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Influence of the yttrium segregation at grain boundaries in the superplasticity of yttria tetragonal zirconia polycrystals

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Abstract

This work presents a general view on the high temperature plastic deformation of yttria tetragonal zirconia polycrystals (YTZP), in the frame of the new modelling effort made by the authors to understand the main features of this system. A critical analysis is made, as well as a future perspective of the possible development of research in this material.

Keywords: Creep; Diffusion; Grain boundaries; Grain size; Superplasticity

1. Introduction

Since the discovery of the superplasticity in YTZP by Wakai et al. in 1986,[1] a considerable effort has been devoted to understand their superplastic behaviour at moderate temperatures. Most works have concentrated on the submicron range of grain sizes, with 2–4 mol% Y_2O_3 and temperature between 1250 and 1450 °C. Several reviews on the mechanical outputs and the subsequent interpretation are available.[2–4]

As a result of these investigations, there are numerous sets of experimental data, which are, in most cases, different and often contradictory for nominally similar materials tested under similar experimental conditions and analysed using the classical creep equation:

$$\dot{\varepsilon} = \mathrm{A}\frac{Gb}{kT}\left(\frac{b}{\mathrm{d}}\right)^{p}\left(\frac{\sigma}{G}\right)^{n} D_{\mathrm{app}} \tag{1}$$

where $\dot{\varepsilon}$ is the steady state creep rate, A is a constant, G is the shear modulus, b the Burgers vector, d is the grain size, σ is the applied stress, p and n are the exponents for grain size and stress respectively, k and T have the usual meaning and D_{app} is an apparent diffusion coefficient controlling the mass transport through the different defects (i.e. vacancies or interstitials) and the different paths operating during diffusion (i.e. lattice, grain boundaries, dislocations). For compounds, all the species and their different diffusional paths must be considered when analysing the diffusion process. The "effective" diffusion coefficient is a combination of those of the different diffusing species, weighted by the contribution of the available diffusion paths. Diffusion theory states that if the diffusion coefficient of one component is much smaller than those of the others, whatever the diffusion path, then the "apparent" diffusion coefficient (D_{app}) corresponds to that of the component under consideration along its faster path In this case D_{app} can be written:

$$D_{\mathrm{app}} = D_o \exp\left(\frac{-Q}{kT}\right) \tag{2}$$

with D_0 a preexponential term and Q the activation energy of the rate controlling process.

Admitted these dependences, several features can be outlined:

(a) The impurities content of the samples can strongly affect the experimental results: The mechanical parameters are very sensitive to the applied stress, particularly in the low stress regime, in high purity samples. In contrast, this sensitivity disappears when the impurities content is higher than a certain amount. In other words, the n value remains equal to 2 in all range of stresses for samples with a sufficient amount of impurities, otherwise n is equal to 2 at high stresses and increases at values as high as 5 when σ decreases.[3–5]

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(b) In high purity materials, the stress for the transition between n equal 2 to higher values is dependent on d and T. In other words, σ increases when d and T decrease.[3,4]
(c) In the pure materials, the activation energy will vary from 500 to 700 kJ/mol when the σ decreases.[3–5] No presence of a glassy phase enhancing grain boundary diffusion was detected.
(d) No testing atmosphere surrounding the sample, or the testing procedure (tension, compression and bending) affects the mechanical behaviour.[6]

A detailed description of these facts can be found in Refs. 3,4.

Supported by the stability of the microstructure during deformation (grain size and shape factor remain unchanged after even few hundred per cent of deformation), it is now accepted that grain boundary sliding (GBS) is the primary deformation mechanism in the superplastic behaviour of fine-grained YTZP.[7–11] However, there is not a consensus about the rate controlling mechanism and several models have been developed to account for the discrepancies in the creep parameters. A critical revision of the different models can be found in Ref. 12.

Nowadays, a quite satisfactory empirical description of the superplastic data of pure sub-micron YTZP has been reported through the introduction of the concept of a threshold stress (σ_0); and the following equation has been derived:[3–5]

$$\dot{\varepsilon} = 3 \times 10^{10} \frac{(\sigma - \sigma_0)^2}{Td^2} \exp\left(-\frac{460\ \text{kJ/mol}}{RT}\right) \quad (3)$$

with σ in MPa, d in μm and σ_0 given by

$$\sigma_0 = 5 \times 10^{-4} \frac{\exp\left(\frac{120\ \text{kJ/mol}}{RT}\right)}{\text{d}} \quad (4)$$

The activation energy in Eq. (3) is very close to the activation energy for cation lattice diffusion,[13–15] suggesting that the superplasticity in YTZP is due to the GBS, being the lattice diffusion of cation (D_{Zr}) the rate controlling mechanism.

The existence of a σ_0 has been widely used in metallic compounds (for more details see Refs. 3–5,12) and has been proved in YTZP through deformation tests at stresses below σ_0.[16] In these conditions, the material is deformed through diffusional creep without GBS accommodation, and in consequence a high cavitation is produced. Despite these evidences, the physical origin of the threshold stress is not clear at present.

In this paper we justify the existence of σ_0 based on the role played by yttrium segregation at grain boundaries and points out the constitutive creep equation for nanostructured polycrystals.

2. Modelling

It is now accepted that yttrium segregates at grain boundaries or at the dislocation cores in YTZP. The origin of this segregation effect is the size difference between the Y^{3+} and the Zr^{4+} ionic radius. The ionic radius of Y^{3+} cations is 20% bigger than that of Zr^{4+} ones.[17] This size effect is the reason for elastic energy in excess around the Y^{3+} cation positions in the lattice. A similar effect has been reported in other ceramic systems, as fine-grained alumina, with small traces of zirconium impurities segregated at the grain boundaries.[18] Segregation phenomena along the dislocation core have been put forth by Gómez-García et al.[19]

The existence of yttrium segregation at grain boundaries has been proved experimentally by means of different analytical techniques: Winnubst et al.[20] made AES measurements, as well as Theunissen et al.,[21] who also made XPS determinations. AES data measured a thickness of the segregated layer of 4 nm, in both works; whereas XPS measurements ranged between 2 and 4 nm. The thickness is in fairly good agreement to the value reported in,[22] which measured 5 nm. Stemmer et al.[23] also agreed to conclude that the segregation layer thickness is around 5 nm through HRTEM observations. Concerning the segregation itself, these authors have reported a strong yttrium enrichment, with a factor of two between the bulk and the grain boundary concentration of this element. This strong segregation effect can even induce the transformation of some grains to the monoclinic phase because of the lower Y-content inside the grains. Hines et al. [24] have analysed the segregation profile by means of EDS spectra, reporting a ratio of Y segregation between 2.3 and 2.7, in fairly good agreement with the previous authors.

As mentioned before, GBS is the primary deformation mechanism in the superplastic behaviour of YTZP, (which at its turn, is governed by the threshold stress, especially at stresses close to σ_0), being the cation diffusion along the lattice as the accommodating process. Both, strain and strain rate will be affected if a local electric field (E) exists as a consequence of segregation of charged chemical ions at the grain boundaries. Assuming a very narrow interfacial region and electrostatic equilibrium, this E can be written, using the classical electrodynamics, as:[25]

$$E = \frac{\rho\lambda}{\varepsilon} \quad (5)$$

being ρ the volume charge density in the thickness of the segregation layer λ.

As the charge density depends on the yttrium segregation, it will be a function of both temperature and bulk concentration (c_b) according to the equation for dilute-solution limit in the high temperature range:[26]

$$\rho = c_b\left[\exp\left(-\frac{\Delta G}{kT}\right) - 1\right] \quad (6)$$

so, Eq. (5) will be:

$$E = \frac{c_b\lambda}{\varepsilon}\left[\exp\left(-\frac{\Delta G}{kT}\right) - 1\right] \quad (7)$$

In this model, the influence of E on strain and strain rate are analysed.

2.1. Influence on the threshold stress

In a previous paper,[27] we proved that the work done (δW) in the relative displacement of one grain respect to each other could be written as:

$$\delta W = C\frac{1}{2}\varepsilon E^2 \delta V \quad (8)$$

where ε is the dielectric constant of the material, δV is the infinitesimal change of the volume between two grains upon sliding an infinitesimal distance $\delta\xi$ ($\delta V = w\mathrm{d}\delta\xi$, with w the thickness of the intermediate region between grains and d the grain size) and C is a geometrical constant that for a cubic grain is 4 (the number of lateral faces).

By substituting Eq. (7) in (8) and taking into account that $\delta W = \mathrm{F}\delta\xi$ the net force per unit area F or threshold stress, this σ_0 can be written as:

$$\sigma_0 = 2\frac{c_b^2\lambda^2}{\varepsilon}\left[\exp\left(-\frac{\Delta G}{kT}\right) - 1\right]^2\frac{w}{\mathrm{d}} \propto \frac{1}{\mathrm{d}}\exp\left(-\frac{2\Delta G}{kT}\right) \quad (9)$$

the minus sign is due to the fact that the force is opposed to the displacement.

The charge effect due to the impurities segregation at grain boundaries not only justifies the existence of the threshold stress in the superplastic behaviour of YTZP but also gives the same grain size and temperature dependence as experimentally observed.[3–5]

2.2. Influence on the diffusion coefficient

As it was demonstrated in Ref. 27 the segregation of Y^{3+} at the grain boundaries is responsible for the appearance of an electric field, and as a consequence an electric potential $\Phi(r)$, which has been calculated in Ref. 28. The gradient of the chemical potential (μ_D) controlling the movement of atoms between the centre of the grains and the boundaries will be now affected by this $\Phi(r)$ and according to thermodynamics, in the limit of dilute solid solutions, this μ_D will be [29]:

$$\mu_D = \mu + z_C e(r) \quad (10)$$

with μ the gradient of the chemical potential in absence of electric potential and z_C the valence of the specie controlling diffusion.

This change in the gradient of the chemical potential will influence the diffusion coefficient controlling superplasticity (D_{Zr}^{eff}) and it can be written as:

$$D_{Zr}^{eff} = \frac{D_{Zr}}{1 + 4\frac{\lambda}{\mathrm{d}}\left[\exp\left(-\frac{z_C e\Phi(r)\lambda}{3\varepsilon_r kTd}\right) - 1\right]} \quad (11)$$

where λ is the thickness of the segregation profile inside the grain (it is the Debye atenuation length), ϕ(R) is the electric potential at the boundaries, e is the electron charge, d the grain diameter (or grain size) and z_D the effective valency of the segregated species.

According to this change in the effective diffusion coefficient, the D^{eff} in Eq. (1) will be now replaced by the expression of Eq. (9).

3. Discussion

It was demonstrated experimentally that the existence of a threshold stress can rationalize the YTZP data in the superplastic regime with a creep equation identical to that found in metals, despite the differences between these two types of materials.[3–5,7] However the physical origin of this threshold stress was not clear. At this point, the yttrium segregation at grain boundaries is postulated as a plausible explanation of its existence.

In this paper, we demonstrate that this segregation can be the origin of the threshold stress with the same grain size and temperature dependence as found experimentally. A good comparison between the experimental and theoretical values of this threshold stress for YTZP can be found in Ref. 25.

If the electric field built up by the segregation is the responsible for the threshold stress, several questions can be asked: 1—Is there σ_0 in any ceramic system when there is segregation at grain boundaries? 2—Is there σ_0 in systems without segregation? 3—During segregation in YTZP, it was assumed that the grain boundaries were ideal sinks for the yttrium segregation. Is there σ_0 when these grain boundaries are no longer ideal sinks for segregation?.

To give answer to the first two questions, it is necessary to study additional ceramic systems and the yttrium-doped ceria and alumina can be good candidates for these studies. Concerning the third question, the YTZP is good if the yttria content approaches the limit for the structural change in the phase diagram.

As it was shown in,[25] when the yttria content is close to the concentration determined by the phase diagram,[30] for which the transformation from tetragonal to monoclinic occurs (c_{min}), there is a critical grain size (d_{crit}) below which, the grains are no longer perfect sources. This critical value is in the range of the nano scale ($d_{crit} < 100$ nm). In these conditions, the increase of the local concentration at grain boundaries will be:[25]

$$\rho = c_g - c_0 = (c_0 - c_{min}) \frac{\left(1 - 2\frac{\lambda}{d}\right)^3}{1 - \left(1 - 2\frac{\lambda}{d}\right)^3} \quad (12)$$

As a consequence, the electrical potential and the threshold stress will be changed.

$$\sigma_0 = 2\frac{c_b^2 \lambda^2}{\varepsilon}\left[\exp\left(-\frac{\Delta G}{kT}\right) - 1\right]^2 \frac{w}{d} \times \left[\frac{\left(1 - 2\frac{\lambda}{d}\right)^3}{1 - \left(1 - 2\frac{\lambda}{d}\right)^3}\right]^2 \left[\frac{1 - \left(1 - 2\frac{\lambda}{d_{crit}}\right)^3}{\left(1 - 2\frac{\lambda}{d_{crit}}\right)^3}\right]^2 \quad (13)$$

A critical examination of this Eq. (13) for the standard concentration of yttria in YTZP has been made in Ref. 25 and give values of σ_0 around 1 MPa, much lower than the stress values obtained when conventional submicron YTZP are deformed at the same conditions.[31,32] A comparison of the dependence predicted by Eq. (9) with that predicted for nanometer-scaled specimens [Eq. (13)] is given in Figs. 1 and 2, respectively. Notice that both plots overlaps in a region around 100 nm; in which a smooth transition should be expected. The detailed dependency cannot be properly reproduced unless the grain distribution function is given. For a model polycrystal in which all grains are exactly equal, the expected transition is sharp, as explained in Ref. 27.

Yttrium segregation can also explain why no threshold stress is observed during high temperature deformation of nano-YTZP. It has been found previously[31,32] that the nano-YTZPs do not follow the mechanical behaviour predicted by the creep Eq. (3). In other words, the creep rates for these ceramics with nanoscale grain size are between one and two orders of magnitude smaller than expected by extrapolation of the creep rate to smaller grain sizes. This important feature has been explained by the change in the diffusion coefficient of the rate controlling species due to the yttrium segregation at grain boundaries. As shown in Eq. (9), D_{Zr}^{eff} is affected by the term $1 + 4\frac{\lambda}{d}\left[\exp\left(-\frac{z_C e \Phi(r) \lambda}{3\varepsilon_r kTd}\right) - 1\right]$

when yttrium segregation occurs. This term becomes negligible when the grain size is larger than 200 nm. For 1150 °C and a grain size of 50 nm the activation energy predicted by Eq. (9) is 7.0±0.2 eV/atom [28], in very good agreement with the experimental results.[31,32]

4. Conclusions

This paper concludes that yttrium segregation at the grain boundaries leads to a threshold stress that enables grains to slide around each other during deformation. In addition to that, all the reported features of the plasticity behaviour can be understood in the light of aliovalent cation segregation phenomena.

A remarkable example is the analysis of the dependence of the threshold stress with the grain size. Whereas the threshold stress is inversely proportional to the grain size in large grains, it is no longer the case when the grain size is smaller than a critical value. This fact correlates quite well with the fact that segregation is dependent on the ability of the grain bulk to become an ideal supplier of dopants. Whereas this is true in large grains, it is unrealistic in very small grains, in which a strong segregation could induce a phase transformation in the whole system. In these last ones, the smaller the grain size is, the smoother the segregation profile; thence the threshold stress decreases down to a negligible value for very small grain sizes in the nanometer scale.

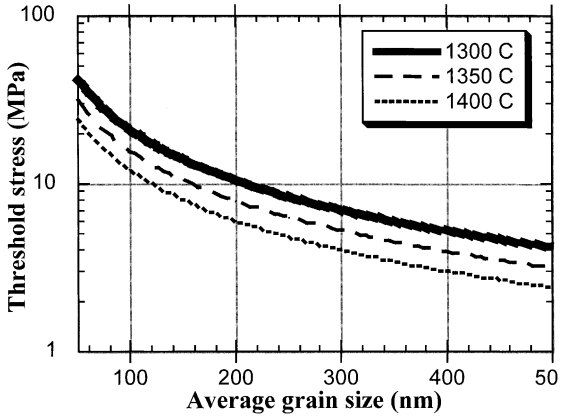

Fig. 1. Theoretical prediction of the dependence of the threshold stress with the grain size in the range of temperatures from 1300 °C up to 1400 °C, in the submicron range of grain sizes. In this range, the grain boundaries behave as ideal sinks for yttrium segregation.

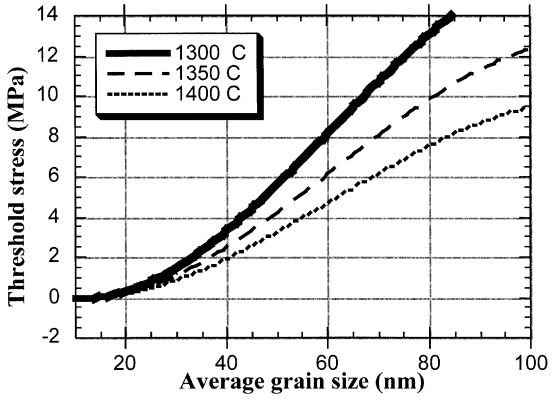

Fig. 2. Theoretical prediction of the dependence of the threshold stress with the grain size in the range of temperatures from 1300 °C up to 1400 °C, in the nanometer range of grain sizes. In this range, grain boundaries are no longer ideal sinks for yttrium segregation, which is restricted by the effective number of sites for yttrium occupation.

This last statement would imply that small grains could still behave as submicron ones provided the bulk behaves as an ideal supplier of the right number of dopants required at the current temperature, according to thermodynamics. This should be true in fine-grained polycrystals with a high enough amount of yttria. On the other hand, it should be clear that no threshold stress would be detected in ceramic systems in which no segregation of charged species takes place. The verification of these last hypotheses in the suitable ceramic systems would be excellent tests to experimentally conclude the assessment of the segregation model.

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