High-temperature elastic properties of *in situ*-reinforced Si$_3$N$_4$

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A high-temperature tensile stress study of a monolithic silicon nitride (Si$_3$N$_4$) was performed with time-of-flight neutron diffraction. A dedicated engineering diffractometer was employed at temperatures reaching 1375 °C. Rietveld refinements of diffraction spectra allowed the determination of (1) the coefficient of thermal expansion tensor during heating and (2) lattice strains during loading. The stress–strain response of individual lattice reflections was used to calculate the single-crystal elastic stiffness tensor of Si$_3$N$_4$ at 1375 °C via a self-consistent model. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1554478]

Si$_3$N$_4$ is one of the most widely used structural ceramics. High strength and good creep resistance make Si$_3$N$_4$ a desirable material for hostile environments, as in gas turbine engines. One promising variety is AS800 (Honeywell Ceramic Components, Torrance, CA), which has an acicular grain structure providing *in situ* reinforcement (ISR). ISR Si$_3$N$_4$ generally has better creep resistance and strength retention above 1000 °C, and higher fracture toughness than non-ISR grades. Previous high-temperature loading studies of ISR Si$_3$N$_4$ have focused mainly on creep experiments[1–3] using more traditional test methods.

Compared to a conventional mechanical test, neutron diffraction (ND) can provide additional information, e.g., lattice strains in multiple orientations, texture, and phase data. While ND has been frequently applied for high-temperature phase identification, there are comparatively few loading experiments at temperature and those reported are at temperatures less than 400 °C.[4,5]

This letter details the characterization of the high-temperature properties of AS800, including the coefficient of thermal expansion (CTE) tensor and the single-crystal stiffness tensor. In the present study, the ND data were collected under load at a very high temperature (1375 °C) as part of an in-depth investigation to quantify the high-temperature behavior of ISR Si$_3$N$_4$.

The experiments employed the SMARTS diffractometer[6] at the Lujan Neutron Science Center, Los Alamos National Laboratory. Commissioned in 2001, SMARTS is dedicated to engineering stress studies. It uses time-of-flight ND, allowing rapid collection of a sample's complete diffraction pattern in multiple orientations. The experiments were conducted using a pin-loaded dog-bone AS800 sample with a gage length of 51 mm and a gage section of 6.4×5.0 mm^2. The incident neutron beam encompassed the entire gage width at the midpoint of the sample. The sample was held horizontally at a 45° angle to the incident beam. Diffraction data were collected in two detectors (at $2\theta = \pm 90°$) measuring strains parallel and perpendicular to the load. First, a preload of 30 MPa was applied and diffraction data were recorded at room temperature, and 200, 500, 800, 1100, and 1375 °C, all under a vacuum of about 10^{-4} Torr. While heating, a high-temperature extensometer measured the macroscopic longitudinal strains. The heating rate was 20 °C/min, and at each temperature a constant extensometer reading was required (indicating no thermal transient effects) before diffraction patterns were collected. Data collection times were 15 min each, the minimum to obtain a high-quality diffraction pattern, in accord with similar methods.[4] At 1375 °C, the sample was subjected to increasing tensile stresses up to 175 MPa. Each stress was held for 45–60 min while multiple diffraction patterns were recorded in succession. The extensometer was not used during the mechanical testing at 1375 °C due to a data acquisition error. After about 7 h at 1375 °C, the sample was unloaded to 30 MPa, then cooled to room temperature. A final scan was performed to compare to the initial room-temperature scan.

Diffraction data were analyzed using the Rietveld method[7] via the GSAS program.[8] The only phase detected in the sample was the hexagonal β-Si$_3$N$_4$. Its space group is $p63/m$ and the literature values for its lattice parameters are $a = 7.608$ Å, and $c = 2.911$ Å.[9] The refined parameters were absorption, peak profile, and background coefficients; lattice and thermal parameters; histogram scale factor; and spherical harmonic (texture) coefficients. Average fitting residual values were about 6%. In addition to a full-pattern Rietveld analysis, some individual reflections were fit as Voigt functions for hkl-dependent calculations, with typical residuals about 8%.

The CTE (α) of β-Si$_3$N$_4$ was determined using several approaches. First, the a and c lattice parameters obtained from full-pattern Rietveld refinements were used. The data shown in Fig. 1 are longitudinal strains, each point being the average of the two to three scans from each temperature;

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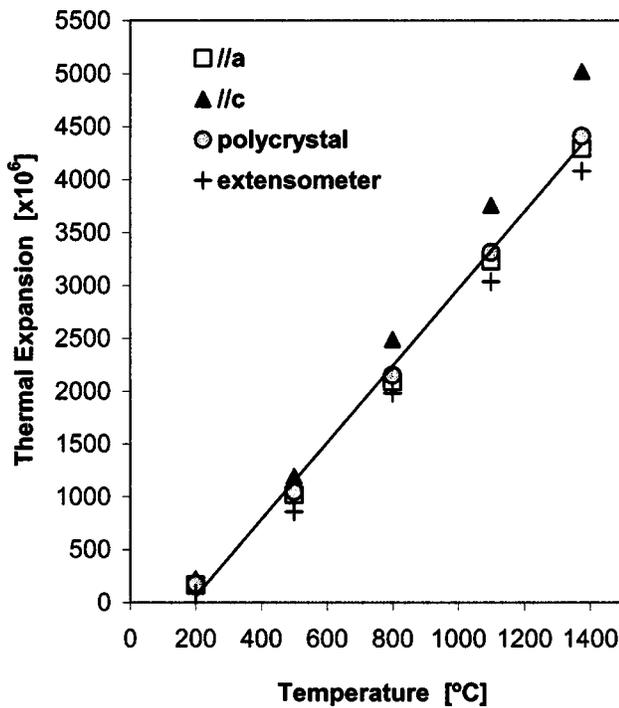
FIG. 1. Thermal expansion of AS800 β-Si$_3$N$_4$ based on longitudinally measured lattice parameters as compared to the macroscopic expansion given by the extensometer. The polycrystalline average data [obtained from $(2a+c)/3$] are fitted with a line to emphasize the near linearity of thermal expansion.

FIG. 2. Average lattice strains resulting from applied tensile stress at 1375 °C. Strains represent the polycrystalline average and were calculated with respect to the lattice constants obtained under a 30 MPa preload at the test temperature. Linear fits yield a Young's modulus of $E=339$ GPa and a Poisson's ratio of $\nu=0.32$.

strains are relative to the initial room-temperature scan. Note the disparity between the CTE values along the a and c lattice parameters due to anisotropy. The thermal expansion appears to be nearly linear over the entire temperature range. The $[(2a+c)/3]$ polycrystalline average in the longitudinal direction has a slope of $\alpha=3.64\times10^{-6}\,°\mathrm{C}^{-1}$, while the transverse data (not shown) yield $\alpha=3.57\times10^{-6}\,°\mathrm{C}^{-1}$. These results are summarized in Table I together with other CTE data.

The symmetric, second-order CTE tensor of β-Si$_3$N$_4$ has two independent components that are parallel to the crystallographic axes, typical of hexagonal structures.[10] For increased precision (by reducing error propagation by avoiding calculating lattice constants first), these components were obtained directly from the d spacings of nine reflections of β-Si$_3$N$_4$.[11] The data from these d spacings were input to the program ALPHA,[11] which uses a least-squares-fitting routine to refine the CTE tensor components based on the crystal structure and thermal expansion response of individual re-

flections. ALPHA yielded: $\alpha_{11}=\alpha_{22}=3.50\,(\pm0.03)\times10^{-6}\,°\mathrm{C}^{-1}$, and $\alpha_{33}=4.06\,(\pm0.04)\times10^{-6}\,°\mathrm{C}^{-1}$. Using $(2\alpha_{11}+\alpha_{33})/3$ gives the polycrystalline average as $\alpha=3.69\times10^{-6}\,°\mathrm{C}^{-1}$, which compares favorably with the CTE obtained from the lattice constants. Honeywell lists the polycrystalline CTE of AS800 as $3.90\times10^{-6}\,°\mathrm{C}^{-1}$ at temperatures up to 1000 °C. The only literature data[12] found on the CTE of β-Si$_3$N$_4$ were for other grades and ranged between 2.90 and 3.60 ($\times10^{-6}\,°\mathrm{C}^{-1}$).

The stress–strain response of the sample at 1375 °C is illustrated in Fig. 2. Lattice strains in directions parallel and perpendicular to the load were obtained from Rietveld refinements and are relative to the data under 30 MPa applied stress. Linear fits yield the Young's modulus, $E=339$ GPa, and the Poisson's ratio, $\nu=0.32$. At each stress level, several diffraction patterns were collected and their data averaged based on the fact that lattice constants did not change with time under constant stress. There was also no change in the texture of the sample after the loading/unloading at 1375 °C.

TABLE I. Comparison of various coefficients of thermal expansion (CTE) obtained in this study to the literature data (values in $10^{-6}\,°\mathrm{C}^{-1}$).

Method	Polycrystal average	$\alpha_{11}=\alpha_{22}$	α_{33}
Rietveld	3.64 (longitudinal)	3.54 (longitudinal)	4.23 (longitudinal)
	3.57 (transverse)	3.49 (transverse)	4.04 (transverse)
Single peak fitting and use of ALPHA[a]	3.69	3.50	4.06
Literature[b] and manufacturer	2.90–3.90	⋯	⋯

[a]Reference 11.
[b]Reference 12.

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TABLE II. Calculated high-temperature single-crystal stiffness tensor components for β-Si$_3$N$_4$ (AS800) compared with room-temperature results from others (values in GPa).

	C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}
Present work	456±31	311±40	144±11	149±40	158±40	238±21
Ref. 17	433	574	108	119	195	127

The ISR Si$_3$N$_4$ is known to experience grain rotation and grain boundary sliding during creep, resulting in an increased alignment of its acicular grains along the loading axis.[2,3] This phenomenon is then expected to induce an increase in peak breadth as well as hkl-dependent residual strains, especially for the $(00\cdot l)$ reflections, due to the elastic anisotropy of the material.[3] In the present study, the comparison of room-temperature diffraction data collected at the beginning and end of the investigation yielded no appreciable change in peak breadth and very low residual strains (the maximum was 190 $\mu\varepsilon$ for the $(00\cdot 2)$ reflection—here $\mu\varepsilon = 10^{-6}$ strain). Finally, the total time spent at high temperature and under high stress was only a few hours, much less than that needed to induce significant creep in this grade of Si$_3$N$_4$.[1] Although there was no additional information from the extensometer, the above observations indicate that the sample experienced very little creep during the test and its deformation was mostly elastic. Calculation of the 1375 °C single-crystal elastic constants of this material was justified by this fact.

The elastic stiffness tensor of AS800 was determined from the neutron data using an elastic–plastic self-consistent (EPSC) polycrystal deformation model.[13] EPSC models have ably predicted the diffraction elastic constants measured by neutron diffraction for several materials,[13–16] inputting only the material single-crystal stiffnesses. In the present case, a reversed calculation was performed using the measured diffraction elastic constants and a least-squares-fitting routine to obtain the best fit for the single-crystal stiffnesses. The starting value for the calculation was the isotropic stiffness tensor obtained from the measured macroscopic Young's modulus and Poisson's ratio (Fig. 2). The multiple patterns from each applied stress were summed into a single pattern, and nine single peak fits were used to refine the stiffness tensor (Table II). Comparing the 1375 °C values to those of Vogelgesang, Grimsditch, and Wallace[17] shows some agreement. As their test was both at room temperature *and* for a different grade of β-Si$_3$N$_4$, discrepancy should be expected. AS800 is known to have some elongated grains (along the c axis) oriented in the tensile direction; this could account for the marked difference in the C_{33} value. A true comparison would require a room-temperature test of this material. The reader should also note that the elastic constants calculated in the present study are sensitive to the assumptions of the self-consistent model. There is significant error in the values shown in Table II. This results from the erratic behavior of the peak positions as a function of stress, likely due to somewhat insufficient counting statistics. Using the data in Table II, the elastic constants for the polycrystal were calculated as $E = 313$ GPa and $\nu = 0.31$, close to the values found from the averaged diffraction data (Fig. 2). Honeywell reports $E = 293$ GPa and $\nu = 0.28$ at 1200 °C. The higher values obtained in this study could be a result of this test being in vacuum, which protected the sample from oxidation known to decrease mechanical properties.[12]

In conclusion, this investigation has demonstrated the capability of the SMARTS diffractometer to perform *in situ* loading tests at high temperature. The anisotropic CTE tensor of a β-Si$_3$N$_4$ polycrystal was computed using single peak fits of the diffraction data, yielding $\alpha_{11} = \alpha_{22} = 3.50 \times 10^{-6}$ °C^{-1} and $\alpha_{33} = 4.06 \times 10^{-6}$ °C^{-1}. The sample was loaded in tension at 1375 °C to 175 MPa. Neutron diffraction data indicated deformation was mostly elastic. The high-temperature stiffness tensor was calculated and its components were comparable to room-temperature values, with some softening in the c axis of β-Si$_3$N$_4$.

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