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THE THERMAL SHOCK RESISTANCE OF SILICON OXYNITRIDE

J. C. Glandus and P. Boch

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J. C. Glandus and P. Boch
Center for Ceramic Research, Univ. of Limoges (France,

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16. Abstract

The thermal shock resistance of Si_2N_2O refractory material was studied. The thermal expansion coeff. is 3.55×10^{-6} at 20-800 and 2.86×10^{-6} m/m/° at 20-200°. The breaking loads are high at high stress. Young's modulus E and the shear modulus G decrease linearly with increasing porosity. For dense material $E_O \simeq 216{,}500$ N/mm^2 and $G \simeq 90{,}600$ N/mm^2. The Vickers hardness of the dense material is comparable to that of sapphire. The exptl. results on thermal shock show that R, the breaking load, stays const. for $T < T_C$ ($T_C \simeq 225°$), the first cracks appear and R decreases sharply for $T = T_C$. As the severity of the thermal shock is increased at $T > T_C$, a small no. of new, large-size cracks appears. The shock's cumulative effect is negligible, and repeated shocks do not change the cracks. It is difficult to describe quant. the degrdn. induced by thermal shock at $T > T_C$, but the low values of thermal expan coeff. and Young's mod. and the high tension breaking load are considered. Sintered Si_2N_2O with 5% MgO shows excellent cracking resistance under thermal shock.

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THE THERMAL SHOCK RESISTANCE OF SILICON OXYNITRIDE

J. C. Glandus and P. Boch

Laboratory of Vibrational Physics
Center for Ceramic Research
University of Limoges, France

1. Introduction /45*

Nitride ceramics are currently the subject of a large number of studies because of their refractory characteristics [1]. Mainly because of their mechanical performance at high temperatures, a vast field of application awaits these new ceramics: Increasing the efficiency of heat engines involves running them at as high a temperature as possible, and in the majority of cases, the materials employed are the limiting factor holding down that temperature.

At present, silicon carbide, SiC, and silicon nitride, Si_3N_4, are the main candidates for such uses. Silicon carbide, which was developed a long time ago, has reached a level of quality that seems difficult to improve upon significantly. In contrast, the nitrides are making rapid progress. Besides Si_3N_4, research is concentrating on the SiAlON system: These "sialons" currently are a center of attraction for those concerned with energy and high temperature materials problems [1,2].

Alumina, Al_2O_3, has many advantages: ease of production and forming, good refractoriness, and perfect resistance in oxidizing atmospheres. Unfortunately, its thermal shock resistance is mediocre, which rules out its use in heat engines that often undergo extreme temperature cycles. It is known [3] that, all other things being equal, the higher the coefficient of thermal expansion is, the more marked is the degradation provoked by thermal shocks. In this area, Al_2O_3 does relatively poorly: Between 0 and 1000°C the average

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*Numbers in the margin indicate pagination in the foreign text.

value of α is 8×10^{-6} m/m/°C [4], compared to 4.5 [5] for SiC and 3 to 3.5 for the nitrides [6]. In addition, the higher the Young's modulus is, the earlier the first cracks appear. Here again, Al_2O_3 does not do well: $E \approx 400{,}000$ N/mm^2 [7], and SiC likewise: $E \approx 400{,}000$ N/mm^2 [8], whereas the nitrides have more favorable figures, less than 300,000 N/mm^2 [9] -- these figures being for completely nonporous materials. Let us add that in certain cases the nitrides hold up well in the face of appreciable surface energies [10]. We are interested in this thermal shock resistance for a new refractory material, silicon oxynitride.

2. Silicon Oxynitride

In contrast to oxides, which are stable in oxidizing atmospheres, nitrides degenerate at high temperature in such atmospheres. The advantage of silicon nitrides (and also of SiC) is that they act to create a protective layer of silica. Along these lines, silicon oxynitride, Si_2N_2O (which is located at one of the boundaries of the SiAlON field), merits particular examination. This refractory material first made its appearance in 1958 [11], but it was only in 1975 that it became a directly usable material, as a result of its preparation in the form of high purity powders and the use of sintering to mold it. The samples available to us were prepared by the Limoges Laboratory of Mineral Chemistry and Heterogeneous Kinetics (ERA no. 539), which was the group that perfected Si_2N_2O in the first place [12,13]. The powder (95% Si_2N_2O, 5% MgO) was sintered under a load of 33 N/mm^2 in a nitrogen atmosphere and at temperatures that reached 1560°C. The cycle of sintering operations is schematized in figure 1. It is thus possible to obtain a 100% densification. /46 Unless specifically stated otherwise, our tests were conducted with a dense material, $\rho \approx 2.83$ g/cm^3.

3. Experimental Techniques, Results, and Discussion

The study we made of Si_2N_2O's thermal shock resistance produced a set of complementary measurements.

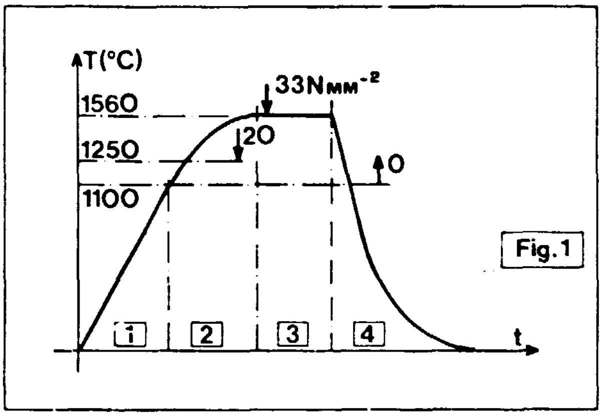

Figure 1

1) The coefficient of thermal expansion was determined by differential dilatometry using prismatic test pieces with a 6 x 6 cm square cross section, a length of 35 mm, and zero porosity. (This coefficient is only very slightly affected by porosity [14]). The average value between 20 and 800°C was 3.55×10^{-6} m/m/°C and 2.86×10^{-6} between 20 and 200°C (figure 2). This low figure ranks with the smallest values found for the nitride family [6]. The essentially covalent nature of the atomic bonding seems to account for the small coefficient of expansion obtained [14].

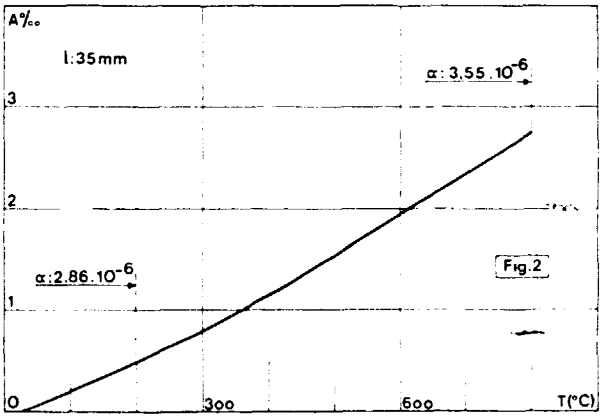

Figure 2

2) The breaking load was determined for compression and biaxial bending [15]. The latter stress led to the value for the tensile breaking load ($\delta c \simeq 950$ N/mm^2). The compression test specimens were cubes 6 mm on a side, and those for biaxial bending were disks 30 mm in diameter and 2.5 mm thick. A Zwick 1461 machine was used in both cases, with a deformation speed of 0.2 mm/min. The values obtained for breaking were high for both compressive and tensile stresses and comparable to those found for hot-pressed Si_3N_4 [10]. The material's surface energy was not measured, but this work is in progress. For Si_3N_4, the value of γ can reach 70 J/m^2 [1,10].

3) The elasticity moduli were evaluated with particular care, and a detailed description of the results will be published elsewhere.

-- Measurements were made using an ultrasonic "pulse-echo overlap" (PEO) technique [16] with transverse and longitudinal waves at frequencies N of 6 and 10 MHz. The samples were cylindrical ones (diameter: 20 mm, length: 16 mm).

-- A "phase comparison" ultrasonic technique [17] checked samples similar to the ones used in the bending tests at N $\simeq$ 10 MHz and 20 MHz.

-- These last test specimens (diameter: 30 mm, thickness: 2 to 3 mm) also participated in plate resonance tests [18], at around 30 kHz.

-- Finally, the dilatometry test specimens were used for making bar resonance measurements, also at around 30 kHz.

This group of tests involved samples of varying porosity P (0%, 0.3%, 3%, 8%, 9.[illegible]%, 12%, 16.5%, 21%, 26.5%). The different techniques employed showed that the samples' anisotropy was very slight, and that the material's texture did not have a preferred orientation. Young's modulus E and the shear modulus G decreased linearly as P increased:

$$\frac{E}{E_o} \approx 1-2.53\ P; \qquad \frac{G}{G_o} \approx 1-2.51\ P.$$

The Poisson ratio μ remained constant at 0.2.

For dense material:

$$E_o \approx 216{,}500\ \mathrm{N/mm^2}; \qquad G \approx 90{,}600\ \mathrm{N/mm^2}.$$

These low moduli (compared to those of Si_3N_4) auger well for the thermal shock resistance of Si_2N_2O.

4) The dense material's Vickers hardness was measured, and the /47 results were comparable to those obtained for a sapphire sample under the same conditions.

SiN_2O_2	$H_{V10N} \approx 1{,}550$
Sapphire	$H_{v10N} \approx 1{,}800$

Other measurements have shown that the hardness increases when the MgO additive is replaced by Y_2O_3.

5) The actual study of thermal shocks was carried out on the samples (diameter: 20 mm, length: 16 mm) used for the PEO ultrasonic measurements. The specimens were exposed to increasing temperatures in an oxidizing atmosphere for a period of one hour. They were then plunged into 20°C water and agitated.

The conventional technique for checking degradation engendered by thermal shocks is to evaluate the breaking load R of test specimens subjected to increasingly severe shocks. As long as the temperature T remains below a critical value T_c, R is constant. For $T = T_c$ the first cracks appear and R decreases sharply [20]. For $T > T_c$, Hasselman's theory gives a good explanation of cracking [21]. This technique has two disadvantages: The destructive tests require a large number of samples, and it is impossible to examine the cumulative effect of multiple shocks. We therefore limited such tests to a few cases, preferring instead to work with ultrasonic nondestructive tests [22,23]. The same sample underwent successive shocks, of constant or increasing severity, and we measured the propagation speed V_L of longitudinal ultrasonic waves and the acoustic attenuation A after each cooling in the water bath. We once again resorted to the PEO method, this time at 6 MHz, for these measurements. Our results were compatible with the preceding data [22,23], in that V_L was not appreciably affected by thermal shocks, in contrast with A. Figure 3 shows that for dense Si_2N_2O, A does not vary (0.4 dB/μs) until $T_c \simeq 225$°C, where it registers a sharp increase ($A \simeq 2.4$ dB/μs). The attenuation remains constant as T increases above T_c. Crack detection confirmed that cracking appeared at T_c: There were a few large cracks extending across the sample. As the severity of the shocks increased, new cracks appeared at $T > T_c$. They were still few in number and of large size. Repeated shocks did not appreciably alter the cracking, which agrees with Hasselman's conclusions [21]. We have started to check the damage caused by destructive compressive stress breaking tests. The usual appearance of the curve obtained is given in figure 4. It has been pointed out that a certain amount of porosity has a beneficial effect on thermal shock resistance [24]. We therefore tested samples with $P \simeq 8\%$ and 16.5% (figure 3). The values obtained for T_c did not differ significantly from those observed in the dense material.

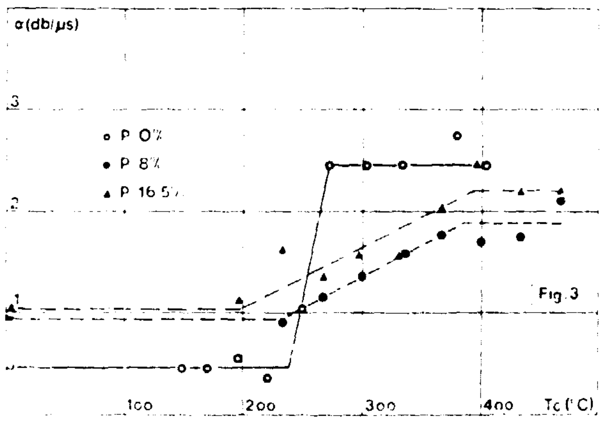

Figure 3

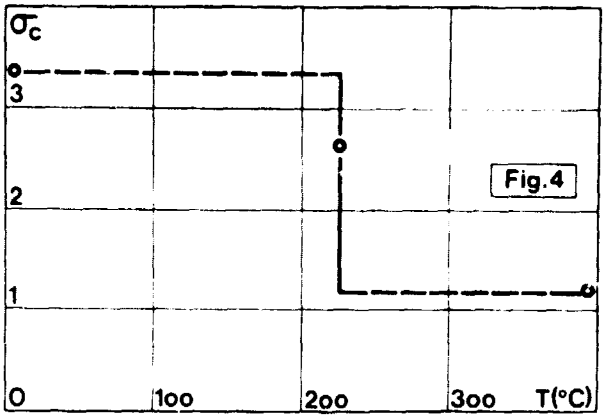

Figure 4

Calculation of the critical temperature T_c was based on the sample's thermal and mechanical characteristics. T_c does not play a direct role; rather it is the difference $T_c - T_{bath} = \Delta T_c$ that does. In fact, it has been mentioned [25] that dipping a sample at temperature T in water leads to a $\Delta T = T - 100$. The boiling point of water imposes a temperature of 100°C on the sample's surface, and the initial temperature of the bath is irrelevant. The relationship /48 between ΔT_c and the other parameters is given by [26]:

$$\Delta T_c \quad \frac{\sigma_t (1-\nu)}{3E\alpha\Psi} \qquad (\sigma_t, \nu, E, \text{ and } \alpha \text{ have already been defined.})$$

$$\psi^{-1} = 1.50 + \frac{3.25}{\beta} - 0.5\exp\frac{-16}{\beta},$$

$\beta = hd/k$ (β = Biot number, h = coefficient of thermal exchange, d= average dimension of the sample, k = thermal conductivity). For dipping in water, $h \simeq 1$ CGS unit [25,26]; $d \simeq 0.8$; measurement of our sample's thermal conductivity is in progress, but for impure i_2N_2O, a figure of $k \simeq 1.38 \times 10^{-3}$ cal-cm^{-1}-°C^{-1}-sec^{-1} has been obtained [27], which is a low value. This leads to $\beta > 500$. The thermal shock is thus very sharp, and $\Psi \simeq 1$. Here, therefore, $\Delta T_c \simeq 125$°C, which implies that $\sigma_t \simeq 287$ N/mm^2, which is in very reasonable agreement with the value of 250 N/mm^2 found in biaxial bending. The term

ΔT_c characterizes the "initiation" of the crack, and must be considered for parts in which no degradation is tolerable. The actual degradation engendered by a shock at $T > T_c$ is difficult to describe quantitatively. Meanwhile, the area of the cracks remains the least arbitrary method of evaluation. We have undertaken such measurements, and they will complete those of surface energy, which are also in progress.

While awaiting these results,it is possible to argue that, given its small coefficient of thermal expansion, its low Young's modulus, and its high tensile breaking load, silicon oxynitride that contains 5% MgO and is scintered under load is a refractory material with excellent resistance under thermal shock.

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