Superplasticity of YTZP: New Approach and Application

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The experimental data available in the literature on superplasticity in YSZP will be presented and critically analyzed in terms of a threshold stress. A new application of the superplasticity has been developed based on the grain boundary sliding, which is the macroscopic deformation mechanism of superplasticity. This technique has been used to join pieces of the same grain size and pieces with different grain sizes to produce a functionally gradient multilayered ceramic composite. Results concerning joining of Y-TZP will be also presented in this paper.

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I. Introduction

Since Wakai and his co-workers first demonstrated the superplastic behavior of a yttria-stabilized tetragonal zirconia polycrystal (YTZP) at high temperature⁽¹⁾, the superplasticity of fine-grained ceramics has been the topic of many investigations (for details see the reviews⁽²⁾⁽³⁾ and cover page of the J. Amer. Ceram. Soc. 97 (May), 1996). The most widely studied ceramics have been zirconia polycrystals partially-stabilized with concentration of yttria from 2 to 6 mol%, with grain sizes $\leq 1 \mu\text{m}$, at temperatures between 1473 and 1723 K and strain rates between 10^{-8} and $10^{-2} \text{ s}^{-1(2)(4)(5)}$.

The mechanical parameters characterizing the superplastic behavior of ceramics have been generally obtained using the creep equation:

$$\dot{\epsilon} = A \frac{Gb}{kT} \left(\frac{b}{d} \right)^p \left(\frac{\sigma}{G} \right)^n D \quad (1)$$

where $\dot{\epsilon}$ is the strain rate, A is a dimensionless constant, G is the shear modulus, b is the magnitude of the Burgers vector, d is the grain size, σ is the stress and D is an appropriate diffusion coefficient which can be written as $D = D_0 \exp(-Q/kT)$ with D_0 a frequency factor and Q is the activation energy; the other parameters have the usual meaning.

As mention before, a considerable amount of research has been performed on YPSZ (yttria partially-stabilized zirconia) showing different and often conflicting creep parameters (stress exponents ranging between 2 and 5, grain size exponents between 1 and 3 and activation energies between 400 and 700 kJ/mol) for nominally similar materials tested under similar experimental conditions. These discrepancies have invoked several interpretations of the mechanisms controlling the superplasticity.

The purity of the material plays an important role in the superplastic behavior of these ceramics. It is now accepted that low-purity YPSZ exhibits a stress exponent of 2 over all stress ranges, whereas for high-purity YPSZ

this exponent increases from a value of 2 for high stresses to values ≥ 3 at the lowest stresses⁽⁵⁾. At the same time, for these high-purity YPSZ, the activation energy decreases with increasing stress as reported in⁽⁶⁾⁽⁷⁾.

Grain boundary sliding has been recognized as the main deformation mechanism for these superplastically deformed materials, however for the purer materials no definitive elemental strain-rate-controlling mechanisms have been definitively identified. In fact, several authors suggest that two different mechanisms, operating sequentially, can explain the different values reported for the creep parameters⁽⁸⁾⁽⁹⁾, whereas our group suggests that only one mechanism with a threshold stress is operating⁽⁵⁾⁻⁽⁷⁾⁽¹⁰⁾.

The main objective of this paper is to critically rationalize the data available in the literature on YTZP in terms of a threshold stress. At the same time, grain boundary sliding, the superplastic macroscopic deformation mechanism, will be used to describe a new application of the superplasticity.

II. Creep Data of Superplastic YTZP

Although YSZP has been extensively studied in the last two decades as a function of yttria concentration, temperature, strain rate, stress, grain size⁽⁴⁾⁽⁵⁾⁽¹⁰⁾, for sake of clarity, data at 1623 K for polycrystals with $d \leq 1 \mu\text{m}$ will be mainly analyzed in this paper.

In order to compare materials with different grain sizes, $\dot{\epsilon}$ will be compensated by d^2 when plotted versus σ (Fig. 1). This value of p has been used because it is the most cited within the regime of $n=2$ (full line in the figure)⁽⁴⁾⁽⁵⁾ although a value of $p=3$ will give the same trend. In this figure, data from polycrystals with grain sizes of ~ 0.4 and $\sim 0.8 \mu\text{m}$ are used. A more complete figure, showing the same trend, can be seen in Ref. (5). From Fig. 1, the following points can be outlined:

- (1) Experimental data show small scatter (less than one decade) at high stress and larger scatter (two orders of magnitude) at lower stresses.
- (2) Some data fit a straight line with a slope of 2 over

Fig. 1 Grain size compensated strain rate vs. stress for YSZP with 2 to 4 mol% Y_2O_3 deformed at 1623 K. Composition, grain size and reference are shown in the legend of the figure.

the stress range reported. A close inspection of the references of these data shown that the samples had the higher impurity contents. Although not shown here, the strain rate of the YPSZ is sensitive to the amount of impurities⁽⁵⁾.

For the other data (samples with higher purity), the experimental data aligned along a straight line with a slope of 2 for the higher stresses but fell systematically below such a line for the lower stresses.

In the low stress regime, a single value of $n \cong 3$ has been reported in most works found in the literature⁽⁴⁾⁽⁵⁾⁽⁹⁾ when $\log \dot{\epsilon}$ vs. $\log \sigma$ plots are used. However, a closer inspection of the values of n obtained from creep experiments at constant load, by which instantaneous change of σ can be performed obtaining single values of n , show that the value of n increases to values >5 when decreasing the stress⁽⁵⁾⁽⁶⁾. **Figure 2** shows a $\log \dot{\epsilon}$ vs. ϵ plot for 3 mol% Y-TZP with $d=0.5 \mu\text{m}$ deformed at 1632 K.

Similar behavior has been observed in a high purity 3YTZP with a grain size of $0.4 \mu\text{m}$ deformed at 1473 K with n decreasing from 4.4 to 2.2 with increasing stress from 20 to 50 MPa⁽¹⁷⁾. At the same time, these authors analyzed the same data on a $\log \dot{\epsilon}$ - $\log \sigma$ plot, obtaining a single value of 2.8, in agreement with what has been pointed out above⁽¹⁷⁾. Clearly, no unique n value can be ascribed to the superplasticity of these materials at low stresses.

Fig. 2 Creep curve for 3YTZP with $d=0.5 \mu\text{m}$ at 1633 K, showing several determinations of the apparent stress exponent.

Fig. 3 Creep curves for 3YTZP with $d=0.5$ and $0.8 \mu\text{m}$ (indicated in the figure) with instantaneous temperature changes to determine the activation energy.

Figure 3 shows creep curves of a 3YTZP samples in which instantaneous temperature changes were used for measuring the activation energy. From the inspection of this figure, together with the values of Q reported in the literature, the activation energy has been found to be stress dependent, and the stress is a function of the temperature and grain size. Values from 700 to 500 kJ/mol with increasing stress and/or grain size has been reported⁽⁵⁾⁽⁶⁾. Lakki *et al.*⁽¹⁸⁾ found values of Q from 600 to 500 kJ/mol when increasing stress for a specific grain size and Wakai *et al.*⁽¹⁹⁾ reported values of 605 and 455 kJ/mol at $\sigma = 20$ MPa in a 3YTZP with grain sizes of 0.5 and $1 \mu\text{m}$, respectively.

A close inspection of Fig. 3 shows that the strain rate

Fig. 4 Strain rate vs. stress for 3Y-TZP with $\bar{L}=0.41 \mu\text{m}$ deformed at 1723 K showing the change in the apparent stress exponent. Data from Ref. (9).

can be extrapolated after a positive or negative temperature change indicating that the different activation energy cannot be ascribed to grain growth. Recently, Owen and Chokshi found a value of the apparent activation energy of 550 kJ/mol independent of the stress⁽⁹⁾. However a close inspection of the plot used to obtain the activation energy indicates that the authors did not take into account the grain growth at lower stresses and higher temperatures. A reanalysis of their data for constant grain size gives values that ranged between 450 and 560 kJ/mol with decreasing stress.

On the other hand, under the assumption of homogeneous deformation, the slope α of the $\log \dot{\epsilon} - \log \sigma$ plot is equal to the stress exponent (see Fig. 2, where the slope decreases when n decreases). It can be observed (Fig. 3) that n increases with increasing Q . From these experimental observations, it can be concluded that n and Q continuously increase when the stress decreases.

Finally, microstructural observations of samples deformed at different stress levels show that the grains retain their equiaxed shape after substantial deformation at low as well as high stresses. No cavitation was found in the superplastic regime. However, deformation of a 3Y-TZP performed at 1623 K and at very low stresses shows significant cavitation for strain as low as 10%⁽²⁰⁾. This change in the microstructural aspect at very low stresses is accompanied by a new change of the apparent stress exponent from values higher than 3 to values lower than 2⁽⁵⁾. A new plot of the values of Ref. (9) at 1723 K for $\bar{L}_0=0.41 \mu\text{m}$ (mean lineal intercept length) taking into account the grain growth shows the same feature (Fig. 4).

III. Mechanism Controlling Superplasticity

The different values of the creep parameters, as a function of the stress reported in the literature and outlined in the preceding paragraph, has been recently rationalized in term of two sequential mechanisms: grain boundary sliding at high stresses ($n=2$) and interface-

reaction grain boundary sliding at low stress ($n=3$)⁽⁹⁾. However, the values of the creep parameters obtaining by instantaneous change of σ or T are not constant with decreasing stress as shown above. These two sequential mechanisms cannot justify the increasing values of the creep parameters n and Q when σ decreases below a critical value which has been found to be grain size⁽⁵⁾⁽⁹⁾ and T ⁽⁵⁾ dependent.

Based on the above observation, it is clear that the transition from high to low stress can only be rationalized on the basis of a threshold stress (σ_0). The incorporation of a threshold stress in eq. (1) has been used by Chaudhury *et al.*⁽²¹⁾⁽²²⁾ in metals as well as by our group⁽⁵⁾⁽⁶⁾⁽¹⁰⁾ in ceramics, to rationalize the change of the creep parameters with the stress. In this approach, the effective stress driving the deformation is not the applied stress σ but rather $\sigma - \sigma_0$, and the creep equation becomes:

$$\dot{\epsilon} = \frac{A}{d^2} (\sigma - \sigma_0)^2 \exp(-Q/RT) \quad (2)$$

with A including all the constants of eq. (1) with the stress and grain size exponents equal to 2, the values reported for the highest stresses where σ_0 is negligible.

The threshold stress dependence with temperature and grain size have been studied for diffusion assisted plastic deformation in metals and ceramics both theoretically and empirically⁽²³⁾⁻⁽²⁶⁾ and the following dependence is mostly found:

$$\sigma_0 = \frac{\phi_0}{d} \exp(Q'/RT) \quad (3)$$

where ϕ_0 and Q' are constants, the other parameters have their usual meaning.

Although at the present the physical origins of the threshold stress are unclear, Murty and Koczek⁽²⁷⁾⁽²⁸⁾ concluded that the inhibitor effect of dispersed particles on grain boundary migration (Zener pinning), which is an integral part of the superplastic deformation, provided a good explanation of the observed temperature- and grain size-dependence of the threshold stress (eq. (3)).

When the applied stress is increased from σ_1 to σ_2 , the apparent stress exponent n_{ap} is obtained from the steady-state values of the strain rate before ($\dot{\epsilon}_1$) and after the stress change ($\dot{\epsilon}_2$), taking into account eqs. (2) and (3), by means of the expression:

$$n_{ap} = \frac{\log [(\sigma_2 - \sigma_0)^2 / (\sigma_1 - \sigma_0)^2]}{\log (\sigma_2 / \sigma_1)} = 2 \frac{\log \left[\frac{\sigma_2 - \sigma_0}{\sigma_1 - \sigma_0} \right]}{\log (\sigma_2 / \sigma_1)} \quad (4)$$

Obviously, the apparent stress exponent will continuously increase when the stress approaches σ_0 if the applied stress instead of the effective stress is used to measure n . This is what is observed in Fig. 2 and was pointed out above.

On the other hand, if we try to measure the activation energy by a fast change of the temperature from T_1 to T_2 by measuring the associated strain rates, $\dot{\epsilon}_1$ and $\dot{\epsilon}_2$, the apparent activation energy will be given by (eqs. (2) and (3)):

Fig. 5 (a) Variation of $\dot{\epsilon}$ vs. σ and (b) $\dot{\epsilon}^{1/2}$ vs. σ for a zirconia-alumina composite (data from Ref. (20)). Dashed lines: linear least squares fit by Berbon and Langdon⁽¹⁹⁾.

$$Q_{ap} = Q + 2R \frac{T_1 T_2}{T_2 - T_1} \log \left[\frac{\sigma - \sigma_{o,T_2}}{\sigma - \sigma_{o,T_1}} \right] \quad (5)$$

where Q is the true activation energy for superplastic flow and σ_{o,T_1} and σ_{o,T_2} are the values of the threshold stress at each temperature. If the threshold stress is not a function of temperature, the second term is zero and the same value of the activation energy (Q) would be obtained at any stress, which is not the case. On the other hand, if σ_o is a decreasing function of T , the apparent activation energy will increase when decreasing σ as outlined above. The values of Q indicate that σ_o depends inversely on temperature.

The threshold stress has been found to be temperature and grain size dependent in YSZP⁽⁶⁾ and can be describe by the equation:

$$\sigma_o = \frac{3 \times 10^{-4}}{d} \exp \left(\frac{120 \text{ kJ/mol}}{RT} \right) \quad (6)$$

where the threshold stress is in MPa for the grain size in μm . By taking $Q = 460 \text{ kJ/mol}$, equations 5 and 6 predict values of Q_{ap} of 710 and 470 kJ/mol for the experimental conditions shown in Figs. 3(a) and (b), respectively.

Recently, the threshold stress concept have been criticize by Berbon and Langdon⁽²⁹⁾, who by re-analyzing data on a zirconia-alumina composite⁽³⁰⁾ claimed that the data are not consistent with a threshold stress because they obtained a negative σ_o . However, it is clear that the points for the higher stress do not fit the power-law of $\dot{\epsilon}$ vs. σ ($n=2$) (Fig. 5(a)). If these points for the higher stresses are neglected in a $\dot{\epsilon}^{1/2}$ vs. σ plot, the correlation factors increase from 0.986 to 0.999 at 1623 K, and from 0.995 to 0.997 at 1673 K and σ_o becomes positive instead of negative, with values of 3 and 1.5 MPa for the testing temperatures of 1623 and 1673 respectively. Fig. 5(b) summarizes these results with the fit of Ref. (29) (dashed lines) and our fit.

The same argument of σ_o negative has been used for Owen and Chokshi⁽⁹⁾ in a 3YTZP deformed between 1623 and 1723 K. They plotted $(\dot{\epsilon} \bar{L}_i^3)^{1/2}$ vs. σ for $\bar{L}_o = 0.66 \mu\text{m}$ and $T = 1723 \text{ K}$ where a significant grain growth ($\bar{L}_i$ is the final mean linear intercept length) occurs at the lowest stresses. They obtained a value $\sigma_o = -12.5 \pm 12.4 \text{ MPa}$. If σ_o is an inverse function of d , it is clear that a threshold stress cannot be obtained with these points when grain growth occurs, which can explain the large scatter reported for⁽⁹⁾.

Since two sequential mechanisms cannot account for the observed values of the creep parameters n and Q and because the analysis performed by Berbon and Langdon⁽²⁹⁾ and by Owen and Chokshi⁽⁹⁾ to obtain σ_o are not correct, it is concluded that the experimental data in Y-SZP can be better understood in terms of a threshold stress.

IV. Applications

Grain boundary sliding has been widely recognized as the dominant strain contributing mechanism in superplasticity in metals as well as in ceramics. The microstructural feature of this mechanism is that during deformation, the grains of the polycrystal change their nearest neighbors, retaining their initial shape constant.

When two parts of a fine-grained ceramics in contact are superplastically deformed, the grains of one part interpenetrate those of the other producing a rapid and perfect junction of both parts. The superplasticity can so be used to joint different parts producing complex structures from simple shapes.

On the other hand, superplasticity is grain size dependent (eq. (1)), so materials with coarse grains will be more creep resistant than those with smaller grains. If two or more layers of the same material with different grain sizes are superplastically compressed, a multilayer composite can be obtained with clean and strong interfaces. The experiments to joint materials is performed in such a way that all the layers are submitted at the same stress (hereafter isostress test).

Fig. 6 Scanning electron micrograph illustrating the two types of junctions: (a) same grain size; (b) different grain sizes. The bar is 2 μm .

Different types of junction can be performed: i) materials with the same composition and grain size $d^{(31)}$ and ii) materials with different composition and/or grain sizes⁽³²⁾⁽³³⁾. **Figures 6(a)** and **(b)** show the two type of junctions described before on a Y-PSZ. In both cases, it can be observed that the grains rotated during deformation producing the junction of both pieces.

To check the strength of the junction, several experiments have been performed:

- (a) Vickers indentations in the interface.
- (b) Compression tests at high temperature, with the stress parallel to the interface (hereafter isostrain test).

When the Vickers indentations were performed at the interface, the cracks which emanate from the corners of the indents either have the same length in the four directions (materials with the same d), or have different length in the case of different materials; the cracks parallel to the interface are shorter than those developed in the material with the lower toughness⁽³¹⁾⁽³²⁾.

The isostrain tests at high temperature showed not evidence of opening of the interface or activation of cavities⁽³²⁾⁽³³⁾. The comparison between cracks obtained from Vickers indentations and the isostrain tests at high temperature, allows us to conclude that the materials have been very well bonded.

On the other hand, it is well known that for the isostrain case, the strain and the strain rate are the same for each layer and if the high temperature mechanical behavior of each layer is described by eq. (1), the stress σ_c is giving⁽³⁴⁾:

$$\sigma_c = \sum_{i=1}^m V_i \left(\frac{\dot{\epsilon}_c}{A_i} \right)^{1/n} \quad (7)$$

where V_i is the volume fraction of each layer, $A_i = A' d_i^{-p} \exp(-Q/kT)$ with A' including all the constants of eq. (1) and n the stress exponent, which we assume the same for all the layers. It is clear that for this type of test, the mechanical behavior is controlled by the hardest layers modulated by the volume fraction.

For the isostress case, the stress is the same for each layer and can be written as:

$$\dot{\epsilon}_c = \frac{\sum_{i=1}^m A_i \sigma^n}{m} \quad (8)$$

with m equal to the number of layers different. In this case the mechanical behavior of the laminated will be controlled by the softer layer deformed at the strain rate imposed by the stress.

These results have interesting implications in the design of materials. For example, a short-crack ceramic can be superplastically joined to a long-crack ceramic to obtain a tough and wear resistant ceramic composite at low temperature or a ceramic composite for structural applications with anisotropic mechanical behavior at high temperature depending how the stress is applied to the composite.

V. Conclusions

The macroscopic and microscopic mechanical characteristics of yttria stabilized (from 2 to 6 mol%) zirconia polycrystals superplastically deformed over a wide range of experimental conditions covering strain rate between 10^{-8} and 10^{-2} s^{-1} , stress from 2 to 250 MPa and temperatures between 1523 and 1723 K can be conclusively rationalized in term of a threshold stress which is grain size and temperature dependent.

The macroscopic deformation mechanism of superplasticity, *i.e.* grain boundary sliding, can be used to joint homogeneous or heterogeneous zirconia layers with strong and clean interface junctions. This technique allows the opportunity of producing materials with complex shape and for functional gradient materials (FGM) with anisotropic mechanical properties at low as well as high temperatures.

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