

Effect of Microstructure on High-Temperature Compressive Creep of Self-Reinforced Hot-Pressed Silicon Nitride

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An experimental self-reinforced hot-pressed silicon nitride was used to examine the effects of microstructure on hightemperature deformation mechanisms during compression testing. At 1575–1625°C, the as-received material exhibited a stress exponent of 1 and appeared to deform by steady-state grain-boundary sliding accommodated by solutionreprecipitation of silicon nitride through the grain-boundary phase. The activation energy was 610 ± 110 kJ/mol. At 1450-1525°C for the as-received material, and at 1525-1600°C for the larger-grained heat-treated samples, the stress exponent was >1. Damage, primarily in the form of pockets of intergranular material at two-grain junctions, was observed in these samples.

I. Introduction

 $S^{\rm ILICON\ NITRIDE\ }(Si_3N_4)$ has potential use in many high-temperature environments. Effective use of Si_3N_4 is hampered by a lack of full characterization of high-temperature mechanical behavior, including integration of failure mechanisms with plastic deformation mechanisms. In this paper, the results of an investigation of compressive creep are reported.

Many creep studies have been performed on self-reinforced silicon nitrides containing an oxide grain-boundary phase.¹⁻⁶ However, most of these tests were conducted in either tension or flexure; neither is directly comparable to results from compression, in which cavitation is greatly reduced. Of the few compression studies, a majority reported testing at low temperatures (i.e., <1400°C), where deformation is invariably accompanied by damage accumulation. Some tests were further complicated by having been conducted in an oxidizing atmosphere, which can enhance cavitation and, in turn, influence creep response.^{2,3}

The dominant creep mechanism for Si₃N₄ containing a grainboundary phase is generally accepted to be grain-boundary sliding (GBS). It has been proposed that GBS occurs by viscous flow of the grain-boundary phase (which acts as a lubricant between the Si_3N_4 grains) or by solution-reprecipitation of Si and N (which occur by diffusion through the grain-boundary phase).⁴⁻⁶ In addition, cavitation at either two-grain or multiple-grain junctions can occur within Si₃N₄ containing a grain-boundary phase; the nucleation and growth of voids are controlled by the same

mechanism that determines deformation.4-6 A new model for tensile creep of Si₃N₄ suggests that the rate of formation and growth of cavities in the deformable second phase controls creep.7 The model predicts that tensile creep increases exponentially with stress, is independent of grain size, is inversely proportional to the effective viscosity of the deformable phase, and is proportional to the cube of the volume fraction of deformable phase. However, it is not clear that the model developed for tensile creep can be applied to this investigation which concentrates on compressive deformation mechanisms in relation to grain size.

II. Experimental Procedure

The starting material used in this study was an experimental hot-pressed Si₃N₄ fluxed with Y₂O₃, MgO, and TiO₂, produced by Dow Chemical USA (Midland, MI). The room-temperature fourpoint flexure strength and chevron-notch fracture toughness measured by Dow were 811 MPa and 7.0 MPa·m^{1/2}, respectively.⁸

The material was received as two 15.25 cm \times 15.25 cm \times 0.6 cm billets. The largest surface was oriented perpendicular to the hot-pressing direction. The original billets were sectioned into four blocks each. To promote grain growth, six blocks were returned to Dow for additional heat treatment at 1900°C under a nitrogen pressure of 5.17 MPa for two different times: 2.67 and 24 h. The resulting three materials were designated as-received (AR) material, short-heat-treatment (SH) material, and long-heat-treatment (LH) material.

The grain-size distributions for the materials were determined from scanning electron microscopy (SEM) of plasma-etched surfaces and were calculated from a diameter based on a spherical approximation of the area measured for each grain.⁹ The materials appeared to have a bimodal grain-size distribution with smaller, equiaxed grains surrounding larger, acicular grains. The average grain sizes, based on the diameter of the spherical approximation of the area, are listed in Table I; ≈ 2000 grains per sample were counted. The large standard deviations were the result of neglecting the bimodal distribution. While the heat treatment increased the average grain size, it can be seen from the photomicrographs in Fig. 1 that as grain growth proceeded, the largest acicular grains impinged on surrounding grains, which prevented them from extending in length, and hence they grew mostly in width. Growth of the large grains occurred at the expense of the small grains. This is consistent with grain-growth studies by Kramer et al., 10 Pyzik and Carroll,¹¹ and Lai and Tai¹² in similar silicon nitrides. The microstructures and the grain boundaries were examined by transmission electron microscopy (TEM) and X-ray energydispersive spectrometry (XEDS).

Steady-state creep behavior can usually be described by an equation of the form^{13,14}

$$\dot{\varepsilon} = A d^{-p} \sigma^n e^{-Q/RT} \tag{1}$$

where $\hat{\epsilon}$ is the steady-state strain rate, A is a constant, d is the grain size, p is the grain-size exponent, σ is the stress, n is the stress exponent, Q is the activation energy, R is the gas constant, and T

S. M. Wiederhorn-contributing editor

Manuscript No. 189354. Received May 7, 1999; approved June 22, 2000. Based in part on the thesis submitted by M. A. Boling-Risser for the Ph.D. degree in materials science and engineering, Northwestern University, Evanston, Illinois, 1998

This research was supported by the U.S. Department of Energy, and by Argonne National Laboratory's Division of Educational Programs, under Contract No. W-31-109-ENG-38.

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 Table I.
 Average Grain Size and Average x-Axis and y-Axis

 Approximations for the Three Materials[†]

	AR Material	SH Material	LH Material
Avg grain size (nm) Avg x-axis (nm) Avg y-axis (nm)	$\begin{array}{c} 0.26 \pm 0.24 \\ 0.53 \pm 0.52 \\ 0.25 \pm 0.17 \end{array}$	$\begin{array}{c} 0.55 \pm 0.51 \\ 0.94 \pm 1.17 \\ 0.43 \pm 0.35 \end{array}$	1.01 ± 0.69 1.61 ± 1.26 0.89 ± 0.48

[†]± values represent 1 standard deviation.



Fig. 1. SEM photomicrographs showing the microstructures of the (a) AR, (b) SH, and (c) LH materials for the surface perpendicular to the hot-pressing direction.

is the absolute temperature. The values of p, n, and Q were determined for steady-state creep in this material system under compressive creep conditions at a constant crosshead speed in an Instron universal tester previously described.¹⁵ All compressive creep experiments were conducted in static N₂ at a pressure of 10⁵ Pa to minimize oxidation and to inhibit volatilization of the grain-boundary material.

Samples were heated at 10°C/min to the test temperature under a small cyclic load (10 N minimum, 20 N maximum). Each sample was held at the test temperature for 15 min to ensure thermal equilibrium. Data were acquired as load *P* versus time *t* and normalized to true stress σ versus permanent true strain ϵ . Strain rates were 5×10^{-7} to 1×10^{-5} s⁻¹; they were established in reference to the initial specimen length. Strain rates of $\geq 1 \times 10^{-5}$ s⁻¹ caused the samples to fracture; strain rates of $<5 \times 10^{-7}$ s⁻¹ could not be reliably maintained. Tests were limited to total strains $\leq 10\%$. After the deformation was complete, the samples were cooled at 10°C/min to room temperature under no load.

Gross fracture occurred at <1450°C.

Samples were compressed between platens machined from the same material as the test specimens. No measurable reaction occurred between the platens and the thoriated-tungsten tooling in the Instron. In all tests, the sample was easily separated from the platens. However, comparison of the measured strain with the strain calculated from the time of the test and known crosshead displacement velocity revealed that at $\geq 1575^{\circ}C$ both the sample and the platens deformed. The resulting depression in each platen was measured optically. Platen deformation was taken into account by treating the platen/sample assembly as a single deforming unit. It was assumed that because the platens were of the same heat-treated material, they would deform at the same rate as the sample. Adding the initial thickness of each platen to the initial sample length yielded an effective initial sample length; adding the depth of each platen depression to the measured sample strain yielded the total strain. Measured strains then agreed with strains calculated from crosshead velocity and time to within 5% of each other. No barreling of the samples was obvious.

SEM of deformed samples indicated that volatilization damage to the samples was limited to the exposed surfaces and affected less than 1% of the material; it was therefore considered to be insignificant. Grain growth did not occur during creep testing. Deformed samples were also examined by TEM and XEDS.

III. Results

(1) Creep Data

Typical σ versus ϵ curves are shown in Fig. 2. True steady-state stress was achieved, as indicated by the work-hardening rate, $d\sigma/d\epsilon$, being zero and the path independence of the stress value. After a new steady-state stress was established in the AR sample at 1600°C at a new strain rate of 2.17 × 10⁻⁶ s⁻¹, it was possible to return to the initial steady-state stress of 22 MPa when returning to the initial strain rate of 8.7 × 10⁻⁷ s⁻¹.



Fig. 2. Characteristic true stress as a function of true strain. This sample of the AR material was tested at 1600°C.

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For most strain rates, steady state was achieved within 2% permanent true strain. In a few instances, apparent steady states could not be achieved because of obvious damage accumulation; the measured load decreased with strain. Data from these tests were not included in our analyses.

Strain rate versus steady-state stress for the AR material is shown in Fig. 3(a). The AR material was tested at 1450°, 1525°, 1575°, 1600°, and 1625°C. We determined that the stress exponent for the AR material was temperature dependent; $n \approx 1.5-2$ at 1450–1525°C, but $n \approx 1$ at ≥ 1575 °C. A stress exponent of 1 is consistent with a diffusional GBS creep mechanism.¹⁷ The increase in stress exponent with decrease in temperature indicated that either another creep mechanism became active or a temperature-dependent threshold stress existed.¹⁸

The SH material was tested at 1525°C and the LH material was tested at 1525° and 1600°C (Fig. 3(b)). At 1525°C, the stress exponent was ≈ 1.5 for all three materials. Note that the SH and LH $\dot{\epsilon}$ versus σ data were nearly identical. The stress exponent for the LH material was ≈ 1.4 at 1600°C. Results are summarized in Table II.

(2) Microscopy

TEM and SEM of samples deformed at \leq 1525°C revealed consistent features. Dislocations were present in the deformed samples (Fig. 4), but not in the undeformed samples. There was some indication of grain translation, but little evidence of cavitation.



Fig. 3. Logarithmic strain rate as a function of logarithmic steady-state stress for (a) AR (open circles = 1625° C, closed circles = 1600° C, open squares = 1575° C, open diamonds = 1525° C, and open triangles = 1450° C) and for the (b) SH (closed triangles = 1525° C) and LH (open circles = 1600° C, open diamonds = 1525° C) materials. Slope resulting in n = 1 is shown for comparison.

Table II.Stress Exponents as a Function of Temperature
for the AR, SH, and LH Materials[†]

Test temperature (°C)	AR Material	Stress exponent SH Material	LH Material
1450 1525 1575 1600 1625	$\begin{array}{c} 1.9 \pm 0.35 \\ 1.5 \pm 0.3 \\ 0.8 \pm 0.2 \\ 0.9 \pm 0.2 \\ 1.4 \pm 0.3 \end{array}$	1.4 ± 0.3	1.5 ± 0.3 1.4 ± 0.3

 $^{\dagger}\text{S}\text{tandard}$ deviations are based on estimated uncertainties in stress, strain rate, and temperature.



Fig. 4. TEM photomicrograph of AR material crept at 1450°C, showing evidence of dislocation activity (primarily in large central grain) and grain translations (examples marked by arrows).

TEM of samples deformed at $\approx 1600^{\circ}$ C stood in contrast. Few dislocations were observed. Grain-boundary sliding was suggested by regions of apparent grain translation. These translations were most obvious at triple points (Fig. 5). Grain faceting could, in principle, impart a similar appearance. However, the apparent translations were not observed in the uncrept AR material, and so GBS is the more likely explanation for the feature shown in Fig. 5

TEM indicated the possibility of grain-boundary buckling and strain whorls caused by grain impingement at some boundaries. These features were most prevalent in the AR material tested at 1450°C, or in the SH and LH samples. Strain whorls have been



Fig. 5. TEM photomicrograph of AR material crept at 1600°C showing evidence of grain-boundary sliding, as indicated by the white arrow, and no evidence of dislocations.

Figure 6 shows a characteristic TEM photomicrograph of a sample deformed under conditions where n > 1. The LH material was compressed at 2×10^{-6} s⁻¹ and 1600°C. The SH and LH materials, and the AR materials tested at ≤ 1525 °C, showed development of lenticular-shaped pockets along two-grain junctions. These pockets were not present in the undeformed material. These pockets were filled with grain-boundary-phase material. The lenticular shape intruded into the neighboring grains, evidence that grain material was being removed from the area through a solution-reprecipitation mechanism.

An XEDS examination of triple points in deformed AR and LH samples indicated no apparent change in the grain-boundary phase due to deformation. Magnesium and zirconium were detected in the triple points. However, examination of the pockets revealed preferential migration of zirconium. The pockets that were most isolated from one another showed the highest concentrations of zirconium.

IV. Discussion

The data and observations for stress versus strain rate could be separated into two categories. The AR material crept at $\geq 1575^{\circ}C$ exhibited a stress exponent that was ≈ 1 , absence of dislocations, and limited cavity formation. The AR material crept at $\leq 1525^{\circ}$ C, and the larger-grained SH and LH materials crept at $\leq 1600^{\circ}$ C, exhibited stress exponents that were $\approx 1.5-2$, relatively high concentrations of dislocations within many grains, and lenticularshaped pockets that were primarily at two-grain junctions. The simplest explanation for the differences is that the AR material tested at the higher temperatures achieved true steady-state creep, but in the other tests, a combination of plasticity and damage accumulation occurred. For a given $\dot{\varepsilon}$ and T in fine-grained materials, a certain steady-state stress may be achieved, in contrast to coarser-grained materials in which the imposed $\dot{\epsilon}$ and T may produce fracture before achieving steady state. Examination of only the creep data may suggest that the n > 1 values could be attributable to the existence of a threshold stress σ_0 :²²

$$\dot{\varepsilon} = A(\sigma - \sigma_0)e^{-Q/RT} \tag{2}$$

Reasonable linear plots of $\hat{\varepsilon}$ versus σ could then be used to calculate σ_0 .¹ However, when a threshold stress was incorporated



Fig. 6. TEM photomicrograph of LH material crept at 1600°C at an initial $\dot{\varepsilon}=2\times 10^{-6}~{\rm s}^{-1}$, which caused damage in the form of lenticular-shaped pockets filled with Zr-rich/Mg-poor grain-boundary-phase material, as indicated by white arrows. Dislocation activity is also evident.

into the analysis of the steady-state data, the results were not consistent. An apparent temperature-dependent σ_0 was calculated. Insertion of the values of σ_0 into Eq. (2) led to contradictory results in which the compensated strain rates were then faster at lower temperatures than were the AR rates at $\geq 1575^{\circ}$ C. Therefore, it seems clear that the two categories of creep response represent steady-state creep and a regime in which damage accumulation was significant. It has been shown that cavitation, at least in tension, can lead to a creep rate that depends exponentially on temperature.⁷

The activation energy Q for the AR material was determined in the temperature regime in which the stress exponent was ≈ 1 . Data from two strain rates were used; it was necessary to interpolate data for 1600°C (Fig. 7). The average value of Q was calculated to be 610 \pm 110 kJ/mol; the error bars in the figure reflect estimates of the accuracy of the measurements and the standard deviations of the line fits. This Q value agrees closely with that for grainboundary sliding accommodated by solution-reprecipitation given by Raj and Morgan,²³ which was based on the heat of solution for Si₃N₄ in the grain-boundary-phase material. Solutionreprecipitation as the primary mechanism of deformation is consistent with the types of pockets formed in the damage regime.

Additional support for the conclusion that the AR material tested at $\leq 1525^{\circ}$ C and the SH and LH materials did not achieve steady state, despite the appearance of an apparent zero work hardening rate in the σ versus ε data, was obtained from calculations of the apparent grain-size exponent *p*. The grain-size exponent was determined to be zero at 1525°C for all materials. There is no known steady-state diffusional creep mechanism that could account for creep rates being independent of grain size. However, the stress at which damage becomes significant is likely to be nearly independent of grain size. Although flexure and compression tests cannot be directly compared, it has been shown that the elevated-temperature fracture stress of this Si₃N₄ was a very weak function of grain size.¹

For a material deforming by steady-state GBS accommodated by diffusion through a liquid phase, the grain-size exponent is expected to be 1 to 3.²⁴ All the creep tests were conducted well above the softening point of the grain-boundary phase, as indicated by the flexure results.¹ It is reasonable to assume, and is consistent with the TEM observations, that GBS occurred and was accommodated by some viscous flow of the boundary phase. However, the strain due to viscous flow in Si₃N₄ has been shown to be limited.^{25,26} Therefore, solution-reprecipitation most likely dominated the deformation.

In the AR materials at 1450–1525°C and the LH and SH materials, GBS could not accommodate all the imposed stress. Stress levels were high, as indicated by the generation of dislocations, and cavitation occurred.



Fig. 7. Steady-state stress as a function of inverse temperature for AR material at two strain rates (squares = $2 \times 10^{-6} \text{ s}^{-1}$ and circles = $1 \times 10^{-6} \text{ s}^{-1}$).

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Before creep testing, the grain boundaries exhibited a uniform thickness and the grain-boundary phase had a uniform composition. There was clear evidence that pocket formation was accompanied by redistribution of the grain-boundary phase. Most important, zirconium migrated preferentially to the two-grain-junction pockets. It has been reported that redistribution of the grainboundary phase from compressive two-grain junctions to tensile two-grain junctions should require that stress be applied for >100 h.²⁷ Our test periods were ≤ 24 h. We can at present offer no credible explanation for why the zirconium and magnesium concentrations of the grain-boundary phase changed with time and location.

V. Summary

For this Si₃N₄ system, the as-received material deformed by the mechanism of grain-boundary sliding at 1575–1625°C; the stress exponent was ≈ 1 and the activation energy was 610 ± 110 kJ/mol. Data and observations were consistent with solution-reprecipitation of the Si₃N₄ as the dominant mechanism of mass flow. At 1450–1525°C for the as-received material, at 1525°C for the short-heat-treated material, and at 1525–1600°C for the long-heat-treated material, the apparent stress exponent increased to 1.5–2, and TEM revealed dislocations and enlarged pockets of grain-boundary-phase material in the crept samples. In these tests, steady state was not achieved and the apparent plasticity was due in part to the damage accumulation.

Acknowledgments

Thanks are extended to Alek Pyzik of Dow Chemical USA, who provided the material for this research and arranged for the postprocessing heat treatments. Thanks to Nestor Zaluzec at Argonne National Laboratory for performing the XEDS experiments, to Craig Sperty for assistance in monitoring the experiments, and to Antonio R. de Arellano-López for his assistance in reviewing the manuscript.

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