

High temperature internal friction measurements of 3YTZP zirconia polycrystals.

High temperature background and creep

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Abstract: This work focuses on the high-temperature mechanic properties of a 3 mol % yttria zirconia polycrystals (3YTZP), fabricated by hot-pressureless sintering. Systematic measurements of mechanical loss as a function of temperature and frequency were performed. An analytical method, based on the generalised Maxwell rheological model, has been used to analyse the high temperature internal friction background (HTB). This method has been previously applied to intermetallic compounds but never to ceramics, except in a preliminary study performed on fine grain and nano-crystalline zirconia. The HTB increases exponentially and its analysis provides an apparent activation enthalpy which correlates well with that obtained from creep experiments. This fact shows on the one hand the plausibility of applying the generalised Maxwell model to ceramics, and on the other hand indicates the possibility of using mechanical spectroscopy as a complementary helpful technique to investigate the high temperature deformation mechanism of materials.

Keywords: Mechanical spectroscopy; ZrO₂; Ceramics; Internal friction; Creep.

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1. Introduction

Ceramics materials possess a unique blend of physical, chemical and mechanical properties (high wear-resistance, hardness, strength, thermal-chemical stability...) which makes them suitable in a wide variety of technological applications, especially under extreme conditions. Moreover, they can exhibit a superplastic behaviour by decreasing the grain size. This fact was first reported for yttria tetragonal zirconia polycrystal [1], and then this material has been the subject of numerous studies [2-5]. As a result of these investigations, grain boundary sliding has been recognized as the main deformation mechanism for yttria tetragonal zirconia polycrystal, with an apparent activation enthalpy between 5 and 7 eV, depending on the experimental conditions [6]. From a physical and technological point of view it becomes essential identifying the deformation mechanisms that operate in a material in order to predict its mechanical response under certain conditions. Creep provides information to understand how a material deforms at high temperatures because some parameters intrinsically related to the operating deformation mechanisms, like the activation energy and the stress exponent, can be obtained from these experiments.

Mechanical spectroscopy is a technique which operates in the an-elastic range, applying an oscillating stress to a specimen and then inducing the structural defects motion (point defects, dislocations...). The mobility of these defects, which is intrinsically related to the mechanical properties of material, can be investigated by this technique.

Furthermore, mechanical spectroscopy has also the advantage of being a non-destructive technique, and therefore very useful when not much material is available and many experiments have to be performed under different conditions. At high temperatures, the HTB analysis provides an apparent activation enthalpy similar to the one measured by creep tests. Thus, Schaller et al. [7] studied 3 mol % yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP), with an average grain size of 0.29 μm , obtaining an apparent enthalpy energy of about 5.6 eV. Donzel et al. [8] studied the same material but with different grain size and they managed to observe a relaxation peak, called Peak II, related to the well-known threshold stress exhibited by this material. A more extended study was performed by Donzel et al. [9] on YTZP with different grain sizes and sintered with different amounts of intergranular phase. They observed another relaxation peak (Peak I) in samples with low purity which was attributed to the glass transition of the amorphous pockets. These two peaks were

already observed in silicon nitride [10-11], where a relationship between standard equation for high temperature strain rate and mechanical loss was established. Recently, a preliminary study performed on micro and nano-crystalline zirconia was reported where nano-3YTZP specimens exhibited a higher increase of the internal friction HTB compared to micro-3YTZP, due to a higher effective grain boundary area associated to the former [12].

In this work we show the experimental results obtained by mechanical spectroscopy performed on 3YTZP and the analysis using the generalised Maxwell model. We compare them to the ones previously obtained by means of others analytical methods, and also to the activation parameters obtained by creep in 3YTZP. So, the purpose of this paper is twofold. Firstly, we want to show that mechanical spectroscopy is a complementary technique together with creep experiments which seems to be very valuable to investigate the high temperature deformation mechanisms, so important for technological applications. And secondly, on the light of the coherent results obtained in this work, the generalised Maxwell model can be applied for the experimental data analysis in ceramics.

2. Experimental details

2.1. Material

High purity commercial 3 mol % yttria-zirconia powder, with 30 nm particle size, was supplied by Tosoh, Japan. Powders were prepared by cold isostatic pressing at 300 MPa. The compact pieces were sintered in a conventional super-kanthal furnace at 1450 °C for 4 hours, with a heating and cooling rate of 600 °C/h. Dense specimens were fabricated with a density, measured using Archimedes' method, close to 100 %.

2.2 Microstructural characterization

The microstructure of the sintered samples was observed by high resolution scanning electron microscopy HRSEM (Model HITACHI S5200, Electron microscopy service, University of Seville, Spain) operating at 5 kV using backscattered and secondary electrons. Prior to observation, the samples were polished with diamond paste of grain sizes down to 1 µm. Then, they were annealed for 30 min at 1400°C to reveal grain boundaries. To study of 3YTZP grain morphology, the grain diameter (d ; defined as $d =$

$(4 \times \text{Area} / \pi)^{1/2}$), and the form factor (F; defined as $F = 4\pi \times \text{Area} / (\text{Perimeter})^2$) were measured from HRSEM micrographs.

2.3. Mechanical spectroscopy

Sintered samples were cut for mechanical spectroscopy with dimensions of 30 mm x 5 mm x 1.3 mm. The equipment used in this work has been developed few years ago [13] and is based on an inverted torsion pendulum. It can measure the internal friction and the dynamic shear elastic modulus in two different working modes: (a) as a function of temperature (300 – 1800 K) at imposed frequency, and (b) as a function of frequency (10^{-3} – 10 Hz) in isothermal conditions. Here we describe its main components:

- An anti-vibratory system to provide stability to the pendulum, composed by three Newport I-2000 laminar flow pneumatic dampers and two synthetic marble flagstones.
- A high vacuum system (10^{-4} Pa) is essential for many reasons: (i) to reduce the noise coming from the transmission of external acoustic vibrations (ii) to avoid overheating of the mechanical system and (iii) to prevent sample oxidation or contamination at high temperatures. This vacuum system consists in a Boc Edwards RV8 rotary vane pump and a Leybold Turbovac 340 M Turbomolecular pump, provided by two pirani and penning vacuum sensors.
- A graphite resistance tubular furnace, which by radiation can heat up to 1800 K. The temperature control system is carried out with a stability of ± 0.1 K by a Eurotherm 3504 PID controller, which regulates the power sent to the furnace by a SM 300-10D Delta Elektronika supply.
- An excitation-detection system. A permanent magnet is excited by two Helmholtz coils driven by a KEPCO power supply, which amplify the sinusoidal signal from a Solartron frequency analyzer. The response signal due to the torsion angle is detected by the displacement of the laser beam spot on a photocell. This response is filtered, magnified and sent to the frequency analyzer which measures the phase lag between the excitation and the response signal. The oscillating strain is measured through an Agilent 34970A voltmeter.

In this work the internal friction of 3YTZP has been measured at temperatures between 800 and 1650 K and oscillating stress frequencies between 0.01 and 3 Hz.

3. Experimental results and analysis

The microstructure of the sintered-3YTZP shown in Fig. 1 predominantly consists of equiaxed grains in the submicrometric size range. The analysis of the grain size and form factor distributions showed an average grain size of 0.6 μm and a shape factor around 0.7. Neither pores nor cavities are observed between grains, which is coherent with the full densification measured by the Archimedes' method.

Fig. 2 shows the mechanical loss measurements performed on 3YTZP as a function of the temperature for an oscillating stress frequency of 0.3 Hz. The dynamic shear elastic modulus variation is also plotted, and its smooth behaviour indicates that nothing strange took place during the test, like a specimen failure, cracks... No peak is observed from 800 to 1300 K, and above this temperature the internal friction experiences an exponential increase, which is relatively monotonous in the whole high temperature background (HTB) region. That indicates the uniqueness of the nature of the microstructural units stimulated during the experiments.

The internal friction versus temperature for different oscillating stress frequencies is shown in Fig. 3. All the measurements have been carried out with an initial oscillating amplitude at room temperature of $\epsilon=10^{-5}$ and a heating rate of 1.5 K/min. It is clear that the internal friction value increases by decreasing the frequency, and in all cases we observe an exponential increase in the high temperature background region. That indicates that in the range of temperatures and frequencies studied here the microstructural units stimulated have the same nature. Thus, only one process is being thermally activated, although it could be the result of the coupling of several individual mechanisms related to the grain boundary sliding.

The high-temperature background (HTB) is determined by viscoelastic relaxation. For mechanical spectroscopy analysis we use the generalised Maxwell model, assuming that the high temperature background HTB of the internal friction Q^{-1} is written as [14]:

$$Q^{-1} = 1/(\omega\tau)^n \quad (1)$$

being ω the oscillating stress frequency, τ the relaxation time and n a parameter that corresponds to the distribution of the relaxation times. The parameter n takes values between 0 and 1, for ideal viscoelasticity. Taking logarithm in Eq. (1) we obtain:

$$\ln Q^{-1} = -n \ln \omega - \ln \tau^n \quad (2)$$

Since viscoelastic behavior is determined by thermally-activated processes, an Arrhenius equation is expected for the relaxation time τ :

$$\tau^* = \tau^n = \tau_0^n \exp(n H_{act}/k_B T) \quad (3)$$

τ^* being the apparent relaxation time. Since the dissipated mechanical work during plastic deformation is proportional to the strain rate, Q^{-1} is proportional to this later quantity. Thus the activation enthalpy displayed in Eq. (3) should be coincident with the activation energy for creep [10]. From the experimental results shown in Fig. 3, we have selected different temperatures and for each one we have reported the internal friction value as a function of the frequency. Then we have plotted the internal friction logarithm versus the frequency logarithm (Fig. 4) following the method developed by Weller et al [15] and recently applied to intermetallic compounds [16-17]. A linear dependence of $\ln Q^{-1}$ versus $\ln \omega$ for each temperature is clearly observed in the HTB (Fig. 4). Furthermore, it is worth emphasizing that this linear dependence has the same slope for all temperatures, indicating that the operating microscopic mechanism is the same in the temperature and frequency range studied here. From the linear regression slope of each isothermal a distribution factor of the relaxation time $n=0.3$ is calculated, and from the interception with the $\ln Q^{-1}$ axis the apparent relaxation time τ^* for each temperature is obtained. Assuming an Arrhenius dependence of τ^* on temperature (Eq. (3)) we can obtain the activation enthalpy of the mechanism involved in the HTB. Fig. 5 shows the $\ln \tau^*$ vs. $1/T$ plot, whose fit provides an activation enthalpy of $H_{act}=6.3 \pm 0.2$ eV and a relaxation time $\tau_0 \sim 4.3 \cdot 10^{-18}$ s. Schaller et al. [7], studied a 3YTZP material sintered at higher temperatures (1643 K) whose mean grain size was about 0.29 μm . Taking the equation for the high temperature background [18], Schaller et al. [7] reported an apparent activation enthalpy energy of about 5.6 eV, a limit relaxation time $\tau_0 \sim 10^{-18}$ s and a broadening factor $1/\alpha$ equal to 3.2. The small value of the limit relaxation time has no physical meaning and has to be corrected by models, which take into account the entropy variations in the grain boundaries at high temperature. This factor is just introduced to take into account that a relaxation peak is broader than a Debye peak. Comparing equations it is easy to notice that the inverse of α corresponds to the distribution factor n in the generalised Maxwell model. As we can see our value $n=0.3$ is in good agreement with $\alpha=1/3.2=0.31$ obtained by Schaller et al. [7]. Also the

relaxation time τ_0 compares well to their value. However, we obtain an apparent activation enthalpy a bit higher. That could be ascribed to the smaller grain size of their samples and also to differences in the experimental conditions since they worked at higher temperatures than in our experiments.

Alternatively to this method we have carried out a similar one, which has some advantages, as we will see later on. Instead of measuring the internal friction as a function of the temperature for several oscillating stress frequencies, as shown before, we have performed measurements of the internal friction as a function of the frequency ω for several temperatures. The $\ln Q^{-1} - \ln \omega$ plot (Fig. 6) is provided with much more data for each isothermal compared to Fig. 4, contributing to a more reliable fit. In fact, this higher amount of data allows us to see the appearing of the Peak II [8], however it is quite weak because of the grain size of our samples and then we can consider a linear dependence of $\ln Q^{-1}$ on $\ln \omega$. Coherently, the linear regression of each isothermal has the same slope, and a value for the distribution factor of the relaxation time $n = 0.29 \pm 0.01$ is obtained. We can see that both methods provide the same value for this parameter. From data plotted in Fig. 6 and taking into account Eq. (2) and Eq. (3), the Arrhenius diagram (Fig. 7) provides an activation enthalpy of $H_{act} = 6.2 \pm 0.2$ eV and a relaxation time of $\tau_0 = 1.3 \cdot 10^{-17}$ s. So, similar values are obtained by using both methods. However, for this sort of calculations, measuring the internal friction as a function of the frequency consumes much less time for the experimental results analysis.

The activation enthalpy value, measured by means of both methods, is in good agreement with the one obtained by other authors by creep experiments, since they reported a value for the activation enthalpy between 5 and 7 eV depending on the creep conditions [6]. On the one hand, this agreement is surprising if we take into account the large difference between creep and mechanical spectroscopy experiments due to the much lower stresses involved in the latter. And, on the other hand it constitutes a proof that mechanical spectroscopy is a helpful non-destructive technique that can provide useful information like activation enthalpy of thermally-activated deformation mechanism, and therefore its use as a complementary technique for creep experiments is obviously of huge worth.

4. Conclusions

Mechanical spectroscopy has been performed in 3 mol % yttria zirconia polycrystals (3YTZP). We have applied two different methods to study the high temperature background, obtaining important parameters such as the activation enthalpy of the deformation mechanism. By means of mechanical spectroscopy we find the same activation energy for YTZP than those obtained by creep experiments. That attests that mechanical spectroscopy, which also has the advantage of being a non-destructive technique, seems to be very useful together with creep experiments to investigate the high temperature deformation mechanisms operating in ceramic materials.

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FIGURE CAPTIONS

Fig. 1. Scanning electron micrograph showing the grain microstructure of YTZP-samples, whose average grain size is 0.6 microns.

Fig. 2. Internal friction and dynamic Young's modulus versus temperature of a YTZP specimen under a oscillating stress frequency of 0.3 Hz.

Fig. 3. Plot of the YTZP set, showing the internal friction vs. temperature for different frequencies, taken from [12].

Fig. 4. Plot of the $\ln Q^{-1}$ as a function of $\ln w$ for different temperatures [12].

Fig. 5. Arrhenius diagram for the high temperature internal background of YTZP specimen [12], whose fit provides an activation enthalpy of $H_{act}=6.3 \pm 0.2$ eV and a relaxation time $\tau_0 \sim 4.3 \cdot 10^{-18}$ s.

Fig. 6. $\ln Q^{-1}$ as a function of $\ln w$ obtained from measuring the internal friction as a function of the frequency for different temperatures.

Fig. 7. Arrhenius diagram plotted from data in Fig. 6. An activation enthalpy of $H_{act}=6.2 \pm 0.2$ eV and a relaxation time of $\tau_0=1.3 \cdot 10^{-17}$ s are obtained. These results are similar to the ones shown in Fig. 5.