

Influence of Grain Size on the Tensile Creep Behavior of Ytterbium-Containing Silicon Nitride

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The effect of grain size on the tensile creep of silicon nitride was investigated on two materials, one containing 5% by volume Yb₂O₃, the other containing 5% by volume Yb₂O₃ and 0.5% by mass Al₂O₃. Annealing of the Al₂O₃-free silicon nitride for a longer period during processing increased the grain size by a factor of 2. This increase did not affect the tensile creep rate; the grain size exponent of the creep rate differed little from zero, $p = -0.20 \pm 1.37$ (95% confidence level). This finding supports the more recent theories of tensile creep for which p = 0 or -1 and rejects the more classical theory of solution-precipitation. In compression, a more limited data set showed $p = -1.89 \pm 1.72$ (95% confidence level). In contrast to the Al₂O₃-free material, a longer term anneal of the Al₂O₃-containing material during processing did not increase its grain size. Despite this, the longer-annealed Al₂O₃containing material crept 10 to 100 times slower than the short-annealed material. The enhancement of creep resistance may be a consequence of SiAlON formation during the additional annealing, which reduces the Al content in the amorphous phase and increases its viscosity. Such changes in chemical composition of the grain boundaries are more effective in controlling tensile creep rate than is the grain size.

I. Introduction

The effect of grain size on the creep of silicon nitride has not been investigated extensively because of the difficulty of growing large grain size materials in such a way that both chemical composition and grain size distribution are unchanged. When large- and small-grain-size materials are self-similar, however, characterizing the grain size dependence of the creep rate can help distinguish between different creep mechanisms. Despite the difficulty in producing self-similar microstructures, some experiments to evaluate the grain size dependence of the creep rate of silicon nitride have been conducted, most of them in flexure^{1,2} and compression.³⁻⁵ However, because silicon nitride creeps by different mechanisms in compression and tension,⁶ these results do not apply to tensile creep. This paper considers results from studies of both tensile and compressive creep. Creep data on ceramics and metals are often fitted by a power-law equation:^{7,8}

$$\dot{\varepsilon} = \dot{\varepsilon}_1 \cdot d^p \cdot \sigma^n \cdot \exp(-Q_1 / RT) \tag{1}$$

where *d* is the grain size, σ is the applied stress, and *T* is the temperature. The constants $\dot{\epsilon}_1$, *p*, *n*, and Q_1 are empirical, determined by fitting Eq. (1) to the experimental data. Their values are often used to gain insight into the creep mechanism.⁸ For diffusional creep mechanisms, p = -1, -2, or -3 and n = 1 or 2, depending on the mechanism.⁹⁻¹⁶ The rate-limiting diffusing species determines the activation energy, Q_1 . Similarly, when creep is by a dislocation mechanism,¹⁷ p = 0 and 1 < n < 5, depending on the mechanism. The activation energy relates to the rate-limiting step for dislocation motion. For silicon nitride, dislocations play little or no role in creep.^{18–25} Stress exponents for tensile creep of silicon nitride are usually much larger than 1, casting doubt on the applicability of diffusional creep mechanisms to tensile creep.

Three more recent models for tensile creep of materials with second phases at their grain boundaries rationalize the large effective stress exponent of silicon nitride. Wakai¹⁶ developed a model in which the velocity of steps across the crystal surface of the wetted grains determines the creep rate. The macroscopic creep behavior takes on different forms depending on the rate-controlling step. When diffusion in the thin film bounding the grains controls the step motion, creep follows classic solution-precipitation models:^{12–15} p = -3 and n = 1. For most of the other scenarios, the creep rate is inversely proportional to the grain size, p = -1, and the stress exponent has values, 1 < n < 2. These stress exponents are lower than those commonly observed for the tensile creep of silicon nitride. However, when the two-dimensional nucleation of surface steps controls creep, the rate takes the form of Eq. (1) with p = -1 and 1 < n < 9.

Another mechanism of tensile creep of silicon nitride assumes that creep occurs when cavities form in the silicate phase, which is located at the silicon nitride multigrain junctions.²⁶ The silicate redistributes through the triple-junction network to produce strain. The mechanism predicts that the cavity volume fraction increases linearly with strain. The tensile creep rate is independent of the grain size (p = 0) and depends exponentially on stress:²⁶

$$\dot{\varepsilon} = \dot{\varepsilon}_2 \left(\frac{\Phi^3}{(1-\Phi)^2} \right) \sigma \, \exp(\alpha \sigma) \exp(-Q_2/RT) \tag{2}$$

where Φ is the volume fraction of silicate phase and α is an empirical constant. The apparent activation energy, Q_2 , is for the silicate redistribution process. At low stress, the tensile creep rate increases linearly with applied stress, while at high stress, it increases exponentially. If the creep data over a limited stress range are expressed as a power-law function, the stress exponent *n* increases from 1 to greater than 7 with increasing stress.

Gasdaska²⁷ developed a creep mechanism that also predicts a large stress dependence of the creep rate. Creep occurs by grain boundary sliding accommodated by solution-precipitation of silicon nitride controlled by the viscosity of glass at the silicon nitride

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two-grain interfaces. At high sliding rates, the viscosity depends on the hyperbolic sine of the applied stress. The creep rate is given by the following equation, which was derived by Luecke and Wiederhorn:²⁶

$$\dot{\epsilon} = \dot{\epsilon}_3 \left(\frac{\delta}{l}\right) \exp(-Q_3/RT) \sinh(\sigma \Omega/RT)$$
 (3)

where δ is the thickness of the glass at the two grain interfaces, l is the distance between sliding interfaces, and Ω is the activation volume for deformation of glass at the interface. For $\sigma\Omega \gg RT$, sinh ($\sigma\Omega/RT$) $\approx \exp(\sigma\Omega/RT)$, so Eqs. (2) and (3) predict a similar dependence of creep rate on stress. The creep rate depends on grain size through the parameter l. If sliding occurs at every grain boundary d = l, the creep rate is inversely proportional to d. If sliding occurs by the motion of clusters of grains and the cluster size is proportional to d, the creep rate is also inversely proportional to d. Therefore, p = -1.

Only Haig *et al.* have measured the grain size dependence of the tensile creep of silicon nitride.^{28,29} In one study,²⁸ they characterized the creep behavior of two billets of gas pressure sintered silicon nitride whose grain size differed by "an order of magnitude." Although the creep rate of the larger grain size material was clearly less than the smaller, the difference in grain size was not quantified sufficiently to accurately estimate *p*. In a second study,²⁹ they made specimens from a single billet of silicon nitride, half of which was annealed in nitrogen to increase the average grain width from 0.5 to 0.8 μ m. They did not report the temperature and other conditions of the annealing treatment. The difference in the creep rates between the two grain sizes was not statistically significant, implying that *p* = 0.

This paper presents the results of a study on the grain size dependence of the tensile creep rate of silicon nitride. Special billets were made for this purpose, with nearly identical composition, differing only in the silicon nitride grain size. Within 95% confidence limits, the grain-size dependence of the creep rate of this material lies in the range $p = -0.20 \pm 1.37$. This finding opposes classical diffusional creep mechanisms and supports the more recent theories for which p = 0 or -1.

II. Experimental Procedure

(1) Materials Processing

The materials investigated were prepared by conventional powder processing techniques. Complete densification was obtained by using 13.14% mass fraction Yb₂O₃ (Ventron, Germany)[¶] as sintering additive. This corresponds to a Yb₂O₃ content of 5% volume fraction, which is used in subsequent sections of the paper to characterize the silicon nitride. The silicon nitride powder (E10, UBE Industries, Japan) had an oxygen content of 1.1% mass fraction, equivalent to a SiO₂ mass fraction of 2.06%. After 1.6% mass fraction SiO₂ (Aerosil, Degussa, Germany) was added, the overall composition lay on the tie line between Si₃N₄ and Yb₂Si₂O₇, so a maximum degree of crystallization of the grain boundary phase could be expected. To investigate the influence of the grain boundary chemistry, a second set of samples was prepared which contained an additional 0.5% mass fraction Al₂O₃ (AKP 53, Sumitomo, Japan). Samples containing only Yb₂O₃ and SiO₂ as sintering additives are denoted as SN5Yb, whereas the Al₂O₃-containing samples are denoted SN5YbAl.

Starting powders were homogenized by attrition milling for 4 h in isopropyl alcohol using silicon nitride milling balls. After the slurries were dried in a rotation evaporator and sieved, the powders were consolidated by cold isostatic pressing at 630 MPa. Complete densification (>99% of theoretical density) required a two-step

sintering program in a gas-pressure sintering furnace with graphite heating elements (KCE, Germany) and a BN crucible. The first step was a constant heating rate of 20° C/min followed by an isothermal sintering time of 15 min at 1780° C under a nitrogen pressure of 0.1 MPa. The second step was a 20 min soak at 1880° C under a nitrogen pressure of 10 MPa. To achieve a larger grain size, the soak time for both compositions (SN5Yb and SN5YbA1) was increased to 180 min. Specimens from the shorter and longer soak times are distinguished by adding the letter S or L, respectively, to the composition indicator. All specimens were heat-treated in air after machining to crystallize the grain boundary phase and to avoid any microstructural change not related to creep. The Al₂O₃-free specimens, SN5Yb, were heat-treated for 250 h at 1350°C and the SN5YbAl samples for 325 h at 1250°C.

(2) Microstructural Characterization

As-sintered and tested specimens were characterized by X-ray diffraction analysis in the range $18^{\circ} < 2\Theta < 54^{\circ}$ (Siemens D 500, Germany, CuK α radiation). The surface oxide layer was removed by grinding about 0.4 mm from the grip of the specimen. Second phase peaks as small as 2% of the largest Si₃N₄ peak could be detected in the X-ray scans. In all, 3 SN5Yb-S, 13 SN5Yb-L, 3 SN5YbAl-S, and 3 SN5YbAl-L specimens were analyzed. For grain size analysis, ground and polished (Masterpolish II, Buehler, Ltd., Lake Bluff, IL) specimens were plasma etched for about 1 min in a mixture of 96% CF₄ and 4% O₂ by volume. The total gas pressure was about 3 kPa and the power was 100 W. Etched surfaces were examined by scanning electron microscopy (SEM) at 10 kV using secondary electrons.

Because of the differences in composition, the contrast between the Si_3N_4 grains (gray) and the ytterbium-containing secondary phase (white) was adequate for the microstructure analysis. SEM images were manually digitized, and then analyzed statistically using a commercial software program (Materials-Pro Analyzer, Media Cybernetics, Silver Spring, MD). Since silicon nitride grains are elongated, planar sections can cut them at any angle. A grain cut normal to its basal plane appears to be equiaxed, whereas one cut parallel to its axis appears to be needlelike. Because of these geometric effects, the silicon nitride grains were divided into two types for analysis. Grains with aspect ratios less than 1.8 were assumed to be end-on, the diameters representing the diameters of the grains. Grains with aspect ratios greater than 2.2 were assumed to be lying on their sides and were analyzed for both aspect ratio and minimum diameter in a second group. About 400 equiaxed grains and 70 elongated grains were measured in each sample.

In addition to characterizing the grain size and grain size distributions, the volume fraction of the intergranular phase was determined by the point count method. From a sample of each material, 10 micrographs were made and a 10 by 10 Cartesian grid was laid over each micrograph to yield 100 points for the count method. The number of points falling on the intergranular phase gave the volume fraction of this phase present in each specimen. The volume fraction determined in this manner was compared with a theoretical volume fraction calculated from the volume sums of each of the oxides present. The calculation was based on the initial mass input for the aluminum containing materials: $Yb_2O_3 =$ 13.14%, $SiO_2 = 3.66\%$, $Al_2O_3 = 0.5\%$, and $Si_3N_4 = 82.7\%$ by mass, from which the volume fraction second phase is 0.118. This number will be on the low side because the volumes of the Yb₂O₃ and the Al₂O₃ are estimated from the crystal density. When dissolved in silicate glasses they will form much more open structures.

X-ray fluorescence spectrometry established an elemental analysis of the four materials. All measurements were made under vacuum using 3 kW X-ray power and a 15 mm diameter beam on a wavelength dispersive X-ray fluorescence spectrometer (Model PW2404, Philips Electronic Instruments). Masking of the fluorescent X-rays assured that only those X-rays coming from the specimen itself were analyzed. As X-ray fluorescence only gives cation concentration, compound forms are assumed: Si was assumed to be Si₃N₄; the remaining elements were set as oxides and summed to 100%.

[¶]Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.



Fig. 1. Three of the materials—SN5Yb-S, SN5YbAl-S, SN5YbAl-L—have approximately the same grain size. The remaining material, SN5Yb-L, has a grain size about twice that of the others.

A qualitative chemical analysis of the grains was conducted using electron energy loss spectroscopy (EELS; Gatan Image Filter) and energy dispersive X-ray spectroscopy (EDS; NORAN Voyager System). We were particularly interested in the distribution of aluminum within the microstructure as a function of the annealing time. Energy dispersive X-ray spectroscopy could not be used to analyze the aluminum concentration at the grain boundaries because of interference between the Yb(m) peak and the Al(k) peak. Since ytterbium is supposedly insoluble in silicon nitride, this interference should not hinder using the EDS for aluminum analysis within the grains.

(3) Mechanical Tests

Tensile creep tests used a pin-loaded, dogbone (SR51) specimen with a 12 mm gauge length and a 2 mm \times 2.5 mm cross section.³⁰ The force was applied through silicon carbide pull-rods that were attached to specimens via α -silicon carbide pins. The load varied less than 1% during the test. The temperature was constant to better than 3°C. Silicon carbide flags marked off the gauge section for a laser detection system (ZYGO, Model 1102, Middlefield, CT, or Lasermike Optical Micrometer, Dayton, OH).

For the SN5Yb material, creep tests to failure were conducted at $1300^{\circ}C < T < 1370^{\circ}C$ over a stress range 75 MPa $< \sigma < 125$ MPa. For the SN5YbAl material, creep tests were conducted over the temperature range $1100^{\circ}C < T < 1250^{\circ}C$ and a stress range of 75 MPa $< \sigma < 100$ MPa. All but two of the SN5YbAl specimens were subjected to a constant stress. The displacement was measured as a function of time until the specimen failed. Reported creep rates are the minimum rates estimated from these data.

 Table I.
 Volume Fraction of Secondary Phase Determined by Point Count Method

	Theoretical	SN5Yb-S	SN5Yb-L	SN5YbAl-S	SN5YbAl-L
Volume fraction	11.8	15.8	12.8	14.9	16.5
Standard deviation		2.6	2.1	2.0	2.3
Number		10	10	10	10



Fig. 2. Histograms of the grain diameters, d and d_{\min} . The insets show the means $(\bar{d} \text{ and } \bar{d}_{\min})$ and standard deviations (in parentheses) of each distribution of grain diameters, as well as the number, N, of measurements.



Fig. 3. Histograms of the aspect ratio (AR) of the elongated grains for all materials tested. The numbers in the figure are the mean aspect ratio, \overline{AR} , the standard deviation of AR (in parentheses), and the number of measurements, *N*.

Stepped temperature tests were made on two SN5YbAl-L specimens to obtain multiple creep rate data. No failure data are reported for these specimens.

Compression creep tests to $\sim 1.5\%$ strain were conducted in a screw-driven universal testing machine at constant load using 2 mm \times 2.5 mm \times 5 mm parallelepipeds machined from the heads of tested tensile specimens. Strain was measured from the displacement of two SiC fibers attached to the loading platens at the ends of the specimen, using a long-working-distance microscope.³¹

III. Results

(1) Microstructure

Figure 1 shows scanning electron micrographs of the four materials. The grain size of the SN5Yb-L is roughly twice as large as the SN5Yb-S. In contrast to the SN5Yb materials, the



Fig. 4. X-ray diffraction analysis of SN5Yb-S, Sn5Yb-L, SN5YbAl-L, and SN5YbAl-S. The specimen numbers are included to the left of each analysis.

 Table II.
 X-ray Fluorescence Analysis of Silicon Nitride Specimens (mass%)[†]

							SRM 1834	
	SN5Yb-S	SN5Yb-L	SN5YbAl-S	SN5YbAl-L	Element	Found	Certified	
С	ţ	İ	İ	İ				
Si ₃ N ₄	83.4 16.4	83.4 16.2	81.5 17.6	81.5 17.5	Si	20.3	20.19	
Al_2O_3	0.03	0.05	0.46	0.46	Al	20.7	20.71	
Na_2O	0.05	0.17	0.19	0.04	Na	0.16	0.14 ^s	
MgO	0.09	0.05	0.04	0.14	Mg	0.09	0.088	
Cl SO ₂	Detected	0.12 0.07	0.13 0.05	0.15 0.04				
P_2O_5				0.01	Р	0.18	0.152	
K_2O Fe ₂ O ₂	0.02	Detected	0.03 0.02	0.02 0.07	K Fe	0.36 0.32	0.42 0.32	
Cr ² CuO		Detected		Detected 0.02	Cr	0.02	0.02 [§]	
					Ti	1.08	1.11	
					Ca Sr	0.09	0.095	
					Zr	0.06	0.047 [§]	
					Ва	0.04	0.062	

[†]Compound forms are assumed, as X-ray fluorescence does not give chemical information. [‡]Detected on the surface of all four samples. [§]Value reported but not certified on certificate of analysis.

Table III. Tensile Creep and Phase Data

Specimen no.	Stress (MPa)	<i>T</i> (°C)	Creep rate (s ⁻¹)	Failure time (h)	Failure strain	Second phases [†]	$I_{215}^{\max}/I_{227}^{\max\ddagger}$
			SN5	Yb-S			
14	100	1300	3.96×10^{-9}	140	0.00413	n.d.	
26	110	1300	8.57×10^{-9}	56.8	0.00285	n.d.	
24	125	1300	3.00×10^{-8}	7.8	0.00168	n.d.	
12	75	1350	8.02×10^{-9}	242.2	0.00998	n.d.	
13	85	1350	1.63×10^{-8}	96.6	0.00877	227	n/a
11	100	1350	$5.81 imes 10^{-8}$	8.5	0.00298	n.d.	
21	75	1370	2.59×10^{-8}	42.5	0.00622	n.d.	
22	85	1370	$7.16 imes 10^{-8}$	11.2	0.00550	227	n/a
15	100	1370	2.05×10^{-7}	2.18	0.00255	n.d.	
			SN5	řb-L			
65	100	1300	1.30×10^{-9}	1039	0.00797	227, 215	0.11
74	125	1300	3.40×10^{-9}	88.5	0.00283	227, 215	0.11
66	75	1350	1.80×10^{-8}	36.8	0.00468	227, 215	0.02
73	75	1350	2.49×10^{-9}	909	0.01176	227, 215	0.15
64	85	1350	3.15×10^{-8}	39.5	0.00636	227, 215	0.23
62	75	1370	9.03×10^{-8}	6.5	ş	227, 215	0.04
61	85	1370	4.32×10^{-7}	0.55	0.0015	227, 215	0.04
76	100	1370	1.29×10^{-7}	4.8	0.00415	227, 215	0.32
			SN5Y	bAl-S			
Untested			_			227	n/a
24	100	1100	1.58×10^{-9}	307	0.00287	n.d.	
23	75	1200	4.42×10^{-8}	15.8	0.00423	227	n/a
22	85	1200	1.12×10^{-7}	5.5	0.0039	n.d.	
15	100	1200	1.17×10^{-7}	4.1	0.00368	227	n/a
14	85	1250	6.95×10^{-7}	0.79	0.00345	n.d.	
16	85	1250	7.98×10^{-7}	0.90	0.00342	n.d.	
11	100	1250	1.20×10^{-6}	0.57	0.00307	n.d.	
21	75	1300	1.14×10^{-6}	1.3	0.00785	n.d.	
			SN5Y	bAl-L			
Untested						227, 215	0.66
4	75	1250	1.80×10^{-9}		¶	n.d.	
1	85	1250	6.80×10^{-9}		¶	227, 215	0.27
4	85	1250	3.60×10^{-9}		ſ	n.d.	
2	100	1250	1.57×10^{-8}	120.1	0.0085	n.d.	
6	75	1300	$6.35 imes 10^{-8}$	31.8	0.0087	n.d.	
1	85	1300	1.16×10^{-7}		ſ		
3	85	1300	1.10×10^{-7}	28.1	0.012	n.d.	
5	85	1350	2.70×10^{-6}	0.65	0.0067	227, 215	0.22

 † n.d. = not determined; 227 = Yb₂Si₂O₇; 215 = Yb₂SiO₅. $^{*}I_{215}^{max}/I_{227}^{max}$ = ratio of the height of the largest peak from Yb₂SiO₅ to that from Yb₂Si₂O₇. n/a = not applicable. 8 Unreliable strain measurement. 1 Stepped stress tests where no failure strains or failure times were measured.

SN5YbAl-S and the SN5YbAl-L have about the same grain size. The long soak time for the Al_2O_3 -containing material did not increase its grain size.

The volume fraction intergranular phase for each of the four materials is presented in Table I along with the standard deviation for each measurement. Three of the materials-SN5Yb-S, SN5YbAl-S, and SN5YbAl-L-have statistically indistinguishable volume fractions of intergranular phase, $\sim 15\% - 16\%$. These three are also the small grain size materials. The volume fraction of the SN5Yb-L, 12.8%, is statistically smaller than the other two. All four of the materials have volume fractions intergranular phases that are larger than the theoretically expected value, 11.8%. Part of this difference is a consequence of the plasma etching procedure which removes the silicon nitride in preference to the intergranular phase and by so doing increases the apparent volume fraction of intergranular phase. Between this and the low theoretical estimate of the volume fraction intergranular phase, a difference of a few percent volume fraction is not surprising. Examination of the intergranular phase by transmission electron microscopy indicates that except for a 1 nm boundary of amorphous phase between the silicon nitride and the intergranular phase, and between the grains of the intergranular crystals, the intergranular phase was all crystalline.

The histograms of grain size and aspect ratio (Fig. 2) bear out the qualitative impressions of Fig. 1. They show that the distribution of diameters, d, of the equiaxed grains and the minimum diameters, d_{\min} , of the elongated grains for SN5Yb-S, SN5YbAl-S, and SN5YbAl-L are the same, but SN5Yb-L is shifted to larger diameters. The aspect ratios range from about 3 to about 10 for all four materials.

X-ray diffraction analysis, Fig. 4, revealed that the silicon nitride was completely β -phase (PDF 33-1160).³² Monoclinic Yb₂Si₂O₇ (PDF 74-2071) was the majority second phase in all specimens characterized (3 SN5Yb-S, 13 SN5Yb-L, 3 SN5YbAl-S, and 3 SN5YbAl-L). Generally, both the SN5Yb-L and SN5YbAl-L specimens also contained monoclinic Yb₂SiO₅ (PDF 40-0386) in varying amounts. Measured by peak height ratio, the 70 series specimens of SN5Yb-L, machined from one billet, contained roughly twice as much Yb₂SiO₅ as the 60 series, which was machined from a second billet. Table III lists the phase compositions and the ratio of the largest Yb₂SiO₅ peak to that of the largest from Yb₂Si₂O₇ for all of the creep-tested specimens. No specimen contained any unidentifiable peaks; however, all creeptested specimens did show a single peak that could be indexed as crystalline SiO₂ (cristobalite, PDF 04-0379). This peak was absent in the specimens that had not been exposed to high temperature. A transmission electron microscopy study³³ on a similar material also indicated the primary phase at the multigrain junctions to be Yb₂Si₂O₇.

X-ray fluorescence analysis (Table II) demonstrated that there were no gross chemical differences in composition between SN5Yb-S and SN5Yb-L, or between the SN5YbAl-S and SN5YbAl-L. The Al_2O_3 -free (SN5Yb) material does have a much lower Al_2O_3 content than the Al_2O_3 -containing (SN5YbAl) material. The column detailing the results of a contemporaneous analysis of a synthetic fused ore (NIST SRM 1834)³⁴ shows some typical detectability limits and accuracies.

The X-ray fluorescence analyses indicated that aluminum was present in both the long- and short-term anneal specimens, but did not give its location within the microstructure. We attempted to locate the aluminum by using both EDS and EELS, but without success. Although results from both techniques were obtained from various grains and from various grain boundaries, the specific presence of aluminum could not be established. One must conclude that the level of aluminum present in the material was below the level of detectability for both techniques. This conclusion is supported by EDS results from a silicon nitride processed with 2% by mass aluminum oxide and 6% by mass yttria. For this material, EDS results from the interior of silicon nitride grains showed no detectable yttrium, as expected, and 0.9% by mass aluminum. On this basis the maximum amount of aluminum expected in our



Fig. 5. Typical creep curves in SN5Yb. Creep curves from SN5Yb-S (a) show the systematic displacement of the curves with applied stress. Curves from (b) demonstrate the scatter in SN5Yb-L data.

current samples would be less than 0.25% by mass, which is below the detection limit on our instrument.

(2) Creep Behavior

Table III summarizes the tensile creep data for the four materials. In general, the creep curves exhibited only primary and secondary creep; distinct tertiary creep occurred in only 2 of the 31 specimens. Figure 5(a) shows several example creep curves for SN5Yb-S. Figure 5(b) demonstrates that the creep behavior of SN5Yb-L was less reproducible than the other three compositions. More than one order of magnitude separates the failure times and creep rates of the two SN5Yb-L specimens tested under identical conditions. Time-to-failure and strain-to-failure decreased with increasing stress at a given temperature for SN5YbAl-L, SN5YbAl-S, and SN5Yb-S. The low reproducibility of the data made it impossible to discern such trends for SN5Yb-L. We assume that the variability is intrinsic to SN5Yb-L, because previous studies on different materials demonstrated that the creep technique could yield creep data with a pooled standard deviation in the creep rate of less than 10%.³⁰ Minimum tensile creep rates as a function of temperature and stress are plotted in Figs. 6 and 7, respectively, for the SN5Yb and the SN5YbAl materials. Figure 8 and Table IV summarize the compression creep data of SN5Yb. Although the data are sparse, SN5Yb-S creeps about 7 times faster than SN5Yb-L at 1350°C.

IV. Discussion

(1) Data Analysis

The goal of this paper is to examine the effect of grain size on tensile creep of silicon nitride. To do this we will examine the



Fig. 6. Minimum creep rates as a function of temperature and stress for Al₂O₃-free specimens: SN5Yb-S and SN5Yb-L.

parameters of the various creep models from the fits of those models to the creep data. For the case of an unknown grain size dependence or a single grain size, Eq. (1) can be rewritten as

$$\dot{\boldsymbol{\varepsilon}} = \dot{\boldsymbol{\varepsilon}}_4 \cdot \boldsymbol{\sigma}^n \exp(-Q_1 / RT) \tag{4}$$

Similarly, if the volume fraction of second phase, Φ , is unknown or not of interest, Eq. (2) can be rewritten as

$$\dot{\varepsilon} = \dot{\varepsilon}_5 \sigma \exp(\alpha \sigma) \exp(-Q_2/RT)$$
(5)

Table V summarizes the coefficients of these fits for both tensile and compressive creep. The fits of Eq. (4) are overlaid on the tensile creep data in Figs. 6 and 7. All four materials have tensile stress exponents that are much larger than 1. The activation energies for SN5YbAl-S and SN5YbAl-L are statistically significantly different. The low reproducibility of SN5Yb-L is reflected by its larger residual standard deviation of the fit, which is 2 to 5 times larger than for the other materials. For the tension data, this probably represents specimen-to-specimen variability. For the compression data, which was generated with only two specimens, the residual standard deviation of the fit probably represents limitations of the compressive strain measurement technique.

Figure 9 compares the tensile creep behavior of all four materials as well as the compression creep behavior of SN5Yb-L, where creep rate is plotted as a function of 1/RT for an applied stress of 100 MPa, evaluated using the fits of Eq. (5) detailed in Table V. The effects of Al₂O₃ and annealing on the creep rate are clearly seen. Adding just 0.5% by mass Al₂O₃ to the silicon nitride increased the creep rate by over 4 orders of magnitude. Annealing of the Al₂O₃-containing material, even though it did not change the grain size, reduced the creep rate by a factor of from 20 to 80. In contrast, although annealing the Al₂O₃-free (SN5Yb) silicon nitride did double its grain size, it did not change its creep resistance.



Fig. 7. Minimum creep rates as a function of temperature and stress for Al₂O₃-containing specimens: SN5YbAl-S and SN5YbAl-L.

(2) Al_2O_3 -Free Material (SN5Yb)

Although the grain sizes (d and d_{\min}) of SN5Yb-L are twice as large as that of SN5Yb-S, the tensile creep rates summarized in Fig. 9 overlap substantially. To answer the question "Does creep rate depend on grain size?," we must turn to statistical tests of the fits to the data. We will use a two-step analysis. In the first step, we will evaluate whether or not a single equation of the form of either Eq. (4) or Eq. (5) can describe the two data sets. If the data can be fitted by a single equation, then we can assume that the two sets of data have a common set of coefficients (\dot{e}_4 , n, and Q_1 , or \dot{e}_5 , α , and Q_2). In the second step, we shall explicitly evaluate the grain size exponent, p, of Eq. (1) using the full data set for both grain sizes, assuming Q and n are the same for both grain sizes.

(A) Step 1: The statistical method used is the analysis of variance method discussed in some detail in Ref. 35, and in many textbooks on linear regression. Two equations, or models, are used to describe the data. One, the so-called reduced model, has a subset of the parameters of the other, the so-called complete model. An F-test is then used to decide whether the reduction in error between the linear regressions of the complete and reduced model is significant. If it is not, then the parameters omitted by the reduced model do not contribute to the fit. For this analysis, the two models tested were (1) a reduced model having the form of either Eq. (4) or Eq. (5) with three parameters, e.g., $\dot{\varepsilon}_4$, n, Q_1 and (2) a complete model having the form of Eq. (4) or Eq. (5) with a total of six parameters, e.g., $\dot{\epsilon}_4^{L}$, $\dot{\epsilon}_4^{S}$, n_L , n_S , Q_1^{L} , Q_1^{S} , where the L and S refer to the large and small grain size. If the reduced (three-parameter) model fits the data as well as the complete (six-parameter) model, the data from both materials form a common set and grain size has no effect on the creep rate. For the power-law creep equation (Eq. (4)), F = 3.02, which is significant at the 7% level. This level is just outside of the traditional 5% level for rejecting the hypothesis that some of the omitted parameters were not zero. For the cavitation creep model (Eq. (5)), which predicts that the creep rate



Fig. 8. Compression creep rate data for SN5Yb-L and SN5Yb-S. The lines are the least-squares fit of Eq. (1) to the creep data. Constants of the fit are summarized in Table V. The solid lines represent SN5Yb-L data; the dashed line represents SN5Yb-S data.

is independent of grain size, F = 3.06, which is also significant at the 7% level. We can conclude that the two data sets are statistically indistinguishable and that grain size has no effect on creep rate.

(B) Step 2: The traditional method for representing the dependence of creep rate on grain size uses the grain size exponent, p, of Eq. (1). To use the full data set of 17 points, we must assume that the activation energy, Q_1 , and the stress exponent, n, of the two data sets are identical. We are justified in this assumption by the results of the analysis of variance conducted in Step 1. Table V shows the results of a multilinear regression of the natural logarithm of Eq. (1) on the SN5Yb data. The grain size exponent, $p = -0.20 \pm 0.64$, is statistically indistinguishable from zero.[¶]

For the compression creep data, an analysis similar to Method 1 shows that a reduced model with four parameters ($\dot{\epsilon}_{4}^{L}$, $\dot{\epsilon}_{4}^{S}$, n, Q_{1}) provides a fit of equal quality to one that employs six parameters ($\dot{\epsilon}_{4}^{L}$, $\dot{\epsilon}_{4}^{S}$, n_{L} , n_{S} , Q_{1}^{L} , Q_{1}^{S}). For this comparison, F = 1.1, which is significant at the 40% level. Therefore, we have good confidence, that in compression SN5Yb-L and SN5Yb-S share a common stress dependence, n, and activation energy, Q. A multilinear regression of the full compression data set yields (see Table VI) the grain size exponent, $p = -1.89 \pm 0.80$, and a stress exponent, $n = 0.89 \pm 0.38$. Figure 8 overlays the data with the fit of Eq. (1).

The tensile creep data of this study are incompatible with standard solution-precipitation models for creep,¹¹⁻¹⁵ because they predict 1 < n < 2. Both Wakai's model of step motion¹⁶ and Gasdaska's model of grain boundary sliding^{27,26} predict high stress exponents for creep. They also predict p = -1, which lies within the 95% uncertainty range of the calculated value of p. Luecke and Wiederhorn's model of cavitation creep²⁶ predicts that the creep rate increases exponentially with stress, in accord with the data, as well as p = 0. This value also lies within the 95% uncertainty range of the measured stress exponent.

(3) Al₂O₃-Containing Material (SN5YbAl)

Two aspects of the results on the Al_2O_3 -containing silicon nitrides were surprising. The longer annealing time, 180 versus 20 min at 1880°C, did not increase the grain size of the SN5YbAl-L compared with the SN5YbAl-S. Also, even though the grain-size distributions, aspect ratios, and chemical compositions were the same for the two materials, the SN5YbAl-L crept much more slowly than the SN5YbAl-S. In this section we will first discuss why the silicon nitride grains did not grow. Then we will review the effect of aluminum oxide on creep and present a hypothesis as to why SN5YbAl-L was more creep resistant.

(A) Grain Growth in Al_2O_3 -Containing Silicon Nitride: The lack of grain growth in the SN5YbAl-L is by far the more difficult result to explain. Although one might argue that the Al_2O_3 somehow poisons the β -Si₃N₄ growth, there is no evidence in the literature that similarly sized silicon nitride reaches a limiting grain size with continued annealing. Mitomo *et al.*,³⁶ Yoon *et al.*,⁵ and Lai and Tien³⁷ measured a $t^{1/3}$ growth law for the widths of the β -Si₃N₄ grains in a Y₂O₃ + Al₂O₃ gas pressure sintered silicon nitride. Using this growth law, the 180 min anneal should have increased the grain width by 100%, which would have been easily measurable, as it was for the SN5Yb. We discount the possibility of gross errors in processing temperature or time, and

Table IV. Compression Creep Data for SN5Yb

Specimen noRun order	Stress (MPa)	Temp (°C)	Creep rate (s ⁻¹)
	SN5	Yb-S	
1–4	300	1370	1.80×10^{-8}
1-1	100	1350	8.70×10^{-9}
1-2	180	1350	1.24×10^{-8}
1–3	300	1350	1.92×10^{-8}
	SN5	Yb-L	
2-2	300	1350	2.76×10^{-9}
3–3	100	1374	4.81×10^{-9}
3–2	100	1395	1.62×10^{-8}
3–5	100	1400	4.30×10^{-9}
2-1	300	1400	3.33×10^{-8}
3-1	300	1400	6.37×10^{-8}
3–4	100	1430	2.60×10^{-8}

⁺⁺Unless otherwise noted, the uncertainty presented is the standard uncertainty. The 95% confidence limits are obtained by multiplying the standard uncertainty by the appropriate value of *t* from a Student *t* table. For 14 degrees of freedom used here t = 2.1245.

Material	$\ln (\dot{\epsilon}_5)$	Q_2 (kJ/mol)	α (MPa ⁻¹)	Residual standard deviation of the fit
		Tension equation (5)		
SN5Yb-S	62.57 (3.13)	1227 (46)	0.0728 (0.0040)	0.13
SN5Yb-L	105.89 (27.90)	1781 (400)	0.0485 (0.0311)	0.98
SN5YbAl-S	36.13 (3.89)	737 (55)	0.0377 (0.0170)	0.42
SN5YbAl-L	73.61 (3.72)	1306 (486)	0.0692 (0.0115)	0.23
Material	$\ln (\dot{\epsilon}_4)$	Q_1 (kJ/mol)	п	Residual standard deviation of the fit
		Tension equation (4)		
SN5Yb-S	36.67 (3.44)	1200 (63)	7.78 (0.53)	0.18
SN5Yb-L	88.80 (22.22)	1776 (386)	5.70 (2.88)	1.03
SN5YbAl-S	24.24 (5.65)	739 (52)	4.43 (1.43)	0.40
SN5YbAl-L	52.68 (5.40)	1300 (49)	6.93 (1.00)	0.24
		Compression equation (4)		
SN5Yb-L	46.55 (19.26)	981 (277)	1.21 (0.51)	0.69

Table V. Coefficients and Standard Errors of the Coefficients of Eqs. (4) and (5) for the Materials Tested[†]

[†]The standard uncertainties of the coefficients are given in parentheses.

are therefore unable to conclude what stopped the grain growth of the SN5Yb-Al.

(B) Effect of Al_2O_3 on the Creep Rate of Silicon Nitride: Figure 9 shows that adding Al_2O_3 affects the creep response dramatically. The Al_2O_3 -free silicon nitrides, SN5Yb-S and SN5Yb-L, are far more creep resistant than those with the small amounts of Al_2O_3 , SN5YbAl-S and SN5YbAl-L. Although there are no studies that detail the effects of deliberate Al_2O_3 additions on the tensile creep of silicon nitride, we can compare typical creep rates between materials containing only Y_2O_3 and/or Yb_2O_3 with those that have added Al_2O_3 . Generally, the former has creep rates in the range 10^{-10} s⁻¹ < $\dot{\epsilon}$ < 10^{-9} s⁻¹ at 1300°C and 150 MPa.³⁸⁻⁴⁰ Under the same conditions, typical creep rates for silicon nitrides made with Y_2O_3 (or Yb_2O_3) + Al_2O_3 are in the range 10^{-7} s⁻¹ < $\dot{\epsilon}$ < 10^{-5} s⁻¹,⁴¹⁻⁴⁴ or 100 to 1000 times larger. Therefore, the addition of Al_2O_3 to silicon nitride is expected to decrease its creep resistance as we observe.

An unexpected result was that SN5YbAl-L crept 10 to 100 times more slowly than the SN5YbAl-S in the range $1200^{\circ}C < T < 1300^{\circ}C$ (Fig. 9). Equation (1) predicts that their creep rates ought to be identical, because their grain size distributions, aspect ratios, and chemical compositions are the same. In addition, a regression analysis similar to that described for SN5Yb shows that the SN5YbAl-S and SN5YbAl-L have statistically significantly



Fig. 9. Comparison of minimum creep rates at an applied stress of 100 MPa. The solid portion of the lines represents an extrapolation of the data set (using the constants in Table V) to the temperature range actually studied.

different activation energies for tensile creep. This improvement in creep resistance for SN5YbAl-L can only be explained by a significant change of the interface chemistry during the extra annealing time at 1880°C.

In this paragraph, we put forward a mechanism that could explain the higher creep resistance of SN5YbAl-L over that of the SN5YbAl-S. The dominant densification mechanism of vitreousbonded silicon nitride is the dissolution of metastable α -Si₃N₄ (95 vol% in the initial powder) and its reprecipitation on preexisting β-Si₃N₄ grains.⁴⁵ In Al₂O₃-containing silicon nitride systems, reprecipitation is combined with the formation of a SiAlON between silicon nitride and Al_2O_3 . The resulting β -Si₃N₄ grains have a core that is free of Al₂O₃, which represents the original β-seed, surrounded by a shell of SiAlON. The core-shell structure is normally visible after plasma etching for materials with higher aluminum oxide contents because silicon nitride etches faster than SiAlON.⁴⁶ We were unable to identify a core-shell structure in the Si₃N₄ grains of the SN5YbAl-S, perhaps because of the small quantity of added Al2O3. For longer sintering times, as for the SN5YbAl-L samples, aluminum and oxygen in the shell should diffuse down their concentration gradients toward the center of the grain and reduce the aluminum and oxygen content in the outer shell of the grains. The simultaneous transfer of aluminum and oxygen from the surrounding amorphous intergranular films to the β -Si₃N₄ grains compensates this inward diffusion to the core. Consequently, the total Al_2O_3 content in the amorphous grain boundary phase will decrease with increasing sintering time. Such a decrease in content of Al₂O₃ in the amorphous phase would increase the viscosity of that phase and could well account for an increase in creep resistance for the SN5YbAl-L material.

V. Summary

A factor of 2 difference in grain size had no effect on the tensile creep behavior of silicon nitride sintered with Yb_2O_3 . This observation is consistent with new theories of tensile creep of silicon nitride, which predict grain size exponents p = 0 or -1. In contrast to the negligible effect of grain size on creep rate,

Table VI. Coefficients and Standard Uncertainties of the Coefficients of Eq. (1) for the Al_2O_3 -Free (SN5Yb) Silicon Nitride[†]

Mode	$ln~(\dot{\epsilon}_1)$	Q_1 (kJ/mol)	р	п
Tension	58.99 (12.44)	1427 (222)	-0.20 (0.64)	6.57 (1.77)
Compression	38.46 (16.64)	836 (231)	-1.89 (0.80)	0.89 (0.38)

[†]The standard uncertainties are given in parentheses

chemical changes of the second phase due either to small additions of aluminum oxide (0.5% mass fraction) or to annealing of the Al₂O₃-containing material have a substantial effect on the tensile creep rate of silicon nitride. From these results, we conclude that the chemical composition of the silicate phases in the silicon nitride is more important than grain morphology in controlling tensile creep behavior.

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References

¹W. Acchar, A. Rendtel, and H. Hübner, "Improvements in the Creep Resistance of Hot-Pressed Silicon Nitride (HPSN)"; pp. 405-10 in Third Euro-Ceramics, Vol. 3. Edited by P. Duran and J. F. Fernandez. Faenza Editrice Iberica S.L., Castellón de la Plana, Spain, 1993.

²T. Hirano, T. Ohji, and K. Niihara, "Effects of Matrix Grain Size on the Mechanical Properties of Si₃N₄/SiC Nanocomposites Densified with Y₂O₃," Mater. Lett., 27, 53-58 (1996).

³P. J. Whalen, C. J. Gasdaska, and R. D. Silvers, "The Effect of Microstructure on the High-Temperature Deformation Behavior of Sintered Silicon Nitride," Ceram.

 Eng. Sci. Proc., 11, 633–40 (1990).
 ⁴S.-Y. Yoon, T. Akatsu, E. Yasuda, and Y. Tanabe, "The Influence of Grain Orientation on a Steady State Creep Rate in Hot-Pressed B-Si₃N₄ Whisker/SiAlON Composite," J. Ceram. Soc. Jpn., 104 [3] 239-42 (1996).

⁵S.-Y. Yoon, H. Kashimura, T. Akatsu, Y. Tanabe, S. Yamada, and E. Yasuda, "Grain Size Dependency on the Creep Rate in Hot-Pressed Silicon Nitride," J. Ceram. Soc. Jpn., 104 [10] 939-44 (1996).

⁶K. J. Yoon, S. M. Wiederhorn, and W. E. Luecke, "Comparison of Tensile and Compressive Creep Behavior in Silicon Nitride," J. Am. Ceram. Soc., 83 [8] 2017-22 (2000).

⁷W. R. Cannon and T. G. Langdon, "Review: Creep of Ceramics, Part 1—Me-chanical Characteristics," *J. Mater. Sci.*, **18**, 1–50 (1983).

⁸W. R. Cannon and T. G. Langdon, "Review: Creep of Ceramics. Part 2-An Examination of Flow Mechanisms," J. Mater. Sci., 23, 1-20 (1988).

⁹F. R. N. Nabarro, "Deformation of Crystals by the Motion of Single Atoms"; pp. 75-90 in Report of a Conference on Strength of Solids (Bristol). The Physical Society, London, U.K., 1948.

¹⁰C. Herring, "Diffusional Viscosity of a Polycrystalline Solid," J. Appl. Phys., 21, 437-45 (1950).

¹¹R. L. Coble, "A Model for Boundary Diffusion Controlled Creep in Ceramic Materials," *J. Appl. Phys.*, **34**, 1679–82 (1963).

¹²G. M. Pharr and M. F. Ashby, "On Creep Enhanced by a Liquid Phase," Acta Metall., 31, 129-38 (1983).

¹³R. L. Tsai and R. Raj, "Creep Fracture in Ceramics Containing Small Amounts of a Liquid Phase," Acta Metall., 30, 1043-58 (1982).

¹⁴R. Raj and C. K. Chyung, "Solution-Precipitation Creep in Glass Ceramics," Acta Metall., 29, 159-86 (1981).

¹⁵J. G. Wang and R. Raj, "Mechanism of Superplastic Flow in a Fine-Grained Ceramic Containing Some Liquid Phase," J. Am. Ceram. Soc., 67, 399 (1984).

¹⁶F. Wakai, "Step Model of Solution-Precipitation Creep," Acta Metall. Mater., 42 [4] 1163–72 (1994).
 ¹⁷J.-P. Poirier, *Creep of Crystals*. Cambridge University Press, Cambridge,

England, 1995.

³W. E. Luecke, S. M. Wiederhorn, B. J. Hockey, R. Krause Jr., and G. G. Long, "Cavitation Contributes Substantially to Tensile Creep in Silicon Nitride," J. Am Ceram. Soc., 78 [8] 2085-96 (1995).

¹⁹R. Kossowsky, D. G. Miller, and E. S. Diaz, "Tensile and Creep Strengths of Hot Pressed Si₃N₄," *J. Mater. Sci.*, **10**, 983–97 (1975). ²⁰F. F. Lange, B. I. Davis, and D. R. Clarke, "Compressive Creep of Si₃N₄/MgO

Alloys, Part 1, Effect of Composition," J. Mater. Sci., 15, 601-10 (1980).

 21 J. Crampon, R. Duclos, and N. Rakotoharisoa, "Compression Creep of $\rm Si_3N_4/$ MgAl₂O₄ Alloys," J. Mater. Sci., 25, 1203-208 (1990).

¹²J. Crampon, R. Duclos, and N Rakotoharisoa, "Creep Behavior of Si₃N₄/Y₂O₃/ Al₂O₃/AlN Alloys," J. Mater. Sci., 28, 909-16 (1993).

 1647–54 (1997).
 ²⁴J. M. Birch and B. Wilshire, "The Compression Creep Behaviour of Silicon Nitride Ceramics," J. Mater. Sci. 13, 2627-36 (1978).

²⁵D. A. Koester, K. L. More, and R. F. Davis, "Deformation and Microstructural Changes in SiC-Whisker-Reinforced Si3N4 Composites," J. Mater. Res., 6, 2735-46 (1991)

²⁶W. E. Luecke and S. M. Wiederhorn, "A New Model for Tensile Creep of Silicon Nitride," J. Am. Ceram. Soc., 82 [10] 2769-78 (1999).

²⁷C. J. Gasdaska, "Tensile Creep in an In Situ Reinforced Silicon Nitride," J. Am. Ceram. Soc., 77 [9] 2408-18 (1994).

²⁸S. Haig, W. R. Cannon, P. J. Whalen, and R. G. Rateick, "Microstructural Effects on the Tensile Creep of Silicon Nitride"; pp. 91–96 in *Creep: Characterization, Damage and Life Assessment.* Edited by D. A. Woodford, C. H. A. Townley, and M. Ohnami. ASM International, Materials Park, OH, 1992.

²⁹S. Haig and W. R. Cannon, "Tensile Creep, Recovery, and Failure of an In Situ

Reinforced Silicon Nitride," unpublished research. ³⁰J. D. French and S. M. Wiederhorn, "Tensile Specimens from Ceramic Components," J. Am. Ceram. Soc., 79 [2] 550-52 (1996).

³¹S. M. Wiederhorn, D. E. Roberts, T.-J. Chuang, and L. Chuck, "Damage-Enhanced Creep in a Siliconized Silicon Carbide: Phenomenology," J. Am. Ceram.

 Soc., 71, 602–608 (1988).
 ³²Powder Diffraction File, International Centre for Diffraction Data, Newton Square, PA. ³³H.-J. Kleebe, M. K. Cinibulk, I. Tanaka, J. Bruley, J. S. Vetrano, and M. Rühle,

"High Resolution Electron Microscopy Studies on Silicon Nitride Ceramics"; pp. 259-74 in Tailoring of Mechanical Properties of Si₃N₄ Ceramics. Edited by M. J. Hoffmann and G. Petzow. Kluwer Academic Publishers, Dordrecht, Netherlands, 1994.

³⁴NIST Standard Reference Materials Catalogue, 1998-1999, NIST Special Publication 260, Standard Reference Materials Program, Office of Measurement Services, Technology Services, National Institute of Standards and Technology, Gaithersburg, MD, 1998.

³⁵W. Mendenhall and T. Sincich; pp. 727–32 in Statistics for Engineering and the Sciences. Prentice-Hall, Upper Saddle River, NJ, 1995.

³⁶M. Mitomo, M. Tsutsumi, H. Tanaka, S. Uenosono, and F. Saito, "Grain Growth During Gas-Pressure Sintering of β-Silicon Nitride," J. Am Ceram. Soc., 73 [8] 2441-45 (1990).

 $^{37}\text{K.-R.}$ Lai and T.-Y. Tien, "Kinetics of $\beta\text{-}Si_3N_4$ Grain Growth in Si_3N_4 Ceramics Sintered under High Nitrogen Pressure," J. Am. Ceram. Soc., 76 [1] 91-96 (1993).

³⁸M. K. Ferber, M. G. Jenkins, and T. A. Nolan, "Comparison of the Creep and Creep Rupture Performance of Two HIPed Silicon Nitride Ceramics," J. Am. Ceram. Soc., 77 [3] 657-65 (1994).

³⁹S. M. Wiederhorn, G. D. Quinn, and R. Krause, "Fracture Mechanism Maps: Their Applicability to Silicon Nitride"; pp. 36-61 in ASTM Special Technical Publication, Vol. 1201, Life Prediction Methodologies and Data for Ceramic Materials. Edited by C. R. Brinkman and S. F. Duffy. American Society for Testing and Materials, Philadelphia, PA, 1994.

40R. F. Krause Jr., W. E. Luecke, J. D. French, B. J. Hockey, and S. M. Wiederhorn, "Tensile Creep and Rupture of Silicon Nitride," J. Am. Ceram. Soc., 82 [5] 1233–41 (1999).
 ⁴¹J. Sankar, S. Krishnaraj, R. Vaidyanathan, and A. D. Kelkar, "Elevated

Temperature Behavior of Sintered Silicon Nitride under Pure Tension, Creep and Fracture"; pp. 19-35 in ASTM Special Technical Publication, Vol. 1201, Life Prediction Methodologies and Data for Ceramic Materials. Edited by C. R. Brinkman and S. F. Duffy. American Society for Testing and Materials, Philadelphia, PA, 1994.

⁴²T. Tanaka, H. Nakayama, N. Okabe, S. Yamamoto, and S. Fukui, "Creep Rupture Map of Engineering Fine Ceramics"; pp. 473–91 in Fracture Mechanics of Ceramics, Vol. 10, Fracture Fundamentals, High-Temperature Deformation, Damage, and Design. Edited by R. C. Bradt, D. P. H. Hasselman, D. Munz, M. Sakai, and V. Ya. Shevshenko. Plenum Press, New York, 1992.

⁴³T. Ohji and Y. Yamauchi, "Tensile Creep and Creep Rupture Behavior of Monlithic and SiC-Whisker-Reinforced Silicon Nitride Ceramics," J. Am. Ceram.

Soc., 76 [12] 3105–12 (1993). ⁴⁴F. Lofaj, A. Okada, Y. Ikeda, and H. Kawamoto, "Creep Processes in the Advanced Silicon Nitride Ceramics," Key Eng. Mater., 171-174, 3931-39 (2000).

⁴⁵M. J. Hoffmann and G. Petzow, "Tailored Microstructures of Silicon Nitride Ceramics," Pure Appl. Chem., 66 [9] 1807-16 (1994).

⁴⁶W. Dressler, H.-J. Kleebe, M. J. Hoffmann, M. Rühle, and G. Petzow, "Model Experiments Concerning Abnormal Grain Growth in Silicon Nitride," J. Eur. Ceram. Soc., 16, 3-14 (1996).

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