

Deformation mechanisms in yttria stabilized cubic zirconia single crystals.

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Abstract

This work **attempts** to give a unified picture of the microscopical mechanisms which control the plastic deformation in yttria stabilized cubic zirconia single crystals, particularly for the soft orientation (uniaxial compression along the $[1\bar{1}2]$ crystallographic axis) at low, intermediate and high temperatures **while also** reviewing and actualizing the existing data for different yttria contents (9,4-32 mol%). The controlling deformation mechanisms are: internal friction within the crystal lattice (Peierls mechanism at low temperatures), pinning of dislocations by localized obstacles and long-range interaction between dislocations (intermediate temperatures) and dislocation viscous glide and climb (recovery creep) at higher temperatures. New aspects of the Portevin le-Chatelier phenomenon during viscous glide, due to the pinning and unpinning of dislocations from their defect clouds (yttrium substitutional atoms), are included.

Keywords: Yttria stabilized cubic zirconia; Single crystals; creep; deformation mechanisms; Portevin le-Chatelier.

1. Introduction.

Yttria fully stabilized zirconia (YFSZ) is an excellent ionic conductor and is used in applications such as solid fuel cells or oxygen detectors. The single crystals are used in jewellery due to their crystalline perfection as substitutes for diamond. YFSZ is also used as a matrix for composite material in structural/functional applications. Therefore the study of the single crystal mechanical properties provides the basis for revealing the deformation mechanisms operating in this system and related composites. Zirconium oxide is found in nature at room temperature with the monoclinic crystal structure, transforming to the tetragonal system at 1443 K and to the cubic system at 2643 K until melting at 2953 K. However, these phase transitions can be lowered to room temperature by doping zirconium oxide with a variety of stabilizers (yttria or other transition and rare-earth oxides). Doping with 3 mol% yttria, for instance, gives the well-known YTZ tetragonal-stabilized-zirconia, where tetragonal phase exists at room temperature. Concentrations of yttria above 8 mol% results in yttria fully stabilized zirconia (YFSZ), which retains the cubic structure at room temperature. The different phases and the different degree of stabilization are the cause of the various phenomena encountered in the yttria-zirconia system: precipitation hardening and softening and solid-solution hardening. Each of these is characterized by a different microscopic controlling deformation mechanism, mainly interaction of dislocations with precipitates, mobile defects or defect clusters [1].

This work reviews the plastic deformation mechanisms in single crystalline YFSZ in a wide temperature range, mainly for the soft orientation, and covers aspects that have not been treated in previous reviews concerning the modelling of dynamic instabilities (PLC effect).

2. Experimental

The single crystals provide an insight on the plastic deformation mechanisms in terms of slip

systems and dislocation activity. Uniaxial compression studies on samples with different crystallographic orientations have been extensively used to assess the different slip systems at a large range of temperatures. These tests have systematically been performed on parallelepipeds cut in specific orientations in order to activate different slip systems and to create and study dislocation activity. At low temperatures, special compression tests were carried out in confining pressure [2,3] to prevent fracture of the samples. At intermediate and high temperatures, conventional uniaxial compression tests were used. Two methods, constant crosshead speed and stress relaxation tests, have been used to obtain the strain-rate sensitivity (m). Creep tests have been performed to estimate the stress exponent ($n=1/m$) and activation energy (Q) of the deformation process, using the constitutive creep equation which relates strain-rate to stress and temperature as follows:

$$\dot{\varepsilon} = A\sigma^n \exp\left(\frac{-Q}{kT}\right) \quad (1)$$

where $\dot{\varepsilon}$ is the steady-state strain-rate, A is a constant which accounts for the microstructural aspects (its value depends on the shear modulus, the Burgers vector and the preexponential term of the diffusion coefficient of the deformation-controlling species), σ stands for the applied stress, Q is the corresponding activation energy, n the stress exponent, k is the Boltzmann constant and T the absolute temperature. The combination of Q and n can be used to determine the deformation mechanism controlling creep.

Microstructural characterization of the as-received samples and of samples deformed in different conditions followed. Transmission electron microscopy (TEM) has been the most useful and

most powerful technique capable of giving an insight into the dislocation structure, the clue to the microscopic deformation mechanisms. Preparation of thin foils for TEM has been achieved by [conventional techniques for ceramic materials involving](#) mechanical polishing followed by Ar ion thinning.

3. Slip systems and deformation mechanisms

The stress-strain behaviour of cubic zirconia single crystals depends strongly on temperature, activated slip plane and dopant concentration. The brittle-to-ductile transition temperature has been estimated between 1273-1473 K for uniaxial compression tests [4]. Since YFSZ has the fluorite structure, comparisons between slip systems of both CaF_2 and YFSZ at different temperatures were made in first approaches, showing great similarity [1,5]. The glide direction is $\langle 110 \rangle$ and the easiest slip plane is $\{100\}$ in most cases. The primary $(001)\langle 110 \rangle$ slip system is activated, at both low and high temperature, when the compression axis is coincident with the $[1\bar{1}2]$ crystallographic direction, or “soft” orientation. This has been explained in terms of dislocation theory [6].

3.1. Low temperature range (500-800 K)

[Samples deformed at low temperatures exhibit long pinned screw dislocations and screw dipoles.](#)

The pinning is attributed to the abundant defect clusters existing in stabilized ZrO_2 .

The elastic approach cannot explain the behaviour at low temperatures and up to the brittle-ductile transition, where dislocation glide is controlled by Peierls potential (lattice friction) and the above mentioned obstacles [7]. Though there are no straight dislocation segments arranged in preferred crystallographic orientations, typical of the Peierls mechanism, the fact that bowed-up

dislocations do not relax after unloading hints to a strong friction and therefore to a Peierls mechanism. The Peierls stress has been roughly estimated in 4500 MPa while the kink energy (also characteristic of the Peierls mechanism) has been found to be 0.9 eV [8]. However, a standard or simplified Peierls model cannot not account for the temperature dependence of the Peierls stress with temperature, nor can it explain the reason why {100} and {111} slip are preferred over {110} slip. These facts are the consequence of more complex electrostatic phenomena at the dislocation core [6].

3.2. Intermediate temperature range (800-1450K)

In this range, a transition from the intrinsic lattice friction below 900K to an extrinsic mechanism controlling the dislocation motion at temperatures above that temperature occurs. The main glide plane of the samples deformed along $[1\bar{1}2]$ at intermediate temperatures is also the primary glide plane (001) [9], the same as for low temperature. The deformation is localized in narrow slip bands separated by nearly dislocation-free regions. Most dislocations are of screw character, in accordance with low-temperature deformation under hydrostatic pressure [2]. However, these screw dislocations are strongly pinned, their zig-zag shape due to the action of localized obstacles. Some of the pinning agents have been identified as jogs of screw dislocations.

Above 900K, a quite high kink density has been found along the dislocations, indicating the Peierls mechanism does not control the dislocation mobility in this range. At higher temperatures, anomalous cyclic fast yield drops (serrations) were observed in the stress-strain curves [10]). The very low values of the strain-rate sensitivity encountered during this anomalous behavior lead to the conclusion that athermal processes dominate around 1423K. *In situ* straining experiments

carried out at the same temperature in a transmission electron microscope did show that dislocations form instantaneously and move very fast [11]. Since overcoming of localized obstacles was not been observed in these in-situ straining experiments, the existence of serrations was explained by rapid dislocation multiplication and their fast passage through the crystal.

3.3. High temperature range (1450 -1800K)

The dependence of yield stress with dopant concentration has been systematically studied in the high temperature range and can be seen in Figure 1 for samples uniaxially compressed along $[\bar{1}12]$ crystallographic axis (easy glide) at 1673 K.

Yield stress increases with dopant concentration, reaches a maximum at 21 mol % yttria and then remains constant. Yield drops observed in the curves are indicative of activation of secondary {111} slip systems. Serrated flow at maximum yield stress has been attributed to Portevin le Chatelier effects (dynamic strain ageing), a process characterized by the locking and unlocking of dislocations from their defect clouds. This phenomenon occurs when the diffusion rate of the defects (in this case the substitutional yttrium atoms) is comparable to the glide velocity of the dislocations; that is the reason why it has only been observed for very particular conditions of strain and temperature, for samples between 15 and 32 mol% yttria [10, 12-14].

Samples deformed at high temperatures contain a majority of edge dipoles, which can also turn into prismatic loops by climb or cross-slip [4]. Secondary slip in {111} is activated after a small percentage of deformation, and finally, as deformation increases, a three dimensional dislocation

network (dislocation forest) is created. This high temperature dislocation structure comes from the equilibrium between dislocation generation and recovery **due to dislocation annihilation**. During recovery, prismatic loops can shrink by climb requiring the emission-absorption of point defects by means of volume diffusion. Cationic diffusion coefficients have been measured as a function of temperature with various methods: self diffusion, creep and dislocation loop annealing (measuring loop shrinkage of individual loops). The results point to zirconium diffusion as the rate controlling mechanism for matter transport in YFSZ [4].

The results of uniaxial compression tests in the high temperature range are shown in Figure 2, which plots strain rate versus the inverse of temperature for several yttria concentrations: 21, 24, 28 and 32 mol%. The values have been normalized to a stress of 100 MPa using the values of stress exponent and activation energy obtained in the creep tests. **A change on the deformation mechanism has been reported at a temperature around 1723 K [15-16]**. The results have been explained by a model developed by Burton in which plastic deformation is controlled **by two sequential mechanisms**: viscous glide of dislocations followed by dislocation annihilation (recovery) by climb. **The slowest process controls strain-rate in each regime**. At temperatures above 1723 K, climb would be the mechanism controlling the plastic behaviour, with many dislocations perpendicular to the (001) **and activation energies between 5 and 6 eV**, while at temperatures below 1723 K glide of dislocations is the deformation controlling mechanism, **with higher activations energies**. Typical values for n and Q from creep tests are summarized in Table 1.

The origin of the low dislocation glide mobility has been attributed to the strong dislocation-point defect interaction due to the size effect produced by the substitutional dopant yttrium atoms. The

defects form Cottrell clouds which constraint dislocation mobility. The velocity due to diffusion of these defects relative to the velocity of moving dislocations plays a fundamental role [17]. When both point defects and dislocations move at comparable rates, episodes of pinning and unpinning of dislocations from their Cottrell clouds occur. This is known as the Portevin - le Chatelier (PLC) phenomenon, and it is characterized by rapid oscillations of stress (sudden stress drops or “serrations” in stress-strain plots). The Portevin - le Chatelier effect is more likely to occur in samples with high yttria concentrations (>15 mol%) and was first suggested by Gallardo-López et al [18] as an explanation to the serrated yielding observed during plastic deformation, which was previously attributed to a synergy between multiplication yield points and thermomechanical softening [19]. An experimental study on such plastic stabilities is also reported by Tikhonovsky et al [14], and more detailed studies on the subject have been carried out [12-13] where the diffusing species responsible for the PLC have been unambiguously identified as solute yttrium atoms, based on numerical estimations of the waiting time of dislocations (time while dislocations remain pinned) and the diffusion time of yttrium atoms, which were found to be comparable and thus representing optimal conditions of PLC instabilities. The frequency and amplitude of the oscillations and the sudden decay of the strain-rate sensitivity are also characteristic of PLC phenomena. The numerical check was based on the standard model for dynamic strain ageing and the PLC effect developed by Estrin and Kubin [20], and the detailed calculus and values assumed for the case of YFSZ can be found in [12].

During dislocation climb, significant dislocation recovery takes place. In the higher temperature regime, the increased creep resistance (lower strain rates Figure 2) of the material with higher yttria content can be explained in terms of a reduced recovery caused by the decrease of the cation diffusion coefficient.

4. Conclusions

The deformation mechanisms for plasticity in YFSZ single crystals when deformed in the soft orientation are governed by the Peierls stress at low temperatures, interaction of dislocations with point defects at intermediate temperatures and a competition between viscous glide of dislocations dragging yttrium defects and climb (recovery creep) at high temperatures.

During the viscous glide regime, PLC phenomena of pinning and unpinning of dislocations from their defects can take place giving rise to dynamic instabilities in the stress-strain curves. This happens when the waiting time of dislocations is of the same order than the diffusion time of the defects.

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List of figures and table captions

Table 1: Activation energy, Q (eV), of the controlling microscopic deformation mechanism, and stress exponents n , for several compositions (dopant contents) and for the two temperature regimes encountered at high temperature.

Temperature (K)	Activation Energy Q (eV)				
	mol% Y_2O_3				
	9,4	21	24	28	32
1673-1773 (glide*)	7.5	9.0±0.5	9.0±0.5	9.6±0.5	9.0±0.5
1773-1973 (climb*)	5.5	5.7±0.4	5.8±0.5	5.9±0.5	5.9±0.5
	Stress exponent (n)				
	mol% Y_2O_3				
	9,4	21	24	28	32
1673-1773 (glide*)	7.3±0.5	5.0±0.3	7.0±0.5	6.5±0.5	7.0±0.5
1773-1973 (climb*)	4.5±0.4	3.2±0.4	4.5±0.5	4.9±0.5	4.8±0.5

*Strain-rate controlling mechanism.

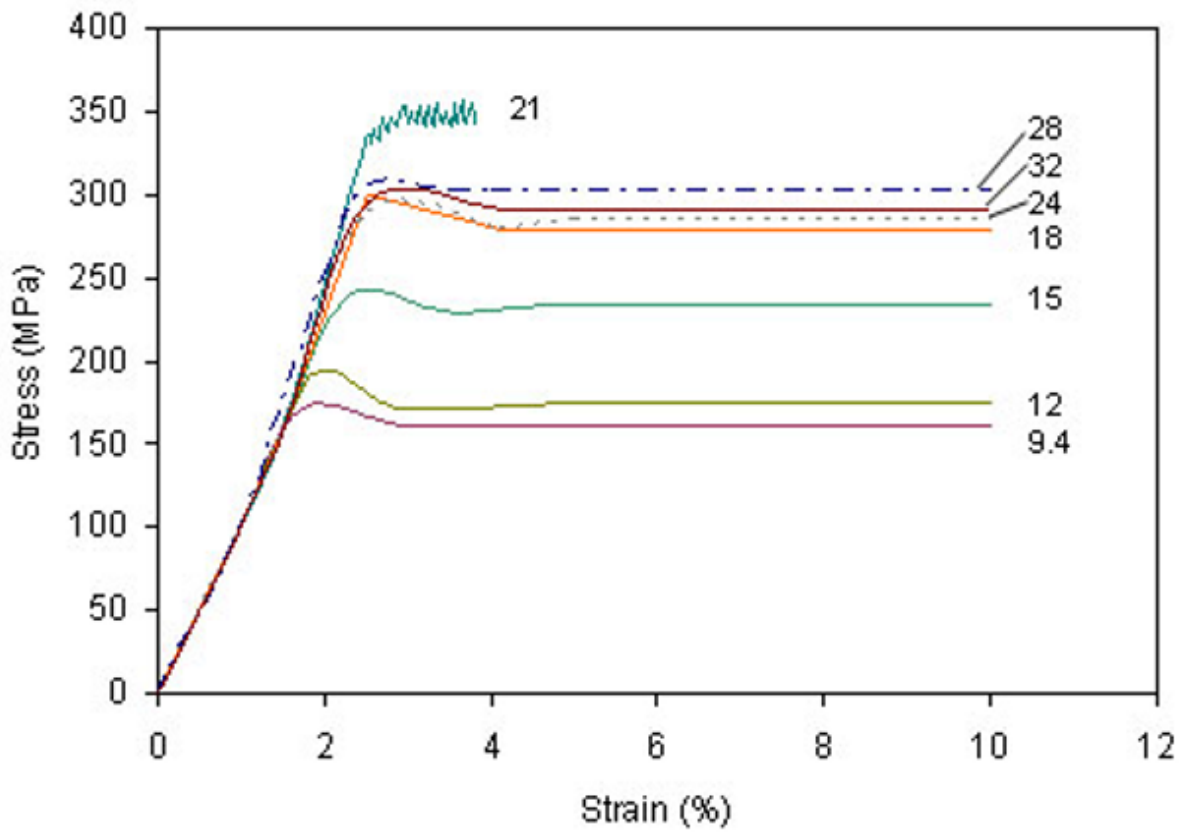


Figure 1: Stress-strain curves showing variation of yield stress for different yttria concentrations in YFSZ at 1673 K. Data collected from [17].

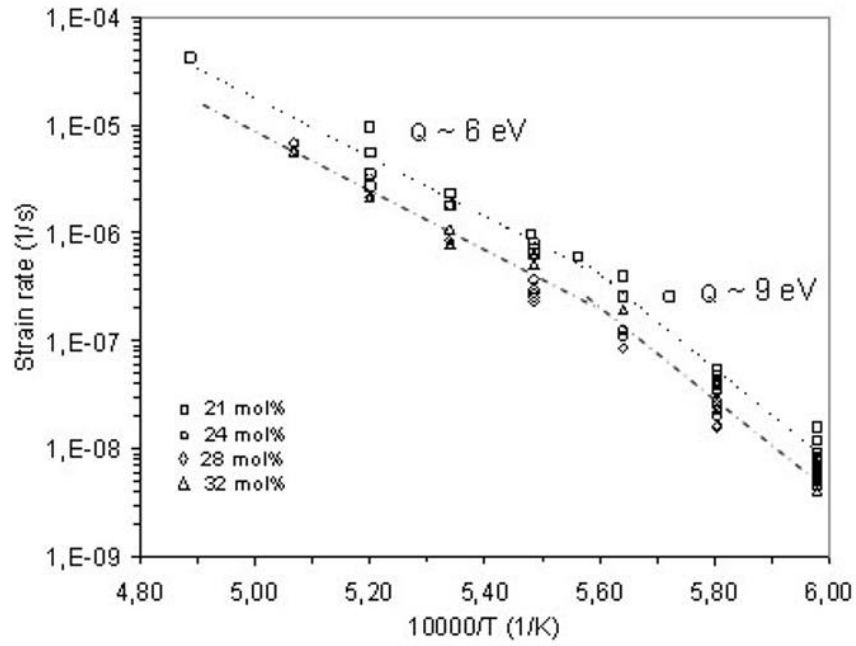


Figure 2: Strain rate versus the inverse of temperature for various yttria contents (21, 24, 28 and 32 mol%) showing the two deformation regimes with different values of activation energy Q .