

Anelastic relaxation associated with the intergranular phase in silicon nitride and zirconia ceramics

A. Lakki and R. Schaller

Ecole Polytechnique Fédérale de Lausanne, Institut Génie Atomique, CH-1015 Lausanne (Switzerland)

Abstract

Mechanical spectroscopy measurements were performed at high temperature in silicon nitride and zirconia ceramics, using a forced inverted torsion pendulum. In both materials a steep modulus decrease is observed together with anelastic relaxation phenomena. They could have their origin in the glassy intergranular phase present in these materials, which is also controlling creep behaviour.

Analysis of the spectra assuming a grain boundary sliding model, shows a good correlation with the results of creep tests performed on the same materials. In zirconia, the activation energy values and the sensitivity to microstructural parameters as obtained by both techniques, are very close. In the case of silicon nitride, the observed irreversible evolution of the mechanical loss spectra with thermal history could be correlated with the crystallization of the intergranular phase.

1. Introduction

Most polycrystalline ceramic materials, including zirconia and silicon nitride, are known to contain an intergranular glassy phase, originating from the residual impurities and sintering aids. This phase is generally believed to influence the high temperature creep behaviour of the materials [1–4], the principal deformation mechanism being grain boundary sliding. The exact micromechanisms are, however, not yet fully understood. An attempt to study the viscosity of the intergranular phase has been undertaken, by using the method of mechanical spectroscopy [5], which is particularly sensitive to the evolution of the microstructure (*i.e.* crystallization) and well adapted to the study of viscous friction mechanisms [6].

2. Experimental details

Two different fine-grained ceramic materials were studied in this work: 2 mol.% Y_2O_3 -doped tetragonal zirconia (ZrO_2) and silicon nitride (Si_3N_4).

The zirconia samples (Laboratoire de Céramique, Département des Matériaux, Ecole Polytechnique Fédérale Lausanne) were prepared by cold isostatic pressing (250 MPa) and air sintering (3 h at 1400 °C) of fine powders (Tosoh Corporation, Tokyo) having two different impurity (SiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O) contents: (a) ≈ 2000 ppm, (b) ≤ 250 ppm. In the “impure”

material, the impurities form a glassy intergranular phase, while in the “pure” material grain boundaries are almost clean [7, 8].

The silicon nitride samples (Céramiques Techniques Desmarquest, France) were obtained by slip-casting and pressureless sintering of commercial Si_3N_4 powder using 10 wt.% (Y_2O_3 , Al_2O_3 , AlN) as sintering aids. These form, by reaction with the residual SiO_2 impurities and the Si_3N_4 matrix, an intergranular phase (YSiAlON) which initially is glassy.

The measurements were carried out in a forced inverted torsion pendulum [9] in the frequency range 1 mHz to 10 Hz and at temperatures between 1100 K and 1600 K. The relative temperature gradient along the specimens is less than 0.5%. The measurements (mechanical loss angle $tg(\phi)$ and normalized elastic shear modulus G/G_{300K}) were performed either as a function of temperature at fixed frequencies or as a function of frequency at fixed temperatures.

3. Results

A typical spectrum obtained for the zirconia samples at high temperature is shown in Fig. 1. One observes an increase in the mechanical loss angle (“damping”) with temperature in parallel with a decrease in the elastic shear modulus. These phenomena are steeper for the samples with higher impurity content (and thus larger quantity of glassy intergranular phase). On the

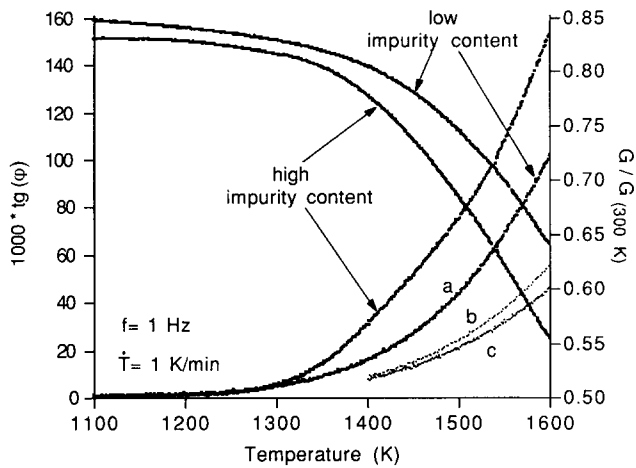


Fig. 1. High temperature parts of the mechanical loss spectra (mechanical loss and normalized elastic shear modulus) of 2 mol.% Y_2O_3 -doped zirconia samples with different impurity content (frequency $f = 1 \text{ Hz}$, heating rate $dT/dt = 1 \text{ K min}^{-1}$). Influence of the grain size d : "pure" material: a, $d = 0.34 \mu\text{m}$; b, $0.69 \mu\text{m}$; c, $1.00 \mu\text{m}$. "Impure" material: $d = 0.40 \mu\text{m}$.

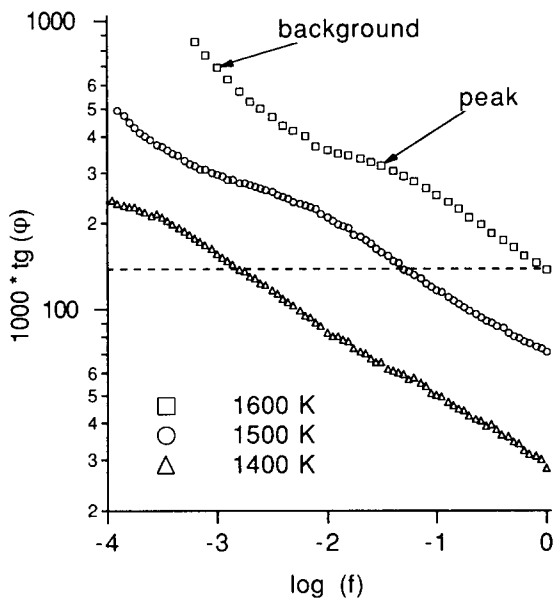


Fig. 2. Isothermal mechanical loss angle spectra as a function of frequency of the less pure zirconia samples. The spectra consist of a peak which is superposed on an exponential background. From the shift of the spectrum the activation energy can be obtained (see Fig. 3).

same graph the influence of grain size is shown: the increase in mechanical loss is found to be approximately inversely proportional to the grain size. To further analyse the spectra, isothermal measurements were performed, shown in Fig. 2. It then appears that the spectrum is, in fact, composed of a mechanical loss peak, superposed on an exponential background. The peak is, however, not well resolved from the background. From the shift of the spectra (either isothermal at

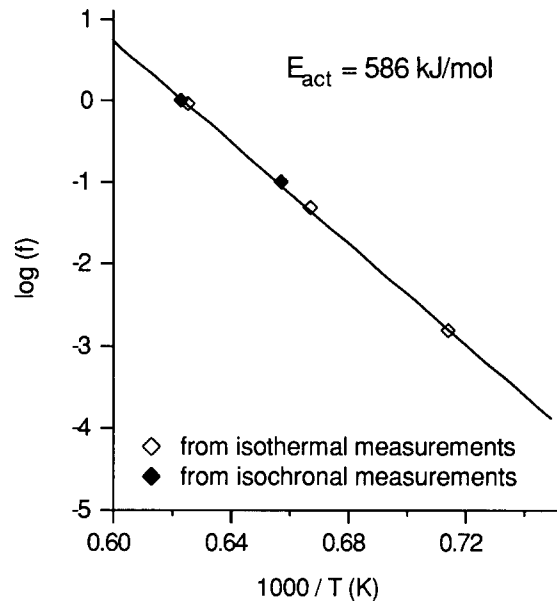


Fig. 3. Arrhenius plots from the shift of the mechanical loss spectra, obtained simultaneously by isothermal and isochronal measurements.

TABLE 1. Comparison of apparent activation energies obtained for zirconia by mechanical spectroscopy and creep tests

| Method | Zirconia | |
|------------------------------|--------------------------|--------------------------|
| | high impurity content | low impurity content |
| Mechanical loss measurements | 586 kJ mol ⁻¹ | 634 kJ mol ⁻¹ |
| Creep tests | 580 kJ mol ⁻¹ | 620 kJ mol ⁻¹ |

different temperatures or isochronal at different frequencies) at a fixed mechanical loss value, the associated apparent activation energy values have been obtained (Fig. 3) and compared with the corresponding creep activation energies [10] (Table 1).

In the case of silicon nitride, the typical spectrum consists of a well-resolved mechanical loss peak, superposed on an exponential background, together with a modulus defect (Fig. 4). These phenomena are present in the "as received" state but disappear irreversibly upon cooling. The peak is a relaxation phenomenon which can be studied by isothermal measurements, some of which are shown in Fig. 5. From these, the associated activation parameters have been deduced (Fig. 6).

4. Discussion

Creep tests performed in the low stress regime ($\sigma < 15 \text{ MPa}$) on the same zirconia materials have shown that the creep rate (at 1623 K, 10 MPa) is higher for the

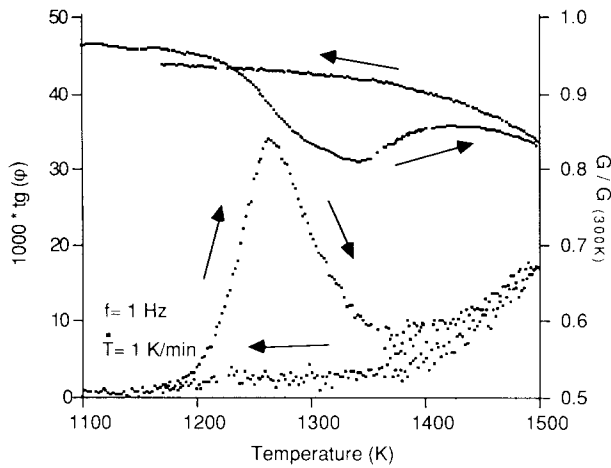


Fig. 4. High temperature mechanical loss spectrum of an $\text{Si}_3\text{N}_4\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-AlN}$ material (frequency $f=1$ Hz, heating rate $dT/dt=1$ K min^{-1}). In the “as received” state, a mechanical loss peak appears, superposed on an exponential background and accompanied by a shear modulus defect. Both phenomena disappear irreversibly in the measurement on cooling.

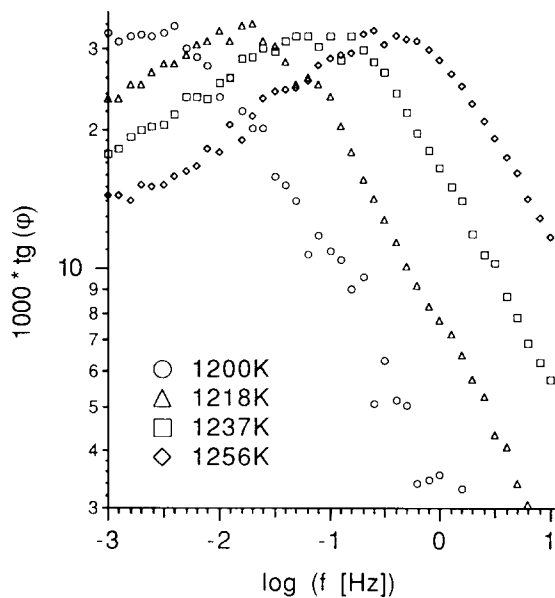


Fig. 5. Shift of the mechanical loss peak of silicon nitride on changing the measurement temperature.

sample containing more impurities; the stress exponent is found close to 2 and the grain size exponent is 1 [7]. These facts, together with the creep activation energy values (see Table 1), led Nauer to the interpretation of the creep at low stress as being due to a grain boundary sliding mechanism. Thus there appears to be a close relation between creep and damping behaviour in these materials as regards (a) the influence of glassy phase content, (b) the dependence on grain size and (c) the activation energy values obtained by the two techniques. If one assumes a grain sliding model to analyse the mechanical loss spectra [10], with a

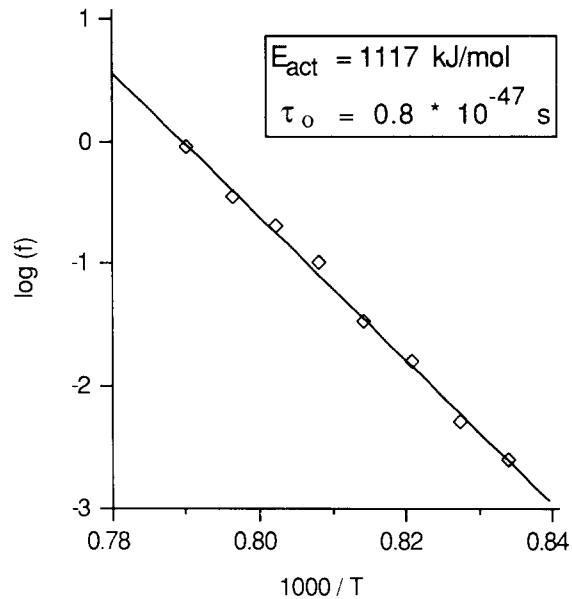


Fig. 6. Arrhenius plot obtained from the shift of the peak of silicon nitride, obtained by isothermal measurements, some of which are shown in Fig. 5.

viscosity term due to the intergranular glassy phase and a restoring force term due to the triple points, one obtains a mechanical loss peak, which evolves into an exponential background when the restoring force vanishes (compare with Fig. 2). In this model, the relaxation time τ is directly related to the viscosity η of the intergranular phase, which can then be estimated to take values of about 10^{10} Pa·s at 1300 K and follows an Arrhenius law, with activation energies as in Table 1. Such viscosity values are typical for glasses above the glass transition temperature ($\eta(T_g)=10^{12}$ Pa·s), i.e. in a temperature range where they are “soft enough” to allow grain boundary sliding to occur.

As was the case for zirconia, the main creep mechanism in silicon nitride is considered to be grain boundary sliding [11]. The difference between the two different ceramics studied in this work is that in silicon nitride the grain morphology is irregular and the thickness of the intergranular layer varies between a few nanometres at thin boundary films and some tenths of micrometres at triple point pockets. In the initial state the whole phase is amorphous. Observation by transmission electron microscopy (TEM) of samples after mechanical spectroscopy measurements (i.e. when the peak had completely disappeared) has shown that the phase had almost completely crystallized except for some residual glassy regions [12]. Thus it seems that the peak is related to the viscosity of the glassy phase and, again using a simple grain sliding model [6] which gives the viscosity per unit grain boundary layer thickness (η/δ) as a function of the relaxation time τ and of a material parameter β ($\beta(\eta/\delta)=\tau/\beta$), one obtains viscosity values

typical for a glass at temperatures above T_g . So one estimates η ($T=1200$ K) $\approx 10^{10}$ Pa·s, η ($T=1300$ K) $\approx 10^8$ Pa·s.

The activation energy obtained by creep tests at 100–200 MPa, $T > 1530$ K, is of the order of 860 kJ mol⁻¹, while the value obtained for the mechanical loss peak (Fig. 6) is 1117 kJ mol⁻¹. This difference could derive on the one hand from the difference between the applied stresses (amplitude 3 MPa in the torsion tests) and on the other hand from the different temperature range ($T < 1300$ K in Fig. 6). In fact, the activation parameters determined in Fig. 6 are apparent values [13], due to the large entropy term in glasses which is temperature-dependent. However, the product $\tau_0 \exp(E_{act}/kT)$ still gives the relaxation time τ which is proportional to η and leads to the afore-mentioned viscosity values.

5. Conclusion

Mechanical loss measurements carried out on two ceramic materials (zirconia and silicon nitride) containing an intergranular glassy phase revealed anelastic relaxation phenomena which seem to be related to the quantity and viscosity of the intergranular phase. In both materials, analysis of the spectra in terms of a grain boundary sliding model led to viscosity values typical for a glass above its glass transition temperature. In zirconia, the agreement between the influence of microstructural parameters and the activation energy values obtained by the mechanical loss spectra and creep tests was very close, indicating that grain boundary sliding is the damping mechanism. In silicon nitride, a relaxation peak is observed, which also seems to correlate with a mechanism of grain sliding, and which

disappears irreversibly when the intergranular phase crystallizes during heat treatment.

Acknowledgments

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