well-known,16-23 the investigation of dislocations in \( \alpha-Si_N_4 \) or α'-SiAlON is limited.) This information will be used to corroborate our understanding of microstructural development.

II. Experimental Procedure

α'-SiAlON with an overall composition of \( Y_{0.33}Si_{1.5}Al_2O_3N _{1.5} \) was prepared from \( \alpha-Si_N_4, AlN, Al_2O_3 \), and \( Y_2O_3 \) powders. The medium size of \( \alpha-Si_N_4 \) particles was 0.48 \( \mu \)m; 85% of the powders were below 1.0 \( \mu \)m. A detailed description of the powder processing and hot-pressing procedure can be found in Ref. 13, in which the present material was referred to as \( 1010 \) composition (corresponding to \( m = 1.0 \) and \( n = 1.0 \)). Full densification was achieved by hot-pressing at 1550°C for 30 min. The as-hot pressed material is superplastic and can be biaxially punch-stretched to larger strains.24,25 The majority of the specimens examined in this study, however, were given a further annealing at 1600°C for 1 h to slightly coarsen the microstructure. Using X-ray diffraction (XRD) analysis, the lattice parameters of \( \alpha-SiAlON \) were determined. The amount of \( \alpha-SiAlON \) and (unreacted) \( \alpha-Si_N_4 \) was estimated from the peak heights of (\( 10\bar{1}2 \)) and (\( 2\bar{1}1\bar{0} \)) reflections. (Overlapping peaks were deconvoluted using FWHM = 0.19° for 29.) In addition, an \( \alpha'-SiAlON \) with an overall composition of \( Y_{0.6}Si_{1.0}Al_2O_3N _{1.5} \) (material 0610 in Ref. 13) was examined to compare the morphology of \( \alpha-SiAlON \) grains in different phase assemblages. The preparation of this material followed a procedure similar to the above.

Foils for transmission electron microscopy (TEM) were prepared from slices cut from the annealed material. The slices were hand-ground to less than 30 \( \mu \)m thick, followed by polishing, dimpling, and ion milling. A thin layer of carbon was evaporated onto these foils to avoid surface charging under the electron beam.

Microscopy was performed using a scanning electron microscope (SEM, Hitachi S-800, Tokyo, Japan) and an analytical transmission electron microscope (TEM, JEO1 2000FX, Tokyo, Japan) equipped with a thin-window energy-dispersive X-ray analysis (EDS, Tracor-Northern, Middleton, WI) system. Dislocations were analyzed using the conventional \( g \cdot b \) criterion, where \( g \) is the operating reflection and \( b \) the Burgers vector.26 At least two nonparallel reflections that rendered the dislocation out of contrast were used to establish the Burgers vector. To eliminate the interference from both the Moiré fringes and the overlapping strain field in a dislocation array, weak-beam (WB) dark-field (DF) imaging was used.27 Diffraction patterns were indexed with the help of computer software (Diffraction II, Vol. 1.2, Microdev Software, Evergreen, CO).
III. Results

(1) General Microstructure

Figure 1 is an SEM micrograph showing the general microstructure of material 1010 after hot-pressing. Measurement of the grain sizes found a distribution between 0.2 and 0.5 μm. Phase analysis by XRD indicated a phase assemblage of 56% α'-SiAlON and 44% α-Si₃N₄. Evidence to be presented in the following further suggests that the smaller grains are unreacted α-Si₃N₄, and the larger grains are α'-SiAlON containing an α-Si₃N₄ core.

The microstructure after annealing is shown in the TEM micrograph of Fig. 2. It also consists of many large grains embedded in a small-grain matrix. Both large and small grains have an equiaxed grain shape. The average size of the large grains is around 1 μm, which is about three times larger than that of the small grains. Large grains with a size up to 3 μm were often found. Phase analysis by XRD indicated that after annealing, α'-SiAlON comprised 90% of the phase assemblage, the balance being α-Si₃N₄.

We examined a large number of grains (about 50%) within the field of view under TEM. The large grains were found to always contain a core with a contrast different from that of the surrounding shell under bright-field (BF) imaging conditions. Several such core-containing large grains, where the core is marked as α and the shell α', can be seen in Fig. 2. The boundary between the core and the shell has a strong contrast, a feature consistent with the presence of misfit strain fields in the lattice. The size of the core is about 0.3 μm, which is somewhat smaller than the size of the starting α-Si₃N₄ powders.

Selected area diffraction (SAD) patterns show that the core and the shell have the same α-Si₃N₄ structure and crystallographic orientation (Fig. 2 inset). The interface between the core and the shell is coherent, as revealed by the continuity of the lattice planes across the interface. For example, continuous (1010) lattice planes are shown in Fig. 3. (We have indicated the position of the interface with arrows.) The interface shows no distinct feature in this image, because it is coherent but not edge-on. Despite their structural similarity, the core and shell compositions are different according to EDS. Figure 4 shows that the core contains only Si and N, while the shell contains Al, Y, and O in addition to Si and N. (Due to the small core size and the possible drift of the foil position during data collection, it was usually difficult to completely avoid the signal contribution from the adjacent grains. We could, however, find some cores for which the shell had been removed during thinning the specimen. They provided the best examples where shell contribution was largely avoided. More generally, we could only see a much lower Al, Y, and O content from the core spectra compared to those from the shell spectra. The detection limit for Al and O in our instrument is about 1.5 wt%.) These findings provide a ready explanation for the lighter contrast (Fig. 2) of the core, which lacks the strong electron-scattering Y. They also identify the core as α-Si₃N₄ and the shell as α'-SiAlON.

Some smaller grains also have a core–shell structure. Others, which contain no core, were sometimes found to have Al, Y, and O. These α'-SiAlON grains may have directly formed without the assistance of a core. On the other hand, if one assumes a slice 0.3 μm thick as representative of the specimen viewed under the TEM, then the probability of sectioning through the shell region (1 μm) without including any part of the core (0.3 μm) is approximately 40%. Taking into account this possibility, it becomes reasonable to suggest that, most likely, every α'-SiAlON grain does contain one α-Si₃N₄ core.

The core–shell structure of α'-SiAlON was also observed in material 0610. After hot-pressing and annealing, this material contained α' and β'-SiAlON in approximately equal fractions, with some residual α-Si₃N₄. Figure 5 shows the microstructure after annealing. It contains both elongated β'-SiAlON grains...
and equiaxed α'-SiAlON grains. The α'-SiAlON grain marked in Fig. 5 again has a core–shell microstructure rather similar in size and proportion to those in material 1010.

(2) Interface Dislocations

Misfit strains exist at the interface due to the compositional difference between the α-Si,N, core and the α'-SiAlON shell. This misfit gives rise to two features. First, Moiré fringes can be seen under appropriate BF diffraction conditions (Fig. 6(a)).

Second, interface dislocations can be seen under WB imaging conditions. One example is shown in Fig. 6(b) for g = 0221.

These dislocations form a network of two arrays, which are better revealed in Figs. 7(a) and (b). Contrast analysis shows that one set of these dislocations is out of contrast under 2310, 1320, and 1100 diffraction conditions but in strong contrast under a 0004 diffraction condition (Fig. 7(a)). Therefore, they have a [0001] Burgers vector, i.e., they are c-axis dislocations. Their edge character is evident from the line direction in Fig. 7(a), which is mostly perpendicular to 0004. The other set of dislocations, which is out of contrast under 0004 and 1012 diffraction conditions, is in strong contrast under 2310 diffraction condition (Fig. 7(b)). They probably have a 1/3[1210] Burgers vector, which is the shortest perfect dislocation Burgers vector in an α-Si,N, structure, and possess an edge character as well. For the 2201, 0221, 1321, and 3521 diffraction conditions, both sets of dislocations are in contrast (Fig. 6(b) for 0221). This is consistent with the [0001] and 1/3[1210] designations for the Burgers vectors.

From the average spacing of Moiré fringes and interface dislocations, the differences in the lattice parameters between the α-Si,N, core and α'-SiAlON shell can be estimated. The average spacing of Moiré fringes for 0002 reflection is 135 Å, which corresponds to a difference of 0.059 Å in the lattice parameters along the c-axis. The average spacing of [0001] and 1/3[1210] dislocations in Figs. 7(a) and (b) are about 460 and 880 Å, respectively. The calculated misfits are 0.069 Å along the c-axis and 0.068 Å along the a-axis. (The Burgers vector of [0001] and 1/3[1210] dislocations are, respectively, 5.62 and 7.75 Å.) According to XRD, the lattice misfits are 0.069 Å along the c-axis and 0.061 Å along the a-axis at room temperature. The reasonable agreement of these data suggests that most of the interfacial strain energy has been relieved by forming the dislocation network.

The micrographs of Figs. 7(a) and (b) contain nodes at dislocation intersections. This could be due to the reaction of two dislocations into, say, a 1/3[1213] dislocation. The dislocation interaction is probably also responsible for the wavy configuration in the dislocation arrays. These aspects, however, were not investigated further.

(3) Inversion Boundary

Two types of planar defects, inversion boundary and δ boundary, have been found in the α/α' core–shell structure. Their configurations are schematically drawn in Fig. 8. We will describe the inversion boundary first and leave the δ boundary to the next section.

An inversion boundary is shown in Fig. 9(a). It appears as a ribbonlike feature winding from the center of the core toward the outer shell. Both ends of the “ribbon” have sliced across the α/α' interface to reach the shell (see arrows in Fig. 9(a)). These planar defects do not usually show any fringe image contrast except under the WB DF imaging conditions. This is probably due to the large extinction distance of this material, which, at the minimum, is about 1000 Å for, say, the (0004) reflection. Trace analysis determines that these defects lie primarily on (0001) planes, but they frequently change from one (0001) plane to another by going through some irrational planes in between. This can also be seen in Fig. 9(a). The regions separated by these planar defects show no contrast difference in any BF imaging conditions (Figs. 9(a–b)), indicating identical crystallographic orientation.

As mentioned in the Introduction, the α-Si,N, structure can have two inversion domains related by a simple inversion. Their impingement results in an inversion boundary, across which a contrast difference arises under DF imaging conditions when Friedel’s law is violated. According to Serneels et al. and Biest and Thomas, an inversion boundary shows no contrast under any BF imaging conditions but gives a strong contrast under certain multiple-beam conditions in which the
Fig. 6. TEM micrographs of an $\alpha/\alpha'$ interface showing (a) Moiré fringes under BF condition and (b) interfacial dislocation network under WB condition.

Fig. 7. WB images of dislocations at $\alpha/\alpha'$ interface with Burgers vector of (a) [0001] and (b) $1/3[1\bar{2}10]$. The [0001] dislocations are visible when $g = 0004$ and the $1/3[1\bar{2}10]$ dislocations are visible when $g = 2310$.

Fig. 8. Growth morphology of $\alpha'$-SiAlON on $\alpha$-Si$_3$N$_4$ showing inversion boundary, $\delta$ boundaries, and misfit dislocations.

crystal projection lacks a center of symmetry. This latter condition is satisfied by $B \sim [12\bar{1}0]$ and $g = \bar{1}0\bar{1}1$, as in Fig. 9(c), where the boundary is visible and a strong contrast across the interface arises in the DF image.

Additional diffraction contrast analysis on this boundary under two-beam conditions, using the structural model to be discussed in Section IV(3), was also performed. Table 1 summarizes the calculated structure factors, the phase angle differences, and the observed image contrast for 10 diffraction conditions. When the phase angle difference between two regions is close to zero, the boundaries are virtually invisible. This is the case in Fig. 9(b), for example, for the 0004 diffraction condition. (The two features marked by arrows in Fig. 9(b) are cracks which formed \textit{in situ} after long exposure to an electron beam.) When the phase angle difference is not zero, a strong contrast for the boundary is always found, even though the two separated regions show no contrast difference, as in Fig. 9(a) for the 1010 diffraction condition. Thus, the structural model described in Section IV(3) and the conclusion that the boundary is an inversion boundary are verified.

The inversion boundary described above was most likely inherited from the starting $\alpha$-Si$_3$N$_4$. Since the growth of $\alpha'$-SiAlON onto the $\alpha$-Si$_3$N$_4$ core is obviously epitaxial, these defects are carried over into the $\alpha'$-SiAlON shell, which has the same space group as $\alpha$-Si$_3$N$_4$. Indeed, the continuation of the inversion boundary across the $\alpha/\alpha'$ interface provides additional evidence for epitaxial growth. The frequency of the occurrence of the inversion boundaries, however, is quite low. This could indicate that the interfacial energy of the inversion
Fig. 9. BF micrographs showing the inversion boundary and its continuity into the shell region. The boundary is (a) visible when \( g = 10\bar{1}0 \) and (b) invisible when \( g = 0004 \). The portions of boundary in the shell region are marked by arrows in (a). The electron-beam-induced microcracks are marked by arrows in (b). (c) DF image showing strong contrast difference between inversion domains. \( B = [12\bar{1}0], g = 10\bar{1}1 \).

Table I. Structure Factor, Phase Angle Difference, and Contrast Analysis of Inversion Boundary

<table>
<thead>
<tr>
<th>Diffraction condition</th>
<th>Structure factor</th>
<th>Phase angle difference</th>
<th>Visibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>10\bar{1}0</td>
<td>7.74</td>
<td>120</td>
<td>Visible</td>
</tr>
<tr>
<td>( \bar{1}10 )</td>
<td>15.79</td>
<td>180</td>
<td>Visible</td>
</tr>
<tr>
<td>011\bar{1}</td>
<td>15.85</td>
<td>60</td>
<td>Visible</td>
</tr>
<tr>
<td>10\bar{1}1</td>
<td>15.87</td>
<td>60</td>
<td>Visible</td>
</tr>
<tr>
<td>202\bar{1}</td>
<td>14.84</td>
<td>120</td>
<td>Visible</td>
</tr>
<tr>
<td>0004</td>
<td>39.12</td>
<td>0</td>
<td>Invisible</td>
</tr>
<tr>
<td>202\bar{1}</td>
<td>14.80</td>
<td>1.5</td>
<td>Invisible</td>
</tr>
<tr>
<td>303\bar{1}</td>
<td>16.83</td>
<td>0.3</td>
<td>Invisible</td>
</tr>
<tr>
<td>303\bar{1}</td>
<td>16.75</td>
<td>0.1</td>
<td>Invisible</td>
</tr>
<tr>
<td>( 2\bar{2}42 )</td>
<td>21.32</td>
<td>0.4</td>
<td>Invisible</td>
</tr>
</tbody>
</table>

boundaries in the starting powder may be quite high. Indeed, the unusual occurrence of beam-induced cracking at these boundaries implies a relatively low cohesive energy which would be consistent with a relatively high boundary energy.

(4) \( \delta \) Boundary (Coherent Domain Boundary)

The inversion boundaries discussed above have a well-defined crystallographic plane and are continuous across the \( \alpha/\alpha' \) interface. We have also observed another type of planar defect which does not lie on any well-defined crystallographic plane and which exists in the \( \alpha\text{-SiAlON} \) shell only. One such defect is already visible in Fig. 9(a) and is marked as \( \delta \). It ends at the \( \alpha/\alpha' \) interface but spans across the entire \( \alpha' \) shell. This latter feature is characteristic of such planar defects. For example, Fig. 9 shows several \( \delta \) boundaries all terminating at the \( \alpha/\alpha' \) interface.

Essentially, no crystallographic difference can be observed under any diffraction conditions between neighboring \( \alpha'-\text{SiAlON} \) regions separated by \( \delta \) boundaries. According to Gever et al., a fringe contrast can still arise from a very small misorientation between the simultaneously excited reflections of the two neighboring growth variants. Such boundaries have been termed \( \delta \) boundaries or coherent domain boundaries in the literature. In our case, it seems plausible that the number of coherent domain boundaries coincides with the number of \( \alpha'-\text{SiAlON} \) nuclei grown from a single \( \alpha\text{-Si,N}_x \) core.

Lastly, since \( \alpha'-\text{SiAlON} \) can also exhibit inversion domains, it can nucleate on the \( \alpha\text{-Si,N}_x \) in either of the two inverted domains. This possibility could exist independently of whether there is a domain boundary in the substrate (much like SiC or GaAs growing on Si). If so, the above \( \delta \) boundaries could actually be inversion boundaries and the domains should have the same contrast. (They look as though they do in the micrographs.) This point, however, was not pursued further in our study. The important point regarding intergrowth kinetics, though, still stands; namely, the number of domain boundaries in the \( \alpha'-\text{SiAlON} \) shell most likely coincides with the number of \( \alpha'-\text{SiAlON} \) nuclei grown from a single \( \alpha\text{-Si,N}_x \) core.
react with residual SiO, on Si,N, surfaces to form a eutectic. Densification because of partial dissolution. About SO% of the large grains nucleation of a'-SiAlON onto the remaining a-Si,N, particles, indicates that the reprecipitation process proceeds by heterogeneous cate that the reprecipitation process proceeds by heterogeneous nucleation, the higher supersatu-
ration level required for homogeneous nucleation would be dif-
ficult to establish. Indeed, with the presence of ample a-Si,N4 seeds and with the relative ease of heterogeneous nucleation, the higher supersatura-
tion level required for homogeneous nucleation would be diff-
cult to establish.

There appears to be no preferential nucleation sites on the surface of the a-Si,N4 particles, nor is there any special growth habit. This is obvious from the observation of several growth habits (separated by b boundaries) around a single a-Si,N4 particle. Energetically, this may be justified by (a) the small difference in the lattice misfit along the c-axis (1.2%) and the a-axis dislocations (1/3[1123]) and some mixed dislocations (1/3[1120]) have been commonly observed in a-Si,N4 and a-axis dislocations ((1120) are smaller than that in a c-axis edge dislocation (0.89 A`). Indeed, since the number of broken Si-N bonds in an a-axis edge dislocation (0.77 A`) is smaller than that in a c-axis edge dislocation (0.89 A`). The core energy should partially compensate for the difference in the elastic energy. It seems then that in an Si,N4 structure, a- and c-axis dislocations should have similar line energy and be able to generate at similar frequencies. This is in agreement with our observations.

With the proper combinations of the two types of dislocations, any strain misfit at the interface between the a-Si,N4 core and the a'-SiAlON shell can be largely relieved. This will facilitate nucleation of epitaxial a'-SiAlON at essentially any surface sites on a-Si,N4. This is partly responsible for the multiple growth variants and the equiaxed grain shape we observed. Meanwhile, since the c-axis dislocation in a-Si,N4 has a much larger Burgers vector than the c-axis dislocation (that is predominant) in b-Si,N4, a higher hardness and a lower fracture energy of a-Si,N4 than those of b-Si,N4 are expected.

(3) Invasion Boundary

The impingement of two inversion domains of a-Si,N4 results in an invasion boundary. In a a-Si,N4 structure, the Si is tetrahedrally coordinated by four N atoms, while N is triangu-
larly coordinated by three Si atoms. Ideally, across the interface between two inversion domains, these bonding requirements should be fulfilled to minimize the interfacial energy.

The atomic arrangements of the four stacking layers forming an a-Si,N4 structure are plotted in Fig. 11, and the coordinates of the atoms are listed in Table II. The reference axes used here

Fig. 10. WB image showing growth variants of a'-SiAlON from a single a-Si,N4. The b boundary between neighboring variants is marked by arrows.
are different from that in the International Table for X-ray Analysis in that the origin has been shifted from the 31c position to the 3-fold axis to make the description of the inversion operation easier. By inspection, it can be easily established that the x- and y-coordinates of the atoms at z = 0 and z = 1/4 are related to each other by an inversion operation through the origin. This observation already provides a clue as to why the domains. As shown in Fig. 12(a), the normal a-Si,N, structure with the stacking sequence of A-B-C-D is converted into its inverted form with the stacking sequence D'-C'-B'-A'.

![Fig. 11. Atomic arrangements of α-Si,N, structure on four successive layers. Si is represented by large circles and N by small circles.](image)

**Table II. Atomic Coordinates in α-Si,N, Structure**

<table>
<thead>
<tr>
<th>Coordinate</th>
<th>N(1)</th>
<th>N(2)</th>
<th>N(3)</th>
<th>N(4)</th>
<th>Si(1)</th>
<th>Si(2)</th>
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<tbody>
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<td>(2/3, 1/3, 1/4)(0, 0, 3/4)</td>
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<td>(0.833, 0.75, 3/4)(0.25, 0.083, 3/4)</td>
<td>(0.917, 0.167, 3/4)(0.417, 0.167, 1/4)</td>
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</tr>
<tr>
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<td>(2/3, 0, 0)(0, 2/3, 0)</td>
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<td>(0, 1/3, 3/4)(2/3, 0, 1/4)</td>
<td>(1/3, 1/3, 0)(0, 2/3, 1/4)</td>
<td>(0.5, 0.917, 1/2)(0.083, 0.583, 1/2)</td>
<td>(0.417, 0.5, 1/2)(0.583, 0.833, 0)</td>
</tr>
<tr>
<td></td>
<td>(0.417, 0.5, 1/2)(0.583, 0.833, 0)</td>
<td>(0.25, 0.417, 0)(0.167, 0.75, 0)</td>
<td>(0.25, 0.417, 0)(0.167, 0.75, 0)</td>
<td>(0.25, 0.417, 0)(0.167, 0.75, 0)</td>
<td>(0.25, 0.417, 0)(0.167, 0.75, 0)</td>
<td>(0.25, 0.417, 0)(0.167, 0.75, 0)</td>
</tr>
</tbody>
</table>

Because the atomic arrangement of the A'(B') layer is similar to that of B(A) layer, the easiest way to maintain the bonding requirements is to form the interface between A/AA' or B/B' layers. In this way, the stacking sequence across the interface becomes C-D-A-A'-D'-C' (see Fig. 12(b)), and all the Si-N bonds across the interface are maintained. (The configurations of the next-nearest-neighbor bonds have to be changed, but this is relatively unimportant as far as energy is concerned.) In comparison, interfaces other than (0001) are not energetically favorable, because they must entail relaxation of some Si positions in order to maintain Si-N bonding continuity across the interface. This provides a ready explanation for the observed (0001) habit plane for the inversion boundary.

**References**


S.-L. Hwang and I-W. Chen, "Reaction Hot-Pressing of SiAlON Ceramics," in review.


