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Elastic properties of silicon oxynitride

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Silicon oxynitride is a refractory material which appears to exhibit good mechanical and thermal properties. This work studies the elastic properties of hot-pressed samples with an addition of 5 wt% MgO. The samples are isotropic and homogeneous, and the three different methods of measurement used, operating in the frequency range 20 kHz to 10 MHz, give similar results. Young's modulus and shear modulus are low (about 22×10^{10} Pa and 9×10^{10} Pa, respectively), which leads to small thermal stresses and thus allows a good thermal shock resistance. The elastic moduli decrease linearly when the porosity increases over the range of 0 to 27%. Poisson's ratio is sensibly a constant equal to 0.2, and the rate of variation is the same for both moduli: 2.5, this value being superior to what could be expected from the usual theories.

1. Introduction

A growing number of investigations are currently being carried out on vehicular gas turbines with high efficiency. Such turbines operate at high temperatures, and the main question is: what material can one use in the hot zones of the turbines? The best materials would be silicon carbide and nitrogen ceramics [1–4], particularly silicon nitride, Si_3N4, or eventually aluminium nitride, AlN.

These materials may become corroded in an oxidizing atmosphere (contrary to oxides) but exhibit interesting mechanical properties: low creep and good thermal shock resistance. In comparison to alumina, which has a thermal expansion coefficient, $\alpha \simeq 8 \times 10^{-6}\,\mathrm{m\,m^{-1}\,{}^\circ C^{-1}}$, and a Young's modulus of 40×10^{10} Pa, nitrogen ceramics have low thermal expansion coefficients and elastic moduli: thus, important thermal gradients may exist inside a sample before cracks develop. In addition, because the fracture energy of nitrogen ceramics is high, the propagation of these cracks is limited.

The Si–Al–O–N compounds as well as Si_3N_4 have been studied. The present work, however, is devoted to silicon oxynitride, Si_2N_2O. Because it is important to know the elastic moduli as well as other mechanical properties, we have studied these. Firstly, the values of the moduli influence the thermal shock resistance; secondly, any calculation of strains in a loaded sample calls for knowledge of the moduli; lastly, the elastic constants are intrinsic properties of material, directly connected to atomic bonding (as is thermal expansion) and thus cannot be improved, in constrast to what could be hoped for the toughness. Our study is essentially concerned with the relationship between elastic moduli and porosity, the main microstructural parameter.

2. Silicon oxynitride

Si_2N_2O was demonstrated to have an orthorhombic lattice, of space group $Cmc2_1$ [5]. Washburn [6] has shown it to be a refractory material. Therefore, a good resistance to oxidation and to molten nonferrous metals or salts would be the main advantage of using Si_2N_2O. In 1971, Billy *et al.* [7] found a method of preparation that yields high purity powders, from the reaction:

$$3Si + SiO_2 + 2N_2 \rightarrow 2Si_2N_2O,$$

from mixed powders ($Si + SiO_2$), which are first heated to 1350° C in an oxidizing atmosphere to prevent the formation of Si_3N_4, and then are nitrided for a few hours at 1450° C. In this way 95% pure Si_2N_2O is obtained, with less than 5% of β-Si_3N_4. Minute quantities of iron, chrominum, nickel and sodium remain after grinding and washing which eliminates silicon and silica. The mean particle size is 3 μm, and is always under

$20 \mu m$. We have chosen this method of preparation, and have hot-pressed the samples, with the addition of an oxide (MgO or Y_2O_3, 5 wt %) to improve the densification, which is difficult in the case of covalently bonded solids [1]. With MgO, a pressure of 33×10^6 Pa and an annealing time of 20 min at 1560° C in a nitrogen atmosphere, lead to a 100% densification, giving a density: $\rho_0 \sim 2.83 \text{ g cm}^{-3}$, which corresponds to the theoretical value. If the annealing time is reduced, a porous state can be obtained, the porosity P varying from 0 to 27%.

3. Experimental results

Three methods were used to measure Young's modulus E and the shear modulus G. We have verified that two moduli are enough to describe the elasticity of the samples, which are highly isotropic. X-ray diffractometry has shown no preferential texture, the sintered grains are randomly oriented and the agglomerate is statistically isotropic. This behaviour of Si_2N_2O is unusual: most of the hot-pressed ceramics are anisotropic, due to the orientation of the load. The methods used were:

(1) An ultrasonic "pulse echo overlap method" [8], with longitudinal or shear waves, in a frequency range 2 to 10 MHz, using cylindrical samples, (diameter = 20 mm, $l = 16$ mm). The apparatus allows measurements to be made as a function of temperature (up to 400° C) and pressure (up to 3×10^{10} Pa), to obtain temperature and pressure derivative of moduli. The acoustic attenuation A has also been measured.

(2) A "phase comparison method" [8], at 10 MHz, using thin samples ($e = 2$ to 3 mm) fixed at the end of a fused silica waveguide.

(3) A method of vibrating discs, between 20 and 40 kHz, using samples (diameter = 30 mm, $e = 2$ mm) resting on four points [9] and vibrating on the first two overtones. The elastic moduli are calculated from the resonance frequencies, and the internal friction Q^{-1} is measured by the decay of the free vibrations. It must be pointed out that this method is well suited to ceramic samples, such discs being easily obtained by sintering. Moreover, the discs can also be used to determine the biaxial strength, in a simple manner.

The microstructure was observed using a scanning electron microscrope, and a mecury porosimeter was used to evaluate the porosity. Three or four-point bend tests or a biaxial test were used to investigate the strength, and similarly, a three-point bend test on a notched beam (25 mm × 4 mm × 4 mm) was used to determine the critical stress intensity factor. Finally, the expansion coefficient was measured by dilatometry, using prismatic samples (35 mm × 6 mm × 6 mm).

4. Results and discussion

Except in the case of dispersive materials, where the elasticity varies as a function of frequency, or in the case of anelastic phenomena that introduce modulus defects [10], the elastic constants are independent of frequency. In fact, the three methods used (corresponding to the frequency range 20 MHz) lead to very similar results, with a scatter of $< 3\%$ for E in the dense material: a reasonable accuracy to expect. The results for the dense material, which was hot-pressed with an MgO addition, are shown in Table I. Added Y_2O_3, instead of MgO, or different sintering temperatures (in the range 1560 to 1750° C) give similar values for E and G (maximal scatter on moduli = 5%). It should be noted that different sintering conditions lead to different intergranular glassy phases.

(1) The results are independent of the method used, confirming that the samples are isotropic: the elastic moduli are very sensitive to the orientation of the crystals and the relationships between E and G and the velocities of travelling waves in an "infinite" medium (in case (1) above) or of stationary waves in a finite medium (case (3) above) give similar results only when the medium is isotropic. This point is reinforced by the fact that the samples were not the same for both experimental methods.

(2) Silicon oxynitride has low values of E and G, in comparison [11–15] to Al_2O_3 or SiC ($E \simeq 40 \times 10^{10}$ Pa), Si_3N_4 ($E \simeq 25 \times 10^{10}$ Pa), and nitrides or sialons (E from 20 to 30×10^{10} Pa). These low elastic moduli reduce the sensitivity of the material to thermal shock. The thermal expansion coefficient obtained was: $\alpha = 2.85 \times 10^{-6} \text{ m m}^{-1} {}^\circ\text{C}^{-1}$ from 20 to 200° C, and $3.55 \times 10^{-6} \text{ m m}^{-1} {}^\circ\text{C}^{-1}$ from 20 to 800° C, which is rather low. Moreover, the tensile strength is acceptable ($\sigma_t \simeq 2.5 \times 10^8$ Pa) and the toughness is rather high (critical stress intensity factor $K_{IC} = 4.4 \times 10^6 \text{ Pa m}^{1/2}$). Thus silicon oxynitride has a good resistance to thermal shock [16, 17].

(3) The temperature dependence of elastic moduli is slight, as shown by the low value of

TABLE I Elastic moduli versus porosity

Moduli	P (%)					
	0	5	10	15	20	25
30 kHz						
E (10^{10} Pa)	22.16	19.41	16.60	13.91	11.16	8.41
G (10^{10} Pa)	9.31	8.17	7.03	5.89	4.75	3.61
10 MHz						
E (10^{10} Pa)	21.56	18.81	16.07	13.33	10.59	7.85
G (10^{10} Pa)	8.97	7.83	6.69	5.55	4.41	3.27
10 MHz (phase comp.) $P = 0$, $E = 22.2 \times 10^{10}$ Pa, $G = 9.08 \times 10^{10}$ Pa						

TABLE II Temperature and pressure derivatives, acoustic attenuation and internal friction for $P = 0$

$\frac{1}{E}\frac{dE}{dT}$ (°C^{-1})	$\frac{1}{G}\frac{dG}{dT}$ (°C^{-1})	$\frac{1}{E}\frac{dE}{dp}$ (Pa^{-1})	$\frac{1}{G}\frac{dG}{dp}$ (Pa^{-1})	A (at 10 MHz) (dB μsec^{-1})	Q^{-1} (at 30 kHz)
-0.75×10^{-4}	-0.75×10^{-4}	-9.5×10^{-12}	-5.3×10^{-12}	0.5	2×10^{-4}

temperature derivative in the case of Si_3N_4 [13], which gives $1/E\ (dE/dT) \simeq 1\,1 \times 10^{-4}\ ^{\circ}C^{-1}$ between 20 and 800° C. The pressure dependence of elastic moduli is also slight. This is related to the low anharmonicity of atomic potentials, shown by the low thermal expansion coefficient. However, the signs of the derivatives are negative, which is unusual. It must be noted, however, that the elastics constants C_{ij} of single crystals only have a simple physical meaning [18], but not the moduli of a polycrystalline aggregate, especially if the lattice is not cubic and if the atomic bonding is essentially covalent, with a directive character. Moreover, the addition of oxide results in a vitreous phase being segregated at the grain boundaries [19], something which must be taken into account. We plan to study this pressure dependence in the future.

(4) Porosity is the main microstructural parameter acting on the elastic moduli. Fig. 1 shows the variations at room temperature of Young's and shear moduli as a function of porosity, from $P \simeq 0$ to $P \simeq 27\%$. E and G decrease linearly as P increases, with the same slope, Poisson's ratio ν being a constant equal to 0.2:

$$\frac{E}{G_0} \simeq \frac{G}{G_0} \simeq 1 - 2.5\,P$$

Several relationships have been proposed: elastic modulus M versus porosity [18], and a great number of ceramics have been tested using different measurement techniques. The oldest data relate to oxides, particularly Al_2O_3 and MgO, and support an exponential law: $M = M_0 \exp(-bP)$. It has been objected that this law does not lead to $M = 0$ when $P = 1$, but this objection seems to be a formal one, because the exponential law agrees well with experimental data for $P \leqslant 30\%$, and because a realistic model of porous material cannot be extrapolated up to $P = 100\%$. However, an extension of the exponential law to high porosity according to $M = M_0\ [1 - \exp\{-b'(1-P)\}]$ has been suggested. Other laws have been proposed [18], especially a homographic law [21] and a linear one: $M = M_0\ (1 - aP)$.

A linear relationship is often found in recent works, for instant in the case of silicon nitride [13] or of various rare-earth oxides (Yb_2O_3, Gd_2O_3, Sm_2O_3, Lu_2O_3, Sc_2O_3, Tm_2O_3 ...) studied by Hunter *et al.* [22]. In the past, the scattering of experimental data was important, and it was not possible to distinguish clearly the exponential from the linear laws. Now the improvement in the accuracy of the experiments enables one to select one of these laws. This improvement is due to the development of high frequency methods for measuring the elastic moduli more accurately than with static method, and also to better quality samples, chiefly with better isotropy and homogeneity. The higher quality is due to improvement in sintering techniques due to our knowledge of all the steps of densification. We particularly think that, amongst the different procedures for obtaining porous samples, the best one consists of variation

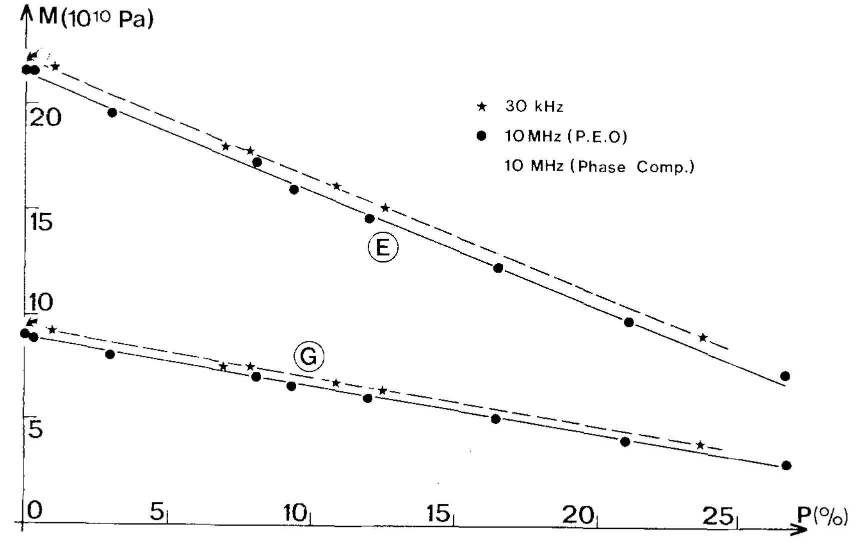

Figure 1 The variation of Young's modulus (E) and shear modulus (G) with porosity (P).

of sintering time. Indeed, other procedures varying the fineness of the powder or the sintering temperature give materials which differ not only in porosity but also in grain size or the nature and distribution of their intergranular phases. It is typical that recent experimental curves do not show the breaks in slope which were noted in older results (these were due to modifications of pore morphology associated with the increase of P). It should also be noted that the old data of a or b was very scattered, giving values from 1.5 to 6; now the a or b values are generally under 3, between 2 and 2.5, and values over 3 are associated with sample irregularities such as inhomogeneous porosity or microcracks. It is supposed [23, 24] that a and b depend on whether the porosity is open or closed, and are sensitive to pore morphology, pore homogeneity, and grain stacking. For spherical pores, a and b would be about 2; non-spherical pores would lead to a more pronounced variation. In effect, some examples [25] suggest that microcracks, which are the limiting case of elongated pores, considerably reduce the moduli.

It is clear from Fig. 1 that a linear law describes our results better than an exponential law. However, recent works [11, 26] claim that the ultrasonic velocities, and not the moduli, vary linearly with P: thus the relation $V \simeq (M/\rho)$ 1/2 and $\rho \simeq \rho_0\ (1-P)$ give E and G as a third power function of P. Thus, we have verified that the linear law is effectively the better one in our case. In particular, the correlation coefficient r of a least squares method is:

$$r_E = -0.9990;$$

$$r_G = -0.9990 \text{ (linear law on } E \text{ and } G)$$

$$r_E = -0.9924;$$

$$r_G = -0.9907 \text{ (exponential law on } E \text{ and } G)$$

$$r_{VL} = -0.9940;$$

$$r_{VS} = -0.9930 \text{ (linear law on } V_L \text{ and } V_S).$$

Such a linear law has been justified by Fate [13] in the frame of Budiansky's theory [27], which links the moduli and the porosity of a material by:

$$\frac{G}{G_0} = 1 - \frac{P}{1-c} \quad \text{and} \quad \frac{B}{B_0} = 1 - \frac{P}{1-d},$$

with G_0, B_0, G, B the shear and bulk moduli of dense and porous materials, c and d being:

$$c = \frac{2}{15}\left(\frac{4-5\nu}{1-\nu}\right) \qquad d = \frac{1}{3}\left(\frac{1+\nu}{1-\nu}\right)$$

if ν is the Poisson's ratio of the porous state. Here, $\nu = 0.2$, which gives $c = d = 0.5$. Thus:

$$\frac{g}{G_0} = \frac{B}{B_0} = \frac{E}{E_0} = 1 \text{ to } 2P \text{ and } \nu = \text{ a constant.}$$

It is only for this particular value of ν that the variation rates of both independent moduli would be the same, this being the case also for Si_3N_4. But for Si_3N_4 the experimental results do give $1{-}2P$, according to the theory, whereas our measurements on Si_2N_2O give $1{-}2.5P$. These measurements were accurate, the various methods gave the same results, and the samples were isotropic, thus we feel that the value of 2.5 may be considered as valid. Concerning the Mackenzie equations [28], which are also often cited, it can be written, neglecting the P^2 term:

$$\frac{G}{G_0} \sim 1 - \frac{15}{7}\left(\frac{1-\nu_0}{7-5\nu_0}\right)P$$

and

$$\frac{E}{E_0} \sim \frac{\nu+1}{\nu_0+1}\left[1 - \frac{15}{7}\left(\frac{1-\nu}{7-5\nu_0}\right)P\right]$$

which for $\nu \simeq \nu_0 \simeq 0.2$ leads to the same results as Budiansky's theory:

$$\frac{G}{G_0} = \frac{E}{E_0} \simeq 1 - 2P.$$

Hence, both Budiansky's theory and Mackenzie's theory seem to be only a first approximation in the description of the elastic behaviour of porous silicon oxynitride. Wachtman [18] pointed out that the theoretical equations correctly predict the slope in normal polycrystalline ceramics being higher numerically. For instance, in the rare earth oxides [22], it is occasionally observed that the "theoretical" and experimental slopes are the same. In fact, non-spherical pores, or different packing types [20] may explain, *a posteriori*, any value of a or b between 1.2 and 9.

Figs. 2 and 3 show the microstructure of porous Si_2N_2O samples, for 8 and 23% porosity. It is difficult to see the grain boundaries, in spite of the fact that etching treatments have been used. It seems that, only the glassy phases are etched, these phases being irregularly distributed: hot-

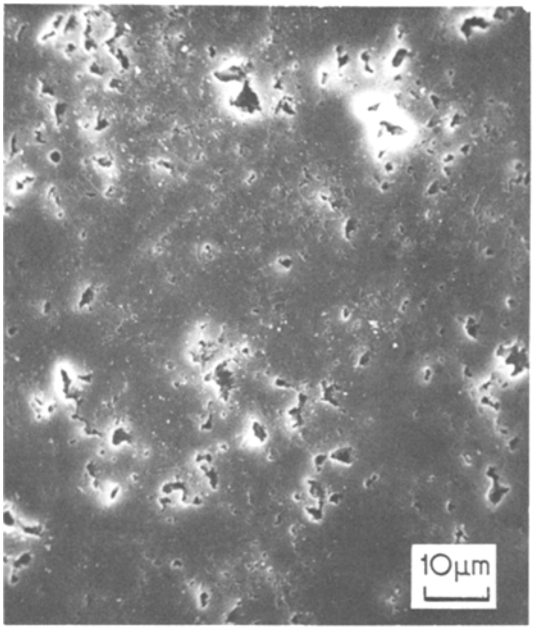

Figure 2 The microstructure of Si_2N_2O with 8% porosity.

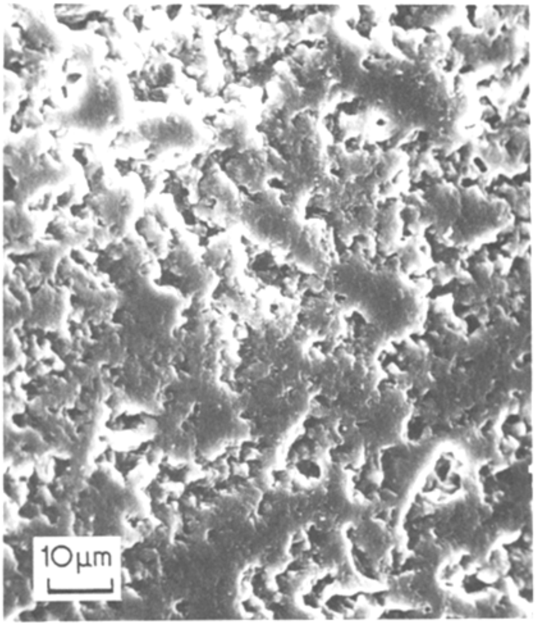

Figure 3 The microstructure of Si_2N_2O with 23% porosity.

pressed nitrides contain boundaries of at least two types, namely those between the crystallites of the initial particles and those between the particles themselves. Of these, the first are probably clean, whereas the second are associated with a glassy phase [19]. However, when it is possible to see such boundaries the grain shape appears to be rather regular, the mean grain size being several microns, identical to the size of the initial particles: the sintering temperature was low, and a secondary recrystallization was not expected. Some large grains (20 μm) are found, but it is plausible that they were in the initial powder. In the 8% porous sample, pores are very homogeneously distributed but in the 23% porous sample, the porosity appears to be homogeneous, but a careful examination shows that some areas are more porous than others. It seems [23] that such heterogeneity has little influence in the present case where the relationship between moduli and porosity is linear. The pores are not spherical, but ellipsoidal in shape, the pore dimension being larger along the directions perpendicular to the direction of the load during hot-pressing than along the latter direction (the c/a ratio of such an ellipsoidal pore being about 3 for $P = 8\%$ and about 1.5 for $P = 23\%$). This point could justify [24] the fact that E and G decrease faster than when the pores are spherical. Moreover, the pore boundaries are irregular, and the term "ellipsoidal" is an approximate one. In addition, the orthorhombic lattice of Si_2N_2O must be responsible for stresses at grain boundaries, due to the anisotropic thermal expansion (contrary to the case of cubic crystals), such stresses not being taken into account in the theoretical models. We propose to alter the sintering conditions, in the hope of obtaining different pore morphology: it is expected that in this way further information will be obtained.

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