

# Measurement of viscosity of the grain-boundary phase in hot-pressed silicon nitride

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An internal friction technique has been used to measure the viscosity of the grain-boundary amorphous phase in commercial hot-pressed silicon nitride. The viscosity in the region of the glass transition (850 to 900° C) was approximately  $5 \times 10^{15}$  P per unit thickness (cm) of the grain boundary, with an apparent activation energy of 163 kcal mol<sup>-1</sup>.

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## 1. Introduction

Hot-pressed ceramics such as silicon nitride and silicon carbide are likely candidates for the next generation of structural materials for elevated temperature applications. Because slow intergranular crack growth is the primary failure mechanism in these ceramics [1], the microstructure features which influence the rate of crack growth are of interest. It has been suggested that the viscosity of the amorphous phase existing in the grain boundaries of these ceramics [2] is an important factor in the rate of crack growth [3] and deformation [13] at elevated temperature. This amorphous phase derives from additives introduced during hot-pressing to promote sintering of the polycrystalline ceramic [2, 4]. The viscosity of the boundary phase is suspected to be sensitive to the purity of the additive. For example, of the two grades of hot-pressed silicon nitride being supplied by the Norton Company, HS130 which is also the higher purity, maintains its flexural strength to higher temperatures than HS110. It is believed [4] that calcium is the impurity which degrades the viscosity of the grain-boundary phase in HS110 and leads to its inferior high temperature properties.

A procedure is described for measuring the

viscosity of the phase segregated in the boundaries of hot-pressed ceramics. Such measurements can be helpful in the prediction of the rate of intergranular crack propagation at elevated temperature. Since many parameters (e.g. trace impurities) can adversely affect the viscosity of a glass, a procedure such as described here, which can be employed for a routine measurement of the viscosity of the boundary phase, can be a useful tool in the development of ceramics for elevated temperature applications.

## 2. The internal friction technique

Over a quarter of a century ago Zener [5] and Kê [6] demonstrated, in torsional pendulum experiments, that polycrystalline metals exhibited a damping peak that was absent in "single crystals" of the same metal. They ascribed the relaxation to sliding at grain boundaries. Recently, Mosher and Raj [7] have shown that the damping peak is indeed a result of grain-boundary sliding and that its relaxation time at a given temperature can be correlated to the "viscosity" of sliding at that temperature; this was accomplished by microstructural control of the sliding viscosity and showing agreement between the experimentally determined relaxation times and predictions based

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on the work of Raj and Ashby [8]. Because the experiment measures sliding rates, only the viscosity per unit thickness of boundary rather than bulk viscosity of the boundary phase is determined. If  $\eta$  is the viscosity of the boundary phase and  $\delta$  its thickness, then the relaxation time [7]

$$\tau = \beta \frac{\eta}{\delta} \quad (1)$$

where  $\beta$  is a parameter depending on the grain size, grain shape and the elastic properties of the bulk material of which the grains consist [8]. For an equiaxed grain structure  $\beta$  is given by

$$\beta = 1.14 \frac{(1 - \nu^2)}{E} d \quad (2)$$

where  $d$  is the grain size and  $E$  and  $\nu$  are Young's modulus and Poisson's ratio for the grains.

The procedure then is to measure  $\tau$  at a given temperature in an internal friction experiment and, knowing  $d$ ,  $\nu$  and  $E$ , calculate the viscosity per unit thickness of the grain-boundary phase.

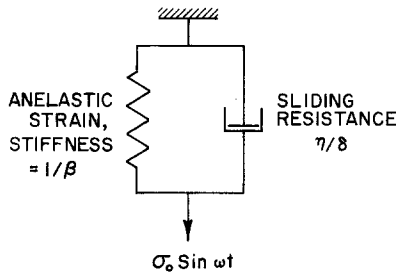


Figure 1 A spring-dashpot model for anelastic strain due to grain-boundary sliding.

The rate of energy dissipation from internal friction can be calculated from the spring-dashpot model shown in Fig. 1. If a cyclic stress  $\sigma_0 \sin \omega t$  is imposed upon the system then the power dissipation per unit volume in the dashpot is given by:

$$P = \frac{\eta}{2\delta d} \frac{(\beta\omega\sigma_0)^2}{(1 + \omega^2\tau^2)} \quad (3)$$

At resonance,  $\omega\tau = 1$ , and substituting from Equations 1 and 2 in Equation 3 we get:

$$P = \frac{\delta}{2d\eta} \sigma_0^2 \quad (4)$$

\*  $\sigma_{\max} \approx Gc\theta/l$  where  $\theta$  is the twist angle,  $c$  is the specimen thickness and  $l$  the length.  $G$  is the sheat modulus [14]. The specimen dimensions, therefore, allowed a maximum twist of  $10^\circ$  for  $\sigma_{\max} \leq G/1000$ .

### 3. Experimental method

#### 3.1. Specimens

Two sets of silicon nitride specimens were tested; one set was made from Norton HS110 and the other from HS130. Specimen configuration was based on constraints imposed by fabrication methods and by the internal friction apparatus. The latter required torsional rigidity such that frequencies in the range 0.5 to 10 Hz were achieved and that relatively large twist angles could be achieved without damage to the specimen. A ribbon-shaped specimen 2 in.  $\times$  0.125 in.  $\times$  0.010 in. satisfied these requirements\*.

Grain sizes were measured, following completion of the internal friction measurements, from scanning electron micrographs of fracture surfaces of each specimen. To compensate for the presence of some non-equiaxed grains, the effective grain size was considered to be the geometric mean of maximum and minimum dimensions of each grain. An average of fifty grains, along with limits representing the observed extremes served to characterize the grain-size distribution.

#### 3.2. Apparatus

Specimens were tested in an inverted torsional pendulum [9] fitted with a 6 in. long cylindrical molybdenum radiation heater surrounded by several concentric molybdenum radiation shields. The temperature was controlled by means of a thermocouple attached to the specimen. A type K thermocouple wire, 0.001 in. diameter, was spot-welded to a small stainless steel foil which was fastened snugly about the midlength of the specimen. The specimen was positioned in the furnace by means of high strength high-purity graphite collets coupled to ceramic rods. Temperature is believed to have been quite uniform along the specimen, although a drop of  $5^\circ\text{C}$  was measured in the graphite collets with respect to the temperature at the centre of the specimen. Axial stress in the specimen was reduced to a minimum by carefully counterbalancing the pendulum bob.

Damping measurements were made with the aid of an optical lever. Because of the higher frequencies involved these were based on a procedure similar to that described by de Morton *et al.* [10] wherein the velocity decrement between successive

swings of the light spot past its rest point provides an equivalent measure of the damping. The application of this procedure measures the times  $t_0$  and  $t_n$  required for the spot to traverse a fixed small distance spanning the rest position during the 0th and  $n$ th cycles, respectively. From these the internal friction is

$$Q^{-1} = \frac{1}{n\pi} \ln \frac{t_n}{t_0}. \quad (5)$$

Measurements were made initially at intervals of approximately  $25^\circ\text{C}$  over the entire range from room temperature to  $1200^\circ\text{C}$  in order to establish the character of the damping spectrum. Subsequent measurements concentrated on the temperature range  $600$  to  $1200^\circ\text{C}$ .

#### 4. Results

Typical damping spectra for the HS110 and HS130 samples are shown in Fig. 2, both taken at a frequency of  $0.73\text{ Hz}$ . The peak for HS110 occurs at a lower temperature than HS130 which was to be expected since HS110 is the grade with a boundary phase of a lower viscosity. Note also that the magnitude of the damping peak is higher in HS130 than in HS110. From inspection of Equation 4 the stronger peak in HS130 may be a result of a larger grain-boundary phase thickness or a smaller grain size in HS130. As shown in Table I, HS130 material has a consistently smaller grain size than HS110.

In all, four specimens from HS130 and three from HS110 were tested. The results are summarized in Table I. A wide variability in grain size was found so the maximum, minimum and the average value of the grain size from fifty measurements from each specimen is reported. The values of  $\eta/\delta$  given in Table I were calculated from Equations 1 and 2 using the following values:  $E = 4.12 \times 10^{12} \text{ dyn cm}^{-2}$  and  $\nu = 0.3$ . Note that  $\delta$ , the thickness of the grain-boundary phase may be different from sample to sample and between HS110 and HS130. The relative values of  $\eta/\delta$  have a meaning only when  $\delta$  is constant for each specimen. No information was available to estimate the value of  $\delta$  for each specimen. In general it is believed to be  $100$  to  $1000 \text{ \AA}$ . Variation of  $\eta/\delta$  with temperature is shown in Fig. 3. The mean activation energy ranges from  $152$  to  $170 \text{ kcal mol}^{-1}$  for HS110 and from  $144$  to  $180 \text{ kcal mol}^{-1}$  for HS130.

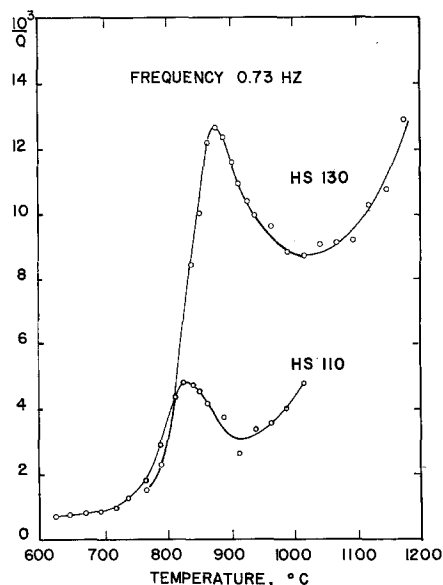


Figure 2 Typical damping spectra for the HS110 and HS130 materials.

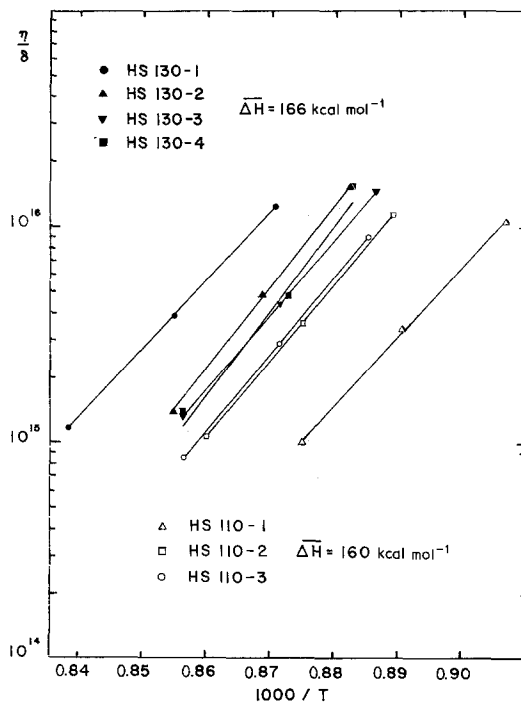


Figure 3 Temperature dependence of viscosity per unit thickness.

#### 5. Discussion

It is to be noted from Fig. 3 that (i) the viscosity per unit thickness from sample to sample, for HS110 and for HS130 can vary by a factor of up to 4, (ii) the average viscosity per unit thickness for HS130 is about one order of magnitude greater

TABLE I Summary of experimental data

Specimen number	Grain size			Grain-boundary damping peak				Boundary viscosity
	Max ( $\mu\text{m}$ )	Ave ( $\mu\text{m}$ )	Min ( $\mu\text{m}$ )	Temperature ( $^{\circ}\text{C}$ )	$\tau$ (sec)	$Q_{\text{max}}^{-1}$	$\Delta H$ (kcal mol $^{-1}$ )	$\eta/\delta$ (P cm $^{-1}$ )
HS110-1	1.97	0.81	0.26	830	0.2180	0.003	149	$1.07 \times 10^{16}$
				850	0.0689			$3.38 \times 10^{15}$
				870	0.0201			$9.85 \times 10^{14}$
HS110-2	1.26	0.69	0.29	852	0.1753	0.003	164	$1.13 \times 10^{16}$
				870	0.0553			$3.58 \times 10^{15}$
				890	0.0162			$1.06 \times 10^{15}$
HS110-3	1.78	0.87	0.39	857	0.1970	0.008	166	$8.99 \times 10^{15}$
				875	0.0622			$2.84 \times 10^{15}$
				895	0.0184			$8.40 \times 10^{14}$
HS130-1	1.40	0.71	0.30	875	0.2195	0.010	149	$1.23 \times 10^{16}$
				897	0.0689			$3.85 \times 10^{15}$
				920	0.0202			$1.13 \times 10^{15}$
HS130-2	1.87	0.65	0.22	860	0.2510	0.013	173	$1.53 \times 10^{16}$
				878	0.0792			$4.84 \times 10^{15}$
				897	0.0227			$1.39 \times 10^{15}$
HS130-3	1.74	0.65*	0.29	855	0.2242	0.012	159	$1.45 \times 10^{16}$
				875	0.0706			$4.44 \times 10^{15}$
				895	0.0204			$1.31 \times 10^{15}$
HS130-4	1.74	0.61	0.29	860	0.2373	0.012	182	$1.51 \times 10^{16}$
				873	0.0727			$4.73 \times 10^{15}$
				895	0.0213			$1.39 \times 10^{15}$

\* Estimate

than for HS110 in the temperature range measured, (iii) the activation energy for the viscosity is unusually large and (iv) the bulk viscosity is approximately  $5 \times 10^{11}$  P for a boundary thickness  $\delta = 1000 \text{ \AA}$ . The spread in  $\eta/\delta$  may be a result of a change in  $\delta$  or a change in  $\eta$  due to trace impurities from one sample to another. The higher viscosity for HS130 than for HS100 correlates well with its better flexural rigidity and with its better resistance to intergranular crack propagation. In view of the large activation energy which is measured we are led to believe that we are making measurements near the glass-transition temperature for the amorphous phase in the boundary. This is also confirmed by the estimate of the bulk viscosity since the viscosity of glasses near the glass transition temperature is about  $10^{11}$  to  $10^{13}$  P.

If the viscosity and the thickness of the grain boundary are known then it becomes possible to build models for intergranular fracture and creep deformation at elevated temperature, and compare results with experimental measurement on creep, fracture and crack growth in hot-pressed ceramics. For example, it has been shown that the deformation of hot-pressed silicon nitride at elevated

temperature derives from grain-boundary sliding which is accommodated by the growth of cavities at triple-line grain-junctions [13]. The temperature dependence of the creep rate can then be expected to be identical to the temperature dependence of the viscosity of the boundary phase. This appears to be supported by the fact that the activation energy measured in the internal friction experiments (approximately 163 kcal mol $^{-1}$ ) is about of the same magnitude as measured in creep experiments (130 to 150 kcal mol $^{-1}$ ) [12, 13].

A simple model for fracture is to consider the growth of penny-shaped voids in a grain boundary across which a tensile stress is applied. The voids may nucleate at inclusions, at pre-existing holes or at triple-line junctions. An intergranular crack may propagate by the growth and coalescence of such voids ahead of the crack tip. For a periodic array of voids in the boundary placed an average distance  $2l$  from each other the time to fracture when a normal stress  $\sigma_n$  is applied across the interface, is given by [11]:

$$\frac{0.9l^2}{\sigma_n \delta} \cdot \frac{\eta}{\delta} < t_r < \frac{232.5l^2}{\sigma_n \delta} \cdot \frac{\eta}{\delta}. \quad (6)$$

The lower bound for  $t_r$  in Equation 6 results when the interfacial tension effects are negligible and the upper bound results when they are dominating [11]. At a stress of  $8 \times 10^9 \text{ dyn cm}^{-2}$ , for a thickness of the boundary phase of  $10^{-5} \text{ cm}$ , for a spacing of the penny-shaped voids (equivalent to the inclusion spacing since the voids will probably nucleate at the inclusions) of  $10^{-4} \text{ cm}$ , and for  $\eta/\delta = 5 \times 10^{15} \text{ P cm}^{-1}$ , the time to failure from Equation 4 is  $1.16 \text{ h} < t_r < 40.3 \text{ h}$ . The value for  $\eta/\delta$  is taken from Figure 3 and it applies at a temperature of approximately  $900^\circ \text{ C}$ . The flexural rigidity of HS110 and HS130 degrades at about this temperature [1]; therefore, a failure time at  $900^\circ \text{ C}$  as estimated above is probably a reasonable value.

## 6. Conclusion

Grain-boundary damping peaks in hot-pressed silicon nitride have been measured. The viscosity per unit thickness of the grain-boundary phase has been calculated to lie in the range  $10^{15}$  to  $10^{16} \text{ P cm}^{-1}$  at a temperature of  $850^\circ \text{ C}$ . Correlation has been established between the high flexural rigidity of a material (HS130 versus HS110) and a high viscosity for its grain-boundary phase.

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## References

1. A. G. EVANS and S. M. WIEDERHORN, *J. Mater. Sci.* **9** (1974) 270.
2. P. DREW and M. H. LEWIS, *ibid* **9** (1974) 261.
3. F. F. LANGE, Scientific Paper 74-9DA-POWDR-P, May 16, 1974, Westinghouse Research Labs, Pittsburgh, Pa. 15235.
4. R. KOSSOWSKY, *J. Mater. Sci.* **8** (1973) 1603.
5. C. ZENER, *Phys. Rev.* **40** (1946) 906.
6. T. S. KÉ, *ibid* **71** (1947) 533.
7. D. R. MOSHER and R. RAJ, *Acta Met.* **22** (1974) 1469.
8. R. RAJ and M. F. ASHBY, *Met. Trans.* **2** (1971) 1113.
9. D. R. MOSHER, *Rev. Sci. Instrum* **40** (1969) 820.
10. M. E. DE MORTON, S. A. LOTT and D. F. STAINSBY, *J. Sci. Instrum* **40** (1963) 441.
11. R. RAJ and C. H. DANG, *Phil. Mag.*, in press.
12. M. S. SELTZER, A. H. CLAUER and B. A. WILCOX, Second Annual Report on High Temperature Creep of Ceramics, Contract F33615-73-C-4111, February 1975.
13. R. KOSSOWSKY, D. G. MILLER and E. S. DIAZ, *J. Mater. Sci.* **10** (1975) 983.
14. S. TIMOSHENKO and J. N. GOODIER, "Theory of Elasticity", 2nd Edn. (McGraw-Hill, New York, 1951) p. 273.

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