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Anelastic Grain-Boundary Sliding in Ceramics. II. Polycrystals with Glassy Boundaries

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Abstract. Systematic experimentation on grain-boundary sliding of ceramics with a glassy film at grain boundaries has been carried out by low-frequency internal friction technique up to $\approx 2200\text{K}$. A model silicon nitride polycrystal was selected for this basic investigation in which the grains were continuously encompassed by a nanometre-sized film of pure SiO_2 glass. The SiO_2 film was also doped with increasing amounts of two different glass-network modifier anions (i.e., F and Cl) in order to systematically lower its bulk viscosity. For comparison, a very dilute sialon material was also tested in which the grain-boundary film was eliminated and the grains were directly bonded. An internal-friction peak, whose top displayed just below the melting point of the grain-boundary glass, was systematically found, the shift of the peak upon frequency variation or dopant addition being closely related to the viscosity change of bulk SiO_2 glass. For comparison, a dilute sialon material, in which the grain-boundary film was eliminated, was also tested. The anelastic peak of internal friction disappeared in this latter material and only a viscoelastic background rising could be detected.

1. INTRODUCTION

Since the early discovery of the grain-boundary peak of internal friction in polycrystalline metals [1], controversy has arisen about its actual origin. According to the original interpretation, the peak should arise from viscous sliding of grain boundaries, the main evidence supporting this thesis being the clear dependence of the peak strength on the amount of grain-boundary surface area present in the specimen or its absence in single-crystals. In the interpretation of grain-boundary sliding in metals, a major hint was provided by the theory of "amorphous cement" [2], according to which a layer of very thin, but finite, thickness should be associated to each grain boundary. In such a layer, the random arrangement of atoms would imply the existence of a "boundary phase" whose properties are those of a vitreous material. There are, however, as a counterpart to this interpretation, a number of physical concerns dealing with the actual meaning of viscosity in a directly bonded polycrystal.

In this paper, we have followed an alternative experimental approach with focussing on highly covalent ceramic polycrystals, namely a silicon nitride and a dilute sialon materials. The goal was to establish a clear relation between the anelastic internal-friction peak in polycrystals and the viscous slip of their internal grain-boundaries. Two basic characteristics may make these materials rather suitable for the above purpose: (1) any intragranular dislocation activity can be reasonably excluded up to very high temperature, at least under the stress level usually applied for internal friction measurement; (2) a glassy film (i.e., an amorphous cement) actually exists at grain boundaries as a thin channel of constant thickness [3] soaked with a low-melting glassy phase. The difference of melting point between the intergranular phase and the crystal grains is generally so large to exclude any conspicuous plastic deformation of the grains in a wide range of testing temperature. Thus, any relaxation peak is likely to be directly related to grain-boundary sliding without being overlapped by transgranular phenomena of diffusive or other origin.

2. EXPERIMENTAL PROCEDURE

Two viable approaches are available to characterize the grain-boundary peak in ceramic polycrystals

with a glassy boundary. One is that of varying the frequency of the measurement and, hence, the temperature at which the peak top is revealed. In such a way, for a fixed composition of the intergranular glass, both the viscosity value and the activation energy of the peak can be monitored according to peak-shift method [4]. Another approach consists of systematically lowering the bulk viscosity of the glassy film by addition of increasing amounts of anion dopant. Then, the temperature shift of the peak top is monitored at a fixed frequency. Also in this latter experiment the goal is to compare the grain-boundary viscosity value, as derived from internal friction experiments, to the viscosity value determined by macroscopic measurements on bulk glasses with the same composition. Particularly effective is thought to be the comparison of the scaling viscosity (i.e., owing to increasing dopant addition) between film and bulk glass. In our investigation, we have followed both the above approaches.

The silicon nitride polycrystal investigated in this study was a hot-isostatically pressed material, prepared from a high-purity powder and fully dense. The SiO_2 film arose from an oxidation process of the raw powder. F or Cl dopant were intentionally introduced into the polycrystal through the addition of pulverized polytetrafluoroethylene (i.e., Teflon) or hexachloroethane, respectively, to the starting ceramic powder. The chemical procedures were optimized in order to leave out into the polycrystal only F or Cl ions, without contemporary introducing hydrogen, which is also a glass-network modifier, and complicates the interpretation of internal friction data. The dilute sialon material was prepared by gas-pressure sintering process (from the same starting silicon nitride powder) upon addition of stoichiometric amounts of AlN and Al_2O_3 phase. Then, upon an optimized annealing cycle, the grain-boundary film could be almost eliminated through transgranular solid-solution effect of the oxygen species. Since the obtained solid-solution was very dilute, no significant softening of the bulk crystal structure of the grains was expected. High-resolution microscopy inspection on the silicon nitride polycrystal [5] revealed the presence of a continuous SiO_2 film 1 nm thick located at grain boundaries. The presence of anions caused a slight widening of the grain-boundary film, namely an increase in thickness of ≈ 0.1 nm. Any glassy film could not be detected at grain boundaries of the dilute sialon material up the angstrom resolution of the electron microscope. The actual segregation of the anion impurities in the glassy- SiO_2 intergranular phase was confirmed by spectroscopy microanalyses performed contemporary to microscopy.

The apparatus utilized for measuring simultaneously internal friction and shear modulus was a torsional pendulum of the same type used by Ke [1]. Nitrogen atmosphere was selected in order to minimize the decomposition process of the present materials during the measurements. Data were automatically collected from room-temperature up to $\approx 2200\text{K}$ at 5K intervals, according to the free-decay method [4]. Experiments were conducted in the frequency range between 3 and 15 Hz on rectangular bars $2 \times 3 \times 50$ mm, in dimensions.

3. RESULTS AND DISCUSSION

Internal friction data for the undoped silicon nitride and dilute sialon samples are shown as a function of temperature in Fig.1. The curves were found to be stable with respect to subsequent cooling and further measurement runs. The curve for the silicon nitride material showed a well-defined relaxation peak located at 1983K, namely nearby the melting point of pure SiO_2 glass. On the other hand, in the dilute sialon material, owing to the elimination of the grain-boundary film, no anelastic peak could be detected. In Fig.2, the peaks detected at different frequencies are shown after the subtraction of the respective viscoelastic backgrounds. The background curves could be precisely defined by virtue of the measurements at very high temperature and fitted by an exponential curve. The peak shifted consistently to higher temperatures with increasing the frequency of the measurement, as explicitly indicated in Fig.2. The activation energy calculated from the peak shift was 410 ± 30 kJ/mol, namely in fairly good agreement with that for the change in viscosity of high-purity SiO_2 glass [6].

The anelastic internal-friction peak component is shown in Fig.3 for the F and Cl doped silicon nitrides, in comparison with that of the undoped samples. As clearly envisaged in these data, anion addition produces a well definite shift of the peak towards lower temperatures. The peaks, representing the grain-boundary relaxation process, tend also to become broader with increasing the amount of dopant incorporated in the material, particularly evident being the effect of the Cl anion. The internal friction peaks of undoped and doped samples were related to the grain-boundary viscosity at the respective peak-top temperature [7], these values being displayed in the plot of Fig.4. In a comparison with the respective viscosity values from macroscopic experiments on bulk glasses, an order-of-magnitude agreement is found. Both the dependence of viscosity upon temperature as found by the peak shift method for pure SiO_2 glass and the scaling of the viscosity value with increasing the F content are almost the same as those of the bulk glass. This evidences may strengthen the thesis of anelastic relaxation by grain-boundary sliding.

A complete quantitative analysis of the peak-width broadening effect upon dopant addition has

been carried out in a separate paper, taking into consideration the peak broadening effect due to the distribution of grain-boundary orientations within the polycrystal [8]. For brevity's sake, we shall limit our treatment here to consider the expression which relates of the full width at half height, W_s , to the activation energy, H , for a single-relaxation (i.e., Debye) peak [4]:

$$W_s = 2(\cosh^{-1}2)R/H \quad (1)$$

where R is the gas constant. Equation (1) indicates that, even under the simplified assumption of single-relaxation peak, a decrease in activation energy, H , related to the change in glass viscosity, will lead to a peak broadening effect. From Fig.4 a decrease in activation energy is indeed envisaged by the lowered slope, H/R , of anion-doped bulk glasses as compared to the undoped one. Hence, physical consistency is recognized in the present experimental results.

The data shown in this paper may provide evidence for relating grain-boundary sliding to the anelastic internal-friction peak of ceramic polycrystals with a glassy film at grain boundaries. In the light of the present evidences, internal friction technique appears to be a powerful tool for characterizing atomistic processes taking place within the intergranular glassy film of polycrystalline ceramics.

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Figure 1: Internal friction curves as a function of temperature for the polycrystalline silicon nitride with pure glassy-SiO₂ film at grain boundaries and the dilute sialon polycrystal in which the SiO₂ grain-boundary film has been eliminated.

Figure 2: Frequency shift of the grain-boundary relaxation peak of polycrystalline silicon nitride with the pure SiO_2 film at grain boundaries. The respective exponential-like backgrounds have been subtracted from the experimental data.

Figure 3: Internal friction peaks of silicon nitride polycrystals with F- or Cl-doped SiO_2 film at grain boundaries. The measurement were done at the frequency of ≈ 13 Hz. The indicated amounts of dopant represent the total wt% of anion in the material.

Figure 4: Arrhenius plot showing a comparison between viscosities of the grain-boundary film, as obtained by internal friction measurement, and viscosities of the bulk glasses by macroscopic measurement. The dopant amounts represent the wt% of dopant segregated in SiO_2 glass.