The microstructure and boundary phases of in-situ reinforced silicon nitride

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Abstract

The microstructure of an in-situ reinforced silicon nitride, gas pressure sintered with La₂O₃, Y₂O₃, and SrO additives and then heat treated, is examined with X-ray diffraction, SEM, and high-resolution TEM. Two crystalline rare-earth apatite phases, La₅Si₃O₁₂N and Y₅Si₃O₁₂N, are identified at the grain pockets and at the two-grain boundaries. The thickness of the crystalline phases at the two-grain boundaries is approximately 1.7 nm, in compliance with the suggested equilibrium intergranular spacing. A glassy phase is also present at the grain pockets and at the two-grain boundaries due to incomplete crystallization of the boundary phases. The thickness of the amorphous phase at the two-grain boundaries varies from 0.7 to 3.0 nm, suggesting that compositional inhomogeneities exist in these areas. Based on the microstructural observations, the structures of the crystalline boundary phases, the equilibrium intergranular film thickness, and the mechanisms causing incomplete recrystallization of the glassy phase in the in-situ reinforced silicon nitride are discussed. © 1998 Published by Elsevier Science S.A. All rights reserved.

Keywords: Microstructure; Boundary phases; In-situ reinforced silicon nitride

1. Introduction

Silicon nitride (Si₃N₄) materials are one class of promising structural materials for high-temperature applications. High resistance to thermal shock, as well as high strength, high fracture toughness, and high resistance to chemical attack, make silicon nitrides suitable materials for turbine engine components operating under extreme conditions. Significant advances in developing silicon nitride gas turbine applications have been achieved in the past few years. A silicon nitride having a pronounced acicular microstructure, known as the in-situ reinforced (ISR) Si₃N₄, shows significantly improved properties including creep resistance, fracture toughness, and strength consistency [1–4]. The superior mechanical properties of ISR silicon nitride are mainly attributed to the in-situ grown β-Si₃N₄ grains with high aspect ratios, as well as their unique grain-boundary structure.

It is known that the bonding between Si and N is basically covalent. The solid-state diffusion is very slow, thus preventing densification of the silicon nitride. However, if a liquid phase is introduced into the system during sintering, high densities are achieved. This liquid phase is introduced by means of oxide sintering additives, which form a eutectic liquid with the oxidized surface layers of silicon nitride powders. After sintering, this liquid phase is usually retained in the glassy intergranular phases which cause a deterioration in the mechanical properties of the material, particularly at elevated temperatures. Five approaches for reducing the detrimental influence of the glassy phase have been suggested: (i) transient liquid-phase sintering where constituents of the glassy phase are absorbed into the silicon nitride grains by solid solution [5], (ii) post-sintering heat treatments to alter the glassy phase composition and structure [6–8], (iii) increasing the refractoriness of the boundary phase [9], (iv) using densification processes such as gas pressure sintering which requires less liquid phase [10], and (v) crystallizing the grain-boundary phase by properly selecting sintering additives and/or heat treatment [11,12]. The
last four approaches have been used extensively in the recent development of high-temperature silicon nitride ceramics, including the ISR silicon nitride material investigated in the present study.

In the last two decades, there has been growing recognition that the properties of Si₃N₄ materials are significantly influenced by the grain-boundary phases present [13–19]. Since a basic understanding of the intergranular phase and structures is essential if improvements in the performance of silicon nitride are to be achieved, extensive research has been done on the characterization of the grain-boundary phases of silicon nitride materials. By adding rare-earth oxide additives to silicon nitrides, Thomas et al. [15,20–23] have found a family of RE₂Si₂O₇ crystalline grain-boundary phases in silicon nitrides which were pressureless-sintered or sintered under relatively low pressures, where RE represents Y, Sm, Gd, Dy, Er, and Yb. On the other hand, a new group of silicon lanthanide oxynitrides of the general formula Ln₅Si₃O₁₂N, called rare-earth apatite or H-phase structure, have been identified by Hamon et al. [24] and Rae et al. [25] in mixtures of silicon nitride and lanthanide oxides hot-pressed at relatively high pressures, where Ln can be Y [25–27], La [24,28,29], Sr [30], Nd, Sm, Gd, and Yb [24].

The purpose of the present research was to study the microstructure of an in-situ reinforced silicon nitride with transmission electron microscopy (TEM). The emphasis of the research, in particular, is placed on the structural characterization of grain-boundary phases by high-resolution electron imaging and electron diffraction in order to gain information on their crucial role in influencing the materials’ high-temperature mechanical properties. This initial work is currently being followed by systematic mechanical testing of this material at relatively high temperatures.

2. Experimental procedure

The in-situ reinforced silicon nitride (AS800) used in the present study is produced by AlliedSignal Aerospace, NJ. Silicon nitride powders are sintered at a temperature above 1750°C in a nitrogen atmosphere with a gas pressure of about 20.7 MPa (3000 psi). The sintering aids include La₂O₃, Y₂O₃, and a small amount of SrO. After sintering, a post-sintering heat treatment is performed. The material thus obtained has a 4-point bend strength of about 500 MPa (72 ksi) at 1400°C and a room-temperature fracture toughness of about 8 MPa m⁻¹² [2].

The as-received material was in the form of a billet, with dimensions of approximately 20 cm x 12 cm x 2 cm. The material was first examined with a Cambridge 360 scanning electron microscope (SEM). Silicon, lanthanum, yttrium, and strontium peaks were identified in the energy dispersive X-ray spectroscopic (EDS) spectrum obtained from the polished surface of the material, and the lanthanum peaks are found to be significantly stronger than the yttrium and strontium peaks (Fig. 1), because La₂O₃ is the major sintering additive. An unetched sample was also analyzed by an XDS-2000 X-ray diffractometer, with a scan rate of 1° min⁻¹. The diffractometer is equipped with a computer analyzer and a line focus Cu tube operated at 40 kV and 40 mA, and has been calibrated using an external silicon standard with a lattice constant of 0.54306 nm at 25°C. Fig. 2 is an X-ray diffraction pattern from the material, showing large peaks from β-Si₃N₄, as well as small peaks from some other crystalline phases. An analysis of these small peaks indicates that they belong to either La₅Si₃O₁₂N or Y₅Si₃O₁₂N, suggesting that crystalline boundary phases may have formed during sintering and/or post-sintering heat treatment. No α-Si₃N₄ peaks are observed in the diffraction pattern, confirming a full transformation from α-Si₃N₄ to β-Si₃N₄ during high-temperature sintering.

Detailed examination of the in-situ reinforced silicon nitride was performed on a JEOL ARM-1000 high resolution TEM, operated at 800 kV, at the National Center for Electron Microscopy (NCEM), Lawrence Berkeley Laboratory, University of California, Berkeley, CA. The microscope has a point-to-point resolution of 1.6 Å and a specimen bi-axial tilting capability of ±40°. The high TEM operating voltage not only improves the resolution and reduces ionization damage, but also allows increased penetration [31]. TEM samples were prepared from the central region of the billet. Standard 3 mm discs were ground down to approximately 100 µm in thickness, polished on both sides to remove the residual stresses, dimpled to near-optical transparency in the central region, and finally ion-
milled to produce large areas sufficiently thin for TEM examination.

The TEM operation conditions for determining the atomic configuration in the vicinity of the ceramic grain-boundaries have been discussed by Clarke and Thomas [32,33]. Accordingly, the boundary has to be tilted to an edge-on position to the incident beam. Furthermore, the interface should be flat with a low density of interfacial steps, and the grains on either side of the interface should be aligned in an orientation suitable for structure imaging or at least for forming one set of lattice fringes. The structure of the grain-boundary phase was determined by using the selected-area electron diffraction (SAED) technique on a JOEL-2000FX TEM.

3. Results

Fig. 3(a) is a SEM micrograph of the polished surface of the silicon nitride specimen. The material contains approximately 90% Si₃N₄ grains and 10% second phase at the grain boundaries and the grain pockets (multi-grain junctions). The grain structure can be clearly seen after the specimen is etched at 400°C in molten NaOH for 4–6 min. As shown in Fig. 3(b), the AS800 silicon nitride consists primarily of acicular Si₃N₄ grains. The acicular microstructure of the material is believed to result from anisotropic growth of the hexagonal Si₃N₄ grains to maximize the area of the low-energy (100) prismatic planes. Because of the high sintering temperature, Si₃N₄ grains with various grain widths and lengths are formed. The average grain width was determined to be approximately 0.8 µm and the aspect ratio is greater than 4. Fig. 4 is a SEM fractograph of the material subjected to high-strain-rate shear, revealing a typical interlocking microstructure, which is highly resistant to deformation. Under compressive loads, the acicular grains interlock, resulting in increased creep resistance by inhibiting grain-boundary sliding. Under tensile stresses, in addition to limiting grain-boundary sliding, the elongated grains improve the stress rupture properties by bridging the microcracks [3].

A similar microstructure is observed in low-magnification TEM micrographs, as shown in Fig. 5(a) and (b). The microstructure is characterized by low-contrast Si₃N₄ grains and a high-contrast boundary phase at the grain pockets. Strain contours, resulting from the residual stresses within the grains and the contact stress between neighboring grains, are observed in the grain-boundary vicinity. Like other silicon nitride materials, some dislocations are found in the specimen, mainly in the large grains. SAED patterns from more than 50 individual grains reveal no evidence of the existence of α-Si₃N₄ grains, which is consistent with the XRD results (Fig. 2). Therefore, a complete transformation from α-Si₃N₄ to β-Si₃N₄ has been achieved by the processing conditions employed. No second phase particles are identified in the microstructure, indicating...
that all the sintering additives were dissolved in the eutectic liquid during the sintering process.

Fig. 6 shows a typical two-grain boundary between two grain pockets. The silicon nitride grains are seen at bright contrast, while the grain-boundary phase appears at dark contrast with near-uniform intensity. The grain boundary appears to be straight and well-defined, having a very small film thickness. High-resolution TEM images and SAED patterns from the boundary areas of the material reveal the presence of an amorphous or glassy phase and fully-crystallized phases, as will be illustrated below.

Fig. 7 is a high-resolution electron micrograph taken at a planar grain-boundary region, showing an amorphous phase at a two-grain boundary. The incident beam is along the \( \langle 012 \rangle \) and \( \langle 001 \rangle \) directions of the two neighboring \( \beta\)-Si\(_3\)N\(_4\) grains, respectively. The (100) and (110) planes are found to be the dominant grain boundary of the \( \beta\)-Si\(_3\)N\(_4\) grains, due to their relatively low energy when compared with other crystalline planes of silicon nitride. The amorphous phase appears to form along a straight grain boundary and shows a slightly light contrast with respect to the \( \beta\)-Si\(_3\)N\(_4\) grains. The thickness of the boundary phase is approximately 1.8 nm, which is typical for amorphous grain-boundary phases in silicon nitrides and is in fairly good agreement with the equilibrium intergranular distance (on the order of 1 nm) between two straight Si\(_3\)N\(_4\) grain boundaries [34].

Fig. 8(a) is a high-resolution TEM image showing a crystalline boundary phase present along a straight grain boundary between two \( \beta\)-Si\(_3\)N\(_4\) grains, at an area approximately 0.1 \( \mu \)m from the grain pocket. The \( d\)-spacings of the lattice fringes of the two \( \beta\)-Si\(_3\)N\(_4\) grains are 0.66 and 0.27 nm, respectively, corresponding to the (100) and (101) fringes of \( \beta\)-Si\(_3\)N\(_4\). The grain-boundary phase shown in Fig. 8(a) exhibits sharp lattice fringes, which are significantly different from those of the neighboring Si\(_3\)N\(_4\) grains regarding \( d\)-spacing and orientation, indicating that a crystalline phase has been formed at the two-grain boundary. The fringes of the crystalline boundary phase orient approximately 45° with respect to the \( \beta\)-Si\(_3\)N\(_4\) (100) planes and approximately 80° with respect to the \( \beta\)-Si\(_3\)N\(_4\) (101) planes. There is a well-defined boundary between the crystalline grain-boundary phase and the neighboring Si\(_3\)N\(_4\) grains. The fringe spacing of the crystalline grain-boundary phase was determined to be 0.24 nm, which does not match any \( d\)-spacing found in silicon nitride (\( \beta\)-Si\(_3\)N\(_4\) or \( \alpha\)-Si\(_3\)N\(_4\)). The thickness of the crystalline boundary phase is approximately 1.6 nm, which is slightly smaller than the thickness of the amorphous grain-boundary phase (1.8 nm) shown in Fig. 7, but still matches well with the equilibrium intergranular distance in Si\(_3\)N\(_4\).
A crystalline grain-boundary phase with a thickness other than 1.6 nm is also identified. Fig. 8(b) is a high-resolution TEM image from another boundary region of the specimen, showing a crystalline phase present along a straight two-grain boundary, at an area near the grain pocket. Compared with the crystalline phase shown in Fig. 8(a), the crystalline boundary phase in Fig. 8(b) shows a similar fringe orientation with respect to the neighboring $\beta$-Si$_3$N$_4$ grains, but a slightly larger fringe spacing (0.26 nm). The thickness of the crystalline boundary phase in Fig. 8(b) was determined to be approximately 1.9 nm, which also is in compliance with the equilibrium intergranular spacing. Kleebe et al. [35] have noted that the intergranular spacing in silicon nitride is independent of the orientation of the neighboring Si$_3$N$_4$ grains, but varies with the composition of the boundary phases. If the boundary-phase composition is indeed the dominant factor controlling the film thickness of a two-grain boundary, the high-resolution TEM images shown in Fig. 8(a) and (b) suggest that there could be more than one crystalline grain-boundary phase formed in the in-situ reinforced silicon nitride.

During high-resolution TEM examination, it was noted that the crystalline boundary phase is often seen at two-grain boundaries near the multi-grain pockets, whereas the boundary phase located at the middle portion of a two-grain boundary is often, if not always, an amorphous phase. The observation suggests that the crystallization of the boundary phase most likely initiates at the grain pockets where the majority of the sintering aids are accumulated. Therefore, a detailed investigation was focused on these areas in order to verify the presence of crystalline boundary phase in the material.

Fig. 9 is a high-resolution TEM image of a three-grain pocket, showing evidence of a crystalline boundary phase present in the pocket. The lattice fringes of a nearby grain shown in this micrograph are...
Fig. 8. High-resolution TEM images revealing the presence of crystalline grain-boundary phase at the two-grain boundaries. The d-spacings of the crystalline boundary phase are determined to be 0.24 nm in (a) and 0.26 nm in (b). The thickness of the boundary phase is approximately 1.6 nm in (a) and is about 1.9 nm in (b). It is noted that the lattice fringes of the boundary phase always orient approximately 45° with respect to the (100) planes of the neighboring β-Si₃N₄ grains.

β-Si₃N₄ (100) fringes which are parallel to the grain boundary, as often seen in silicon nitride. The boundary phase shows two sets of lattice fringes, approximately perpendicular to each other. The fringe spacings of the boundary phase were determined to be 0.32 nm (horizontal fringes) and 0.33 nm (vertical fringes), respectively. The d-spacings and the orientations of the boundary phase fringes do not match those of either β-Si₃N₄ or α-Si₃N₄. Instead, they are in good agreement with the (210) and (112) lattice planes (d₁ = 0.317 nm; d₂ = 0.334 nm; and the inter-plane angle = 86°) of silicon lanthanum oxynitride (La₃Si₂O₁₂N). It is interesting to note that a residual glassy phase, which is a few molecular layers thick, is formed at the interface between the crystalline boundary phase and the β-Si₃N₄ grain. Thomas and coworkers [21,23] also noted the presence of a thin glassy layer at the grain pockets, between crystalline RE₂Si₂O₇ boundary phases and Si₃N₄ grains. The formation of the thin glassy interfacial layer is attributed to the impurities present in the starting Si₃N₄ powders and sintering additives.

The structures of the crystalline boundary phases are also identified by using an SAED technique. The camera length of the microscope was carefully calibrated for each period of operation, by using the standard diffraction patterns obtained from the central regions of the β-Si₃N₄ grains. Due to the small intergranular area, the amount of the crystalline phase segregated at a two-grain boundary is not sufficient to produce a two-dimensional electron diffraction pattern for structural analysis. Most SAED patterns obtained at the two-grain boundaries only show one-dimensional reflection spots, which are not enough to positively identify a given crystal structure because the d-spacing determined from these spots could match several possible crystalline structures. This is illustrated in Fig. 10, which is an SAED pattern from a two-grain boundary where a crystalline boundary phase is identified by high-resolution imaging. It shows a strong (012) standard diffraction pattern from one β-Si₃N₄ grain and a line of sharp (100) spots from the neighboring β-Si₃N₄ grain. In addition, some diffraction spots with significantly lower intensity (arrows) are observed around the origin. The d-spacing of these spots was determined to be 0.548 nm, which does not belong to Si₃N₄. Although this d-spacing matches the (011) spacing of La₃Si₂O₁₂N, it also matches several other possible compounds. Therefore, a detailed SAED study is focused on the two-dimensional diffraction patterns obtained from the

Fig. 9. A crystalline boundary phase present at a grain pocket, showing the two-dimensional lattice fringes. The fringe spacings of the boundary phase are 0.32 and 0.33 nm, respectively, corresponding to the (210) and (112) d-spacings of La₃Si₂O₁₂N. A residual glassy phase with a thickness of few molecular layers is found at the interface between the crystalline boundary phase and the β-Si₃N₄ grain.
Fig. 10. SAED pattern from a two-grain boundary area. It consists of a $\langle 012 \rangle$ standard diffraction pattern from a $\beta$-Si$_3$N$_4$ grain, a line of sharp (100) spots from the neighboring $\beta$-Si$_3$N$_4$ grain, and some low intensity spots (arrows) from the crystalline boundary phase.

relatively large grain pocket areas where a crystalline boundary phase has been identified by high-resolution TEM imaging.

Fig. 11(a) is an SAED pattern from a grain pocket surrounded by three $\beta$-Si$_3$N$_4$ grains. Although the two-dimensional diffraction spots from this area show a relatively lower intensity when compared with those from the $\beta$-Si$_3$N$_4$ grains, they are relatively sharp, indicating that the material at the grain pocket has been well crystallized. The diffraction pattern shown in Fig. 11(a) consists of two sets of spots, perpendicular to each other. The spots along the horizontal direction have a $d$-spacing of 0.838 nm, while the spots along the vertical direction have a $d$-spacing of 0.402 nm. They correspond to the reflections from the (100) and (121) planes of La$_5$Si$_3$O$_{12}$N. The direction of the incident beam is thus determined to be the $\langle 012 \rangle$ direction of La$_5$Si$_3$O$_{12}$N. Based on an analysis of the SAED patterns from the specimen, La$_5$Si$_3$O$_{12}$N is found to be the dominant crystalline boundary phase at the grain pockets, presumably due to the high content of La$_2$O$_3$ in the starting powders. Another crystalline boundary phase identified in the material is silicon yttrium oxynitride (Y$_5$Si$_3$O$_{12}$N), as shown in Fig. 11(b). The SAED pattern shown in Fig. 11(b) is from a relatively large grain pocket surrounded by four $\beta$-Si$_3$N$_4$ grains. Two $d$-spacings are identified from this two-dimensional diffraction pattern. One is 0.474 nm (spots along the horizontal direction) and the other is 0.390 nm. The inter-spot angle is approximately 66°. The $d$-spacings and spot orientation determined from Fig. 11(b) matches well with the $\langle 123 \rangle$ standard pattern from Y$_5$Si$_3$O$_{12}$N, while the three spots nearest to the origin are reflections from the (210), (121), and (111) crystal planes of Y$_5$Si$_3$O$_{12}$N.

The diffraction patterns shown in Fig. 11(a) and (b) also suggest that the crystalline boundary phases at the grain pocket are single crystals, formed by large-scale growth of a single nucleus. This is consistent with the crystallization behavior of the RE$_2$Si$_2$O$_7$ boundary phases observed at the grain pockets [22]. Based on the two crystalline structures identified at the grain pockets, the lattice fringes of the crystalline phases at the two-grain boundaries as shown in Fig. 8(a) and (b) are most likely the (103) fringes of La$_5$Si$_3$O$_{12}$N and the (212) fringes of Y$_5$Si$_3$O$_{12}$N, respectively. Based on X-ray diffraction spectrum, high-resolution TEM images, and SAED patterns, it is therefore concluded that crystalline grain-boundary phases of La$_5$Si$_3$O$_{12}$N and Y$_5$Si$_3$O$_{12}$N have been formed in the in-situ reinforced silicon nitride examined in the present study.

Even though SrO is one of the sintering additives used in preparing the subject material, no evidence of a crystalline silicon strontium oxynitride (Sr$_5$Si$_3$O$_{12}$N) phase is found at the grain boundaries of AS800 silicon.
Fig. 12. High-resolution TEM images of the amorphous phase at the grain pockets. It is noted that the curved \(\beta\)-Si\(_3\)N\(_4\) grain boundary has a stronger bonding with the amorphous phase than the straight boundaries.

Fig. 13. Schematic packing drawing of the rare-earth apatite structure viewed along the \(c_o\) axis [36]. In this structure, an oxygen site in the SiO\(_4\) tetrahedron is replaced by a nitrogen atom and each oxygen or nitrogen atom is surrounded by six lanthanum (or yttrium) ions. Electrical neutrality is maintained by producing a vacancy in every second Si–O–N tetrahedron. The formation of crystallization phases instead of amorphous phases at some grain boundary areas is considered as one of the important reasons resulting in the superior strength of AS800 silicon nitride at elevated temperatures. Y\(_5\)Si\(_3\)O\(_{12}\)N, for example, is found to be stable up to about 1750°C [26], which is significantly higher than the melting temperatures of most glassy phases identified in silicon nitride.

Our observations have shown that the second phases present in the two-grain boundary regions could be either crystalline phases or amorphous phases. The same is true for the grain pockets. It is noted in the present study that not all the grain pockets examined are filled with crystalline boundary phases. Instead, some of them are still filled with the amorphous phase. The high-resolution TEM images of the amorphous phase at the grain pockets indicate that the interface between the \(\beta\)-Si\(_3\)N\(_4\) grain and the amorphous phase usually is well-defined along the curved boundaries (Fig. 12(a)) but is less well-defined along the straight boundaries (Fig. 12(b)). The composition of the amorphous phase at the grain pockets is unknown at present. But the contrast of the amorphous boundary phase does vary from one location to another, suggesting a compositional inhomogeneity of the amorphous phase at the grain boundaries.

4. Discussion

Both crystalline boundary phases identified in AS800 silicon nitride, La\(_5\)Si\(_3\)O\(_{12}\)N and Y\(_5\)Si\(_3\)O\(_{12}\)N, belong to a rare-earth apatite family with a hexagonal crystal structure. Their lattice constants are also very similar. For La\(_5\)Si\(_3\)O\(_{12}\)N, \(a_o\) is 0.9684 nm and \(c_o\) is 0.7275 nm. For Y\(_5\)Si\(_3\)O\(_{12}\)N, the corresponding parameters are 0.9436 and 0.6822 nm, respectively. The most widely studied apatite structure is fluorapatite, Ca\(_5\)P\(_3\)O\(_{12}\)F. Previous studies have shown that substitution of rare-earth cations into the fluorapatite structure would not alter the symmetry of the unit cell but would result in a slight change of the lattice parameters. For rare-earthapatites, the lattice parameters usually increase with increasing ‘ionic’ radii of the cation [30].
The thickness of the crystalline phases at the two-grain boundaries is relatively stable, varying from 1.5 to 1.9 nm, with an average value of approximately 1.7 nm. The thickness of the amorphous phases at the two-grain boundaries, on the other hand, shows variation over a wide range. The high resolution TEM images shown in Fig. 14(a) and (b) illustrate two extreme cases observed in the present study. In Fig. 14(a), the thickness of the amorphous film is approximately equal to the (100) d-spacing of $\beta$-Si$_3$N$_4$, i.e. about 0.7 nm. In Fig. 14(b), on the other hand, the amorphous phase shows a thickness greater than 3.0 nm. The variation of the amorphous phase thickness observed in AS800 silicon nitride suggests that the amorphous boundary-phase chemistry may vary from one area to another. In the pioneering work on ceramic intergranular spacing, Clark [34] indicates that thin intergranular films should maintain an equilibrium thickness at the two-grain boundary of polycrystalline ceramics. According to an analysis of the interfacial energies and the force balance normal to the grain boundary, the presence of an equilibrium intergranular film thickness is the result of two competing interaction forces: (1) an attractive van der Waals force between the grains on either side of the boundary which tends to thin the film, and (2) a repulsive force, due to the structure of the boundary phase, against the van der Waals force. An equilibrium film thickness on the order of 1 nm is proposed based upon the short-range balance of these two interaction forces. Furthermore, it is concluded that for a given ceramic material, the final film thickness is ultimately dependent on the composition of the starting liquid. This is confirmed by the different film thicknesses of the La$_5$Si$_3$O$_{12}$N and Y$_5$Si$_3$O$_{12}$N crystalline boundary phases (Fig. 8(a) and (b)) observed in the present study. Therefore, the wide fluctuation of the intergranular amorphous film thickness observed in AS800 silicon nitride indicates that there exist significant compositional inhomogeneities at the boundaries of $\beta$-Si$_3$N$_4$ grains. This is most likely due to the limited viscosity of the liquid phase in these regions, as well as the presence of impurities from the starting powders. Based upon the high-resolution images obtained in the present study, it is thus suggested that there may be several amorphous boundary phases with different compositions present at the two-grain boundaries of AS800 silicon nitride.

During the processing of AS800 silicon nitride, attempts have been made to eliminate the glassy phase at the grain boundaries, such as adding rare-earth oxides suitable to form crystalline phases, using gas pressure sintering which requires less liquid phase, and performing post-sintering heat treatments to assist crystallization at the grain boundaries. However, the results obtained in the present study still show the presence of an amorphous phase at the grain boundaries and the grain pockets (Figs. 7, 12 and 14), suggesting that complete recrystallization of boundary phases in silicon nitride is hard to achieve. Such a limited recrystallization at the grain boundaries of ceramics is attributed to two factors. The first one is the difficulty for the crystalline phase to nucleate at the grain boundaries. Bernard-Granger et al. [37] have found that nucleation of the boundary phase in silicon nitride takes place in some discrete places at the interface between the boundary phase and Si$_3$N$_4$ grains. Once created, nuclei grow into the boundary phase by displacement of well-faceted crystallization fronts. Therefore, nucleation is heterogeneous and is not an easy step in the crystallization process. For the crystallization to initiate, the nucleation needs, at the same time, local composition fluctuations, with respect to the average composition, in order to reach locally the composition of a crystalline phase, and probably a propitious orientation with respect to the neighboring silicon nitride grains to favor an 'epitaxial' nucleation and growth.
The second barrier to the crystallization of the boundary phase in ceramics is due to the increase of the strain energy during phase transformation. As suggested by Raj and Lange [38], complete crystallization of small amounts of the glassy phase segregated at the grain boundaries is much more difficult than crystallization of a bulk material of the same composition. This is because the glassy phase segregated at the grain boundaries is constrained from flowing over distances larger than the grain size, since the channels through which the liquid must move are quite small, usually on the order of a few nanometers, as can be seen from the high resolution TEM images shown in Figs. 7, 8, 12(b) and Fig. 14. The initial glassy phases resulting from the sintering aids, therefore, are essentially confined within rigid ceramic crystals. As a result, the glassy phase has to sustain hydrostatic stress (shear stresses are unlikely because they will be relaxed by the fluid flow within the intergranular region). Any change in the volume upon crystallization will set up hydrostatic stresses so that the strain energy associated with it must be accounted for in the crystallization process. In general, volume change during the phase transformation from a glassy to a crystalline phase in a confined region will give rise to strain energy which would oppose the transformation. The strain energy introduced depends upon the difference in the specific volumes of the crystalline and the glassy phases, the bulk moduli of the two phases, and the size of the crystalline phase formed. Stress and strain energy calculations performed by Raj and Lange [38], complete crystallization of small amounts of the glassy phase segregated at the grain pockets, and along the two-grain boundaries at areas near the pockets. (2) The thickness of the crystalline phases at the two-grain boundaries is approximately 1.7 nm, confirming that there is an equilibrium film thickness for the second phase at the two-grain boundary. (3) The glassy phase is also observed at the grain pockets and at the two-grain boundaries, indicating that the crystallization of the boundary phases is incomplete. (4) The thickness of the amorphous phase at the two-grain boundaries varies from 0.7 to 3.0 nm, suggesting that significant compositional inhomogeneities of the boundary phases exist in these areas. (6) The superior high-temperature strength of the material is believed to result from the partial crystallization of the boundary phases.

5. Conclusions

The following conclusions can be drawn from the present study on the microstructure of the in-situ reinforced silicon nitride: (1) Crystalline rare-earth apatite boundary phases (La$_2$Si$_3$O$_7$N and Y$_2$Si$_3$O$_7$N) have been identified at the grain pockets, and along the two-grain boundaries at areas near the pockets. (2) The thickness of the crystalline phases at the two-grain boundaries is approximately 1.7 nm, confirming that there is an equilibrium film thickness for the second phase at the two-grain boundary. (3) The glassy phase is also observed at the grain pockets and at the two-grain boundaries, indicating that the crystallization of the boundary phases is incomplete. (4) The thickness of the amorphous phase at the two-grain boundaries varies from 0.7 to 3.0 nm, suggesting that significant

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