High-Temperature Deformation and Microstructural Analysis for Si₃N₄–Sc₂O₃

Deock-Soo Cheong and William A. Sanders

Lewis Research Center
Cleveland, Ohio

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ABSTRACT

Limited past studies have indicated that Si$_3$N$_4$ doped with Sc$_2$O$_3$ may exhibit high-temperature mechanical properties superior to Si$_3$N$_4$ systems with various other oxide sintering additives. High-temperature deformation of samples was studied by characterizing the microstructures before and after deformation. It was found that elements of the additive, such as Sc and O, exist in small amounts at very thin grain boundary layers and most of them stay in secondary phases at triple and multiple grain boundary junctions. These secondary phases are devitrified as crystalline Sc$_2$Si$_2$O$_7$. Deformation of the samples was dominated by cavitation processes rather than movements of dislocations. Thus, the excellent deformation resistance of the samples at high temperature can be attributed to the very small thickness of the grain boundary layers and the crystalline secondary phase, as suggested earlier.

INTRODUCTION

In 1977 Andersson and Bratton (Ref. 1) investigated the effectiveness of several oxide densification aids for Si$_3$N$_4$. They were seeking oxide additives which would yield fully dense hot pressed Si$_3$N$_4$ with good strength retention up to 1370 °C. One of 14 oxides evaluated was Sc$_2$O$_3$ selected because of its high silicate melting point (Ref. 2). Andersson and Bratton (Ref. 1) were unable to fully densify Si$_3$N$_4$ with Sc$_2$O$_3$ for strength testing, but suggested that it probably had the greatest potential for high-temperature strength retention. This conclusion was based on the inverse relationships found...
between the ionic radii of rare earth metals in the silicate $M_2Si_2O_7$ with both the 1400 °C flexural strength and the incipient melting point of corresponding $Si_3N_4-M_xO_3-SiO_2$ eutectic mixtures. Ionic radius was selected as a variable since it is indicative of the bond strength of a rare earth silicate with the $M_2Si_2O_7$ structure. The $Si_3N_4-Sc_2O_3-SiO_2$ combination had the highest incipient eutectic point, and Sc had the smallest ionic radius among rare-earth elements. Negita (Ref. 3) pointed out that Sc is one of several metals whose oxides successfully sinter $Si_3N_4$ where the oxide metal ions have electronegativities less than about 1.5 and ionic radii less than 0.1 nm. It was suggested that ionic materials with these characteristics introduced into the grain boundary phase of a $Si_3N_4$ material promote faster diffusion and sintering. This improved sinterability results from the introduction of these ionic materials which cause surface energy relaxation owing to the nondirectional and long-range properties of the ionic bond. It was further suggested that based on geometrical considerations, metal ions with radii 0.1 nm can substitute for silicon or migrate in channels parallel to the c-axis in the $\beta$-$Si_3N_4$ structure, also promoting sintering (Ref. 3).

In 1981, Morgan and co-workers (Ref. 4) suggested that $Sc_2O_3$ might be an appropriate sintering aid for $Si_3N_4$ since $Sc_2O_3$ was unlikely to form quaternary metal silicon oxynitrides when added to $Si_3N_4$. These metal–silicon–oxynitrides can expand upon oxidation causing cracking (Ref. 5). In the work of Morgan et al., $Si_3N_4-SiO_2-Sc_2O_3$ compositions were hot pressed at 1600 to 1800 °C to determine phase relations, and no quaternary phases were found by x-ray diffraction analysis. Subsolidus tie lines were only found to exist between $Si_3N_4$ and $Sc_2O_3$, $Si_3N_4$ and $Sc_2Si_2O_7$, and $Sc_2Si_2O_7$ and $Si_2N_2O$. A composition of $Si_3N_4$-18 mol % $SiO_2$-8 mol % $Sc_2O_3$ was selected for hot pressing trials and to provide material for oxidation and compressive creep tests, both at 1400 °C.
It was found that a 4-hr hold at 1800 °C under 29 MPa pressure was required to nearly complete the $\alpha \rightarrow \beta$ Si$_3$N$_4$ phase transformation. Sluggish densification and transformation kinetics were suggested to be indicative of high eutectic temperature within the Si$_3$N$_4$-SiO$_2$-Sc$_2$O$_3$ system. The composition proved to be very resistant to oxidation at 1400 °C (0.44 mg/cm$^2$ weight gain in 285 hr), and exhibited 1400 °C compressive creep stress exponents pointing to creep dominated by diffusional processes at stresses less than 275 MPa and dominated by cavitational processes at higher stresses. The likelihood of cavitational processes acting at stresses >275 MPa was substantiated by a decrease in the density of the test specimen as a result of testing. The creep resistance of the Si$_3$N$_4$-SiO$_2$-Sc$_2$O$_3$ material was found to be one to two orders of magnitude superior to that of Si$_3$N$_4$/MgO materials. Morgan et al. found that the microstructure of their Si$_3$N$_4$-SiO$_2$-Sc$_2$O$_3$ material consisted of a $\beta$-Si$_3$N$_4$ matrix of highly prismatic morphology with a Sc$_2$Si$_2$O$_7$ crystalline phase surrounding the $\beta$-Si$_3$N$_4$ grains. A very thin (~1 nm) continuous intergranular glassy phase and a few large glass pockets were also noted.

Also in 1981, Dodsworth and Thompson (Ref. 6) conducted studies on the suitability of Sc$_2$O$_3$ as a densifier for Si$_3$N$_4$. Si$_3$N$_4$ with 2 wt % Sc$_2$O$_3$ was hot pressed at 1700 °C, but could not be fully densified if pressureless sintered at 1700 °C. Higher temperatures required for densification by pressureless sintering could not be applied due to volatilization of silicon monoxide. Oxidation resistance of hot pressed Si$_3$N$_4$ containing 2 wt % Sc$_2$O$_3$ for 120 and 100 hr at 1000 and 1400 °C, respectively, was excellent with weight gains of only 0.02 and 0.25 mg/cm$^2$, respectively. Creep tests of hot pressed Si$_3$N$_4$ with 2, 5, and 10 wt % Sc$_2$O$_3$ at 1225 °C, 77 MPa showed that creep was enhanced as the level of additive was increased. However, this trend was reversed for the same materials devitrified for 120 hr.
In a study of oxynitride glasses containing scandium, Tredway and Loehman (Ref. 7) found that Sc$_2$O$_3$ is thermodynamically compatible with Si$_3$N$_4$ based on the formation of oxynitride glasses without decomposition, and that melts can be made in which Si$_3$N$_4$ is soluble. Thus, the solution-precipitation sintering mechanism for Si$_3$N$_4$ would be operative. Tredway and Loehman pointed out a limited glass forming region for scandium oxynitride glasses and suggested that the intergranular phase in Si$_3$N$_4$ sintered with Sc$_2$O$_3$ might crystallize more readily than is the case for other sintering additives. Crystallization of the grain boundary glass in sintered Si$_3$N$_4$ has been suggested as a technique for increasing high-temperature strength (Ref. 8).

In another study of scandium-containing oxynitride glasses, Mecartney (Ref. 9) found that pieces of hot pressed Si$_3$N$_4$ joined with a glass containing Sc$_2$O$_3$ showed that scandium had diffused down the grain boundaries of the hot pressed Si$_3$N$_4$ and had crystallized as groups of small precipitates in pockets. This occurred without heat treatment. The ready crystallization of the oxynitride glass was absent when Sc$_2$O$_3$ was excluded. It was suggested that under appropriate annealing conditions the crystallization of Sc$_2$O$_3$-containing grain boundary glasses could be made more uniform and extensive resulting in a sintered Si$_3$N$_4$ material with improved creep resistance.

In the present investigation, 2.2 wt % Sc$_2$O$_3$ doped Si$_3$N$_4$ test bars were deformed in a stepped temperature mode to 1400 °C under various loads, and the microstructural analysis of these samples was performed with TEM, HREM, EDS, x-ray Diffractometry, and SEM. The primary object of this study was to understand the microstructures of the undeformed and the deformed samples and to relate these findings to the observed high-temperature deformation behavior.
EXPERIMENTAL PROCEDURES

Materials and Processing

Si$_3$N$_4$\(^1\) (97.7 g) and Sc$_2$O$_3$\(^2\) (2.3 g) powders were ground together as a 100-g charge in a 1-liter SRBSN (Sintered Reaction Bonded Silicon Nitride) mill\(^3\) filled with HPSN (Hot-Pressed Silicon Nitride) media\(^4\). The media charge was 800 g of 1 by 1 cm HPSN cylinders and the grinding fluid was 1/2 liter of pure ethanol. Grinding time was 100 hr. After milling, the powder-ethanol slurry was transferred to a drying apparatus employing a heated water bath and a vacuum connection for removal of ethanol vapor\(^5\). The powder was further dried in a drying oven at 110 °C. The softly agglomerated powder was then crushed using HPSN hardware and sieved through a 149 μm screen. Specific surface area of the powder determined by the 3-point BET method was 19.8 m$^2$/g.

Quantitative chemical analysis of the ground powder gave 3.56 percent oxygen and 0.80 percent carbon. Semi-quantitative spectrographic analysis indicated ppm levels of 1000 Y, 730 Fe, 440 Al, 60 Ca, and 50 Cu. Phase content calculations were based on initial charge composition, Si$_3$N$_4$ pickup from the milling hardware, oxygen analysis and reduction of some SiO$_2$ by carbon assumed to occur during sintering. Phase composition of the powder in weight percent was 93.8 Si$_3$N$_4$, 3.8 SiO$_2$, and 2.4 Sc$_2$O$_3$. In mole percent, the composition was 87.7 Si$_3$N$_4$, 10.1 SiO$_2$, and 2.2 Sc$_2$O$_3$. Phase analyses of the powders and samples after sintering were done with x-ray diffractometry using Cu-K$\alpha$ radiation.

\(^{1}\)Kemanord Industrikemi, Engineering Ceramics, P95H Ljungaverk, Sweden (Superior Graphite Co., Chicago, ILL.)

\(^{2}\)Johnson Matthey, 11216, Seabrook, N.H.

\(^{3}\)Garrett Ceramic Components Division, Torrance, CA.

\(^{4}\)Iscar Ceramics, Livonia, MI.

\(^{5}\)Rotavapor, Prieser Scientific, Louisville, KY.
The sieved powder was pressed into bars at 21 MPa using double-acting tungsten carbide-lined dies. Two lengths of die-pressed bars were pressed, 3.8 and 5.7 cm. The common green bar cross-section was 0.79 by 0.45 cm. Green bars were vacuum sealed in latex tubing and isostatically cold pressed at 414 MPa to a density of 1.80 g/cm³, 58 percent of the calculated theoretical density of 3.12 g/cm³.

Weighed and measured bars were sintered 15 at a time in a tungsten cup with a loose-fitting lid in a water cooled double-wall furnace heated with a tungsten mesh element. Bars were separated from one another and the tungsten cup with high purity BN discs. The sintering temperature of 2140 °C was maintained for 4 hr with 5 MPa nitrogen overpressure. The shrinkage during sintering process was uniform at ~18 percent for length, breadth, and thickness, with sinter weight loss of ~3 percent.

Test bars were longitudinally ground with a 400-grit diamond wheel and the four long edges were beveled 0.12 mm. Final test bar dimensions were 3.0 by 0.56 by 0.28 cm for the fast fracture test, and 4.5 by 0.56 by 0.28 cm for the stress rupture test. The density of the machined test bars was 3.18 g/cm³. This value exceeds that of the theoretical density value of 3.12 calculated based on the law of mixtures assuming the presence of three phases, Si₃N₄, SiO₂, and Sc₂O₃ in the as-ground powder. The density of the grain boundary phase is not known, but to explain the density differences, it is suggested that the specific volume of the grain boundary phase is less than the summed specific volumes of the SiO₂ and Sc₂O₃ phases.

\[ \text{Theoretical density was calculated by the law of mixtures for the compounds Si}_3\text{N}_4, \text{SiO}_2 \text{ and Sc}_2\text{O}_3. \]
Mechanical Testing

Four point flexural strength tests were conducted at a crosshead speed of 0.51 mm/min with inner and outer spans of 9.53 and 19.05 mm, respectively. Room temperature tests were conducted with steel fixtures. Elevated temperature tests were conducted using SiC fixtures in a SiC muffle furnace mounted on a testing machine. All tests were conducted in air.

Four-point flexural stress rupture tests were conducted on lever arm ceramic compression creep test machines. Test bars were loaded under constant dead weight in air in a stepped-temperature exposure mode starting at 1100 °C. Every 24 hr the temperature was raised 100 °C within 5 min and held for 24 hr. At 1400 °C the test bar was held under load at least 72 hr unless failure occurred. Flexural stress rupture fixtures were SiC with inner and outer spans of 19.05 and 38.1 mm, respectively. A creep measurement system included an LVDT displacement transducer with a 3-point extensometer made of Al₂O₃ gaging rods with SiC points. The SiC points contacted the test bar tensile surface at the center and beneath the inner load points. Relative deflection was measured and strain calculated by a data acquisition system. The strain calculation for a test bar in four-point bending assumed a constant radius of curvature between the inner load points. Strain was calculated using the simple relation, \( \varepsilon_{\text{max}} = 4h \times \frac{d}{a^2} \), where \( \varepsilon_{\text{max}} \) is the maximum strain in the outer fiber, \( h \) is the bar thickness, \( d \) is the relative deflection of the bar center with respect to the inner load points, and \( a \) is the inner span length (Ref. 10). Test temperatures, durations, and applied loads are summarized in Table 1.

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7Instron Corporation, Canton, MA.
8Applied Test System Inc., Series 2390, Butler, PA.
Microstructural Characterizations

SEM

In order to study grain morphology, and distributions of grain boundaries and secondary phases, the silicon nitride grains were etched using a plasma etching technique (Ref. 11). Contrary to conventional chemical etching processes, this process etches Si$_3$N$_4$ grains in preference to other secondary crystalline or glassy phases. The microstructure of the etched sample was observed with SEM (JEOL 840 operated at 30 kV). The fracture surface of stress rupture bar 3 (Table 1) which failed after 8 min under a load of 350 MPa at 1400 °C was coated with Au, and then studied by SEM.

TEM

Microstructural analyses of samples were performed by using TEM (Philips 400T operated at 120 kV). Foils of deformed and undeformed samples were prepared by following the conventional TEM sample preparation procedures. For an undeformed sample, the microstructure of a cross-section of the bar was investigated. A section perpendicular to the cross-section was also studied in order to fully characterize the microstructure of the sample. Microstructural analysis of deformed samples was conducted on both tension and compression surfaces of samples deformed in four-point flexural stress rupture. When a sample failed, an additional foil was prepared near the fracture surface. The Burgers vector of dislocations was determined by using diffraction contrast (Two Beam Condition) experiments. Since secondary phases at triple junctions were very small, the CBED (Convergent Beam Electron Diffraction) was employed to study the crystal structure of the phase. In addition to BF (Bright Field) imaging, DF (Dark Field) imaging technique was also used to examine continuous amorphous intergranular phase. During TEM sessions, chemical analysis of
Si$_3$N$_4$ grains and intergranular phases was performed by EDS (Energy Dispersive Spectrometry), equipped with a SiLi Detector.

**HREM**

Since grain boundary phases are a critical factor for mechanical properties of Si$_3$N$_4$, especially at high temperatures, HREM (JEM 4000EX operated at 400 kV) was employed to study the structure of the matrix, secondary phase, and grain boundary phases. To accurately estimate the thickness of the grain boundary, the foil was tilted so that the electron beam was parallel to the grain boundary. The foil was also oriented so that two grains were in a strong diffracting condition in order to have high contrast lattice fringes.

**RESULTS AND DISCUSSION**

X-ray diffractometry traces for the starting powder and the sintered sample are shown in Figs. 1(a) and (b). The starting powder was predominantly composed of $\alpha$-Si$_3$N$_4$ (space group, P31c) and a small amount of $\beta$-Si$_3$N$_4$ (marked by arrows in Fig. 1(a)). The amount of $\beta$-Si$_3$N$_4$ was ~9 percent, calculated by following the method of Gazzara and Messier (Ref. 12). All the $\alpha$-Si$_3$N$_4$ transformed to $\beta$-Si$_3$N$_4$ (space group, P6$_3$/m) and a small amount of Sc$_2$Si$_2$O$_7$ formed during sintering at 2140 °C for 4 hr under 5 MPa N$_2$ pressure. The whole spectrum in Fig. 1(b) is from $\beta$-Si$_3$N$_4$, except two peaks (open arrow) for Sc$_2$Si$_2$O$_7$. The first peak ($2\theta = 28.539^\circ$) corresponds to 111 reflections, and the second peak ($2\theta = 30.548$) is from 021 reflections of Sc$_2$Si$_2$O$_7$. Microstructural and crystallographic information about Sc$_2$Si$_2$O$_7$ will be discussed with the TEM analysis.

The morphologies of Si$_3$N$_4$ grains and grain boundary phases were delineated by etching the Si$_3$N$_4$ grains. Shown in Fig. 2 are $\beta$-Si$_3$N$_4$ grains, thin grain boundaries, and a secondary phase at multiple grain boundary junctions of the etched sample. Particularly interesting in this micrograph are the many long
acicular grains of hexagonal cross-section which form interlocking structures. Such interlocking structures can provide toughening by crack deflection, which is the major toughening mechanism of monolithic Si₃N₄ materials (Ref. 13).

The Sc₂O₃-Si₃N₄ material was characterized in fast fracture flexure tests at room temperature and 1370 °C. The results are presented in Table 2 and indicate that the material has a strength of 748 MPa at room temperature, and 496 MPa at 1370 °C. The standard deviations of the strengths are 48 and 44 MPa, respectively. The strength of Sc₂O₃-Si₃N₄ material compares favorably with the fast fracture strengths of Si₃N₄ densified with Y₂O₃, CeO₂, La₂O₃, Sm₂O₃, and ZrO₂ at room temperature and shows some advantage at 1370 °C, as shown in Fig. 3 (Refs. 14 and 15). As listed in Table 1, Sc₂O₃-Si₃N₄ bars were tested in stepped-temperature flexural stress rupture at 1350 °C/300 MPa (bar 9) and 1400 °C/250 MPa (bar 8) for durations of 91 and 96/hr, respectively, without failure. The plastic strains of the test bars were 0.86 and 1.48 percent. However, another test bar failed under a stress of 350 MPa after only 8 min at 1400 °C with a plastic strain of 0.35 percent.

The fracture surface of bar 3 which failed under 350 MPa at 1400 °C was observed with SEM (Fig. 4). The surface was relatively rough at high magnification, showing crack deflection (marked D) and in some cases acicular grain pull-out (marked as P). The roughness of the fracture surface of a material is directly related to the fracture toughness of a material (Ref. 16). The fracture surface roughness implies that the crack-propagation path is longer and thus needs more energy for crack propagation, i.e., tougher material. There are many sites where the crack propagated around large acicular grains (marked D) in Fig. 4. These sites are where large acicular grains protrude from the fracture surface or where there are imprints showing the location of such grains prior to fracture. This is good evidence of crack
deflection. Also apparent in the micrograph is the interlocking grain structure.

Detailed microstructure analyses of undeformed and deformed samples were also performed by using TEM. Figure 5(a) shows the general microstructure of a cross-sectional area of an undeformed bar, and Fig. 5(b) shows an area which is perpendicular to this cross-section. There are no apparent differences between the two microstructures, indicating that the interlocking structures are homogeneous and acicular grains were distributed at random. The sample was very dense except for a few localized areas showing scattered pores. The grains with hexagonal shape are cross-sections of the acicular grains. The cross-section corresponds to the basal plane, (0001), as shown in the diffraction pattern, inset in Fig. 6. Thus β-Si₃N₄ grains grow in a preferred orientation, along the c-axis. The six-sided surfaces of the grains are the prismatic planes of the HCP structure. CBED (Convergent Beam Electron Diffraction) (Fig. 7) showed that secondary phases at multiple junctions were crystalline, and that the crystal structure was monoclinic which was confirmed with XRD results. The CBED analysis consistently demonstrated these results at about 50 other sites. The zone axis of the CBED inset in Fig. 7 is [112]. There were no indications of amorphous phases in the samples, but this may be due to the limit of detectibility of TEM. Mecartney (Ref. 9) has suggested that Sc enhances crystallization of the glassy phase in the Sc₂O₃-MgO-Si₃N₄ system. And Tredway and Loehman (Ref. 7) proposed that the intergranular phase in Si₃N₄ with Sc₂O₃ crystallizes more readily than intergranular phases in Si₃N₄ resulting from the use of other additives. Preliminary result of interrupted sintering experiments (Ref. 17) showed that the glassy phase in the Sc₂O₃-Si₃N₄ system crystallizes more easily than that in Y₂O₃-Si₃N₄ system. The secondary phase, Sc₂Si₂O₇, is also highly refractory by virtue of a high
eutectic temperature (Ref. 2). Thus the excellent high-temperature mechanical properties for Sc₂O₃-Si₃N₄ material can be attributed to high refractoriness and enhanced crystallization of secondary phases.

Apparent inside the Si₃N₄ grains are many grown-in dislocations. Diffraction contrast experiments showed that the Burgers vectors of dislocations is predominantly [0001]. Some grains showed a very high density of dislocations and larger and/or longer grains tend to exhibit more dislocations in this sample (Fig. 8). Burgers vectors of dislocations in Si₃N₄ determined by other researchers (Refs. 18 to 21) agree with the results obtained in this study. Butler (Ref. 18) and Kossowsky (Ref. 19) reported a Burgers vector of (0001). Lee and Hilmas (Ref. 20) reported Burgers vectors for Si₃N₄ of (0001), 1/3(1210), and 1/3(1123) in the Y₂O₃-Si₃N₄ system after heat treatment at 1500 °C to crystallize the glass phases with formation of the secondary phase, Y₂Si₂O₇. During crystallization and phase transformation of the secondary phase, Si₃N₄ grains deform due to a volume change associated with the phase transformation, and dislocations were formed. Lee and Hilmas attributed the decrease of volume to closer packing of atoms during the phase transformation. Dense dislocation networks and tangles were formed during the heat treatment and annealed out after further heat treatments.

For test bar 8 which experienced the greatest strain, 1.48 percent, the microstructures of two sides, tension (Fig. 9(a)) and compression (Fig. 9(b)), were studied in order to elucidate the deformation behavior of the sample. The significant difference between the two surfaces is the incidence of cavitation. The tension side exhibits many more cavities than the compression side and most cavities exist at triple grain junctions and multiple grain junctions, supporting the mechanism of a cavitational process (Ref. 4) through grain boundary sliding during creep. Kossowsky et al. (Ref. 19) studied the
tensile and creep properties of hot-pressed Si₃N₄, and reported that the deformation at high temperatures, above 1000 °C, is controlled by grain boundary sliding. Morgan et al. (Ref. 4) performed compressive creep tests of hot-pressed Sc₂O₃-Si₃N₄ at 1400 °C and obtained results suggesting that cavitation processes were dominant for stress >275 MPa by showing a decrease of sample density after the tests. Since the stress used in this study, 250 MPa, was close to that of Morgan et al., the cavitation process, suggested by Morgan et al. (Ref. 4), would be operative. In addition to cavity formation at grain boundary junctions, grain boundary separation was observed on a TEM foil, obtained close to the fracture surface of the failed bar 3 (Fig. 10). Grain boundary separation, occurring by growth of cavities during increasing deformation, finally resulted in sample failure (Ref. 22). Also observed in both the tension and compression sides of bar 8 were dislocations, most of which have a Burgers vector of [0001]. Dislocations in deformed Si₃N₄ samples were observed by earlier investigators (Refs. 18 to 21). There were no noticeable differences in dislocation structures between the two sides of the samples, and these dislocations were also observed in undeformed samples. The microstructures of the two sides of less deformed bars, 7 and 9, were also studied with TEM. The microstructures were similar to those of bar 8. Thus the major mechanisms of creep in this system are cavitation and grain boundary sliding, rather than deformation inside grains.

The structural analysis of grain boundary and secondary phases was extended with HREM. Figure 11 (from bar 8) shows the boundary structure between a Si₃N₄ grain and the secondary phase. The upper grain provides lattice fringes for a secondary phase and the lower grain is a Si₃N₄ grain. Lattice fringe spaces of Si₃N₄ and the secondary phase correspond to 2.53 and 2.68 Å, respectively. The lattice fringes in Fig. 11 are too close to measure
the thickness of the grain boundary. Similarly Morgan et al. (Ref. 4) reported that the thickness of the grain boundary for their Si$_3$N$_4$-Sc$_2$O$_3$ material was $\sim$1 nm. Thus, our HREM showed no apparent evidence of amorphous intergranular phases and extremely thin grain boundaries, which is consistent with our results for TEM. Earlier investigators (Refs. 4 and 9) reported the formation of amorphous (glass) phases involving Sc$_2$O$_3$, which were not observed in our samples. The discrepancy can be attributed to differences in composition, sintering temperatures and methods, and other additives. Morgan et al. (Ref. 4) observed amorphous films at grain boundaries. Those glass phases may be retained due to the low sintering temperature, 1600 to 1800 °C. Glass pockets at grain junctions reported by Mecartney (Ref. 9) were formed due to additional additives, Al$_2$O$_3$ and MgO.

Chemical analysis of samples was performed with EDS during TEM sessions. Figure 12(a) shows the typical elemental trace for a Si$_3$N$_4$ grain. No Sc was detected inside the Si$_3$N$_4$ grain. However a very small amount of Sc was observed at grain boundaries of the sample (Fig. 12(b)). For the secondary phase, the intensity of the Sc peak was almost the same as the Si peak (Fig. 12(c)). In some cases, the Sc peaks were smaller than those of Si, which may be caused by overlap of the secondary phases and the Si$_3$N$_4$ grains. The intensity of the O peak of the secondary phase is distinct, but there were negligible amounts of O at grain boundaries and in Si$_3$N$_4$ grains. The relatively small O peak in this case can be caused by absorption effects in the low energy regions. Therefore, Sc from the additive was mostly detected in grain boundary junctions and formed the secondary phase with SiO$_2$. Very small amounts of Sc were observed in the thin grain boundaries.
SUMMARY OF RESULTS

1. The major deformation mode in flexural creep testing under 250 MPa at 1400 °C of 2.2 wt % Sc₂O₃-Si₃N₄ material was due to cavitational processes and grain boundary sliding as is the case for other monolithic Si₃N₄ materials rather than deformation of Si₃N₄ grains.

2. Elements of the additives, Sc and O, were concentrated at triple and multiple grain boundary junctions and formed the secondary phases, which were identified as crystalline Sc₂Si₂O₇ having the monoclinic structure. No evidence of continuous amorphous phases was obtained with TEM and HREM. A very small amount of those elements were detected at grain boundaries. The grain boundaries between two Si₃N₄ grains, or those between grains and secondary phases are very thin (<1 nm).

3. Many dislocations were observed in samples with and without creep tests. These dislocations have mostly Burgers vector of (0001). Large and/or long Si₃N₄ grains tend to show more dislocations.

CONCLUSION

Excellent mechanical properties of Si₃N₄ with Sc₂O₃ may be attributed to high refractoriness and crystallization of the secondary phase, and the very thin grain boundaries.

REFERENCES


17. D.-S. Cheong and W.A. Sanders, in progress.


### TABLE I. - STEPPED TEMPERATURE FLEXURAL STRESS RUPTURE TESTS

OF Si$_3$N$_4$-SiO$_2$-Sc$_2$O$_3$ IN AIR

<table>
<thead>
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<th>Test bar number</th>
<th>Stress at tensile surface, MPa</th>
<th>Test duration</th>
<th>Final strain, percent</th>
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<tr>
<td>7</td>
<td>200</td>
<td>24 hr at 1100, 1200, 1300 °C; 72 hr at 1400 °C</td>
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</tr>
<tr>
<td>8</td>
<td>250</td>
<td>24 hr at 1100, 1200, 1300 °C; 96 hr at 1400 °C</td>
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<td>300</td>
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</tr>
<tr>
<td>3</td>
<td>350</td>
<td>24 hr at 1100, 1200, 1300 °C; 0.13 hr at 1400 °C</td>
<td>0.35 Failure</td>
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</table>

### TABLE II. - FLEXURAL STRENGTH OF Si$_3$N$_4$-Sc$_2$O$_3$ TESTED IN AIR

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<thead>
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<th>Average strength, MPa</th>
<th>Standard deviation, MPa</th>
</tr>
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<td>48</td>
</tr>
<tr>
<td>1370</td>
<td>496</td>
<td>44</td>
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</table>

**Figure 1.**—X-ray diffraction traces for Si$_3$N$_4$-Sc$_2$O$_3$.  

(a) Starting powder.  

(b) Ground surface of sintered bar.
Figure 2.—SEM microstructures of plasma-etched Si₃N₄-Sc₂O₃.

Figure 3.—Flexural strength vs temperature for Si₃N₄-MₓOᵧ compositions.

Figure 4.—Fracture surface of stress-ruptured Si₃N₄-Sc₂O₃ (Bar 3) (Noted P; Pull-out acicular grain, D; Crack deflection).
(a) Center of bar cross section.

Figure 5.—TEM micrographs of undeformed Si$_3$N$_4$-Sc$_2$O$_3$ bar showing similarities.

(b) Section perpendicular to the cross section.

Figure 6.—TEM micrograph of hexagonal $\beta$-Si$_3$N$_4$ grain with corresponding diffraction pattern for HCP basal plane (0001).

Figure 7.—TEM micrograph with CBED pattern for monoclinic secondary phase at triple point of sintered Si$_3$N$_4$-Sc$_2$O$_3$. 

(b) Section perpendicular to the cross section.

Figure 5.—TEM micrographs of undeformed Si$_3$N$_4$-Sc$_2$O$_3$ bar showing similarities.
Figure 8.—Dislocations in deformed $\text{Si}_3\text{N}_4$-$\text{Sc}_2\text{O}_3$, having Burgers vector of [0001].
Figure 9.—TEM micrograph of deformed Si$_3$N$_4$-Sc$_2$O$_3$ ($\epsilon_P = 1.48$ percent).

Figure 10.—TEM micrograph of a foil close to the fracture surface of bar 3, showing grain boundary separation in addition to cavitation.

Figure 11.—Lattice fringe image of secondary phase (upper grain) and matrix (lower grain). Very thin grain boundary is also between two lattice fringes.
Figure 12.—EDS analyses of matrix, grain boundary, and secondary phase.
Limited past studies have indicated that Si₃N₄ doped with Sc₂O₃ may exhibit high-temperature mechanical properties superior to Si₃N₄ systems with various other oxide sintering additives. High-temperature deformation of samples was studied by characterizing the microstructures before and after deformation. It was found that elements of the additive, such as Sc and O, exist in small amounts at very thin grain boundary layers and most of them stay in secondary phases at triple and multiple grain boundary junctions. These secondary phases are devitrified as crystalline Sc₂Si₂O₇. Deformation of the samples was dominated by cavitation processes rather than movements of dislocations. Thus the excellent deformation resistance of the samples at high temperature can be attributed to the very small thickness of the grain boundary layers and the crystalline secondary phase, as suggested earlier.