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Dislocation Climb Controlled Deformation of Y_2O_3-Doped Cubic ZrO_2 Single Crystals

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Abstract

Constant strain rate tests have been performed on cubic ZrO_2 single crystals stabilized with 9·4 mol% Y_2O_3 in an argon atmosphere at temperatures up to 1750°C. Crystals were oriented along the ⟨112⟩ direction for easy {001}⟨110⟩ slip. Mechanical data have been correlated with transmission electron microscopy observations in order to characterize the strain rate-controlling mechanism. At temperatures above 1500°C, a recovery mechanism by dislocation climb has been obtained with an activation energy of about 510 kJ/mol, corresponding to the cation diffusion.

Tests mit konstanter Dehnungsrate wurden an kubischen ZrO_2-Einkristallen, die mit 9·4 mol% Y_2O_3 stabilisiert waren, unter Argon bei Temperaturen bis zu 1750°C durchgeführt. Die Kristalle waren in ⟨112⟩ Richtung orientiert, um einfaches {001} ⟨110⟩ Gleiten zu ermöglichen. Mechanische Daten wurden mit Beobachtungen aus der Transmissionselektronenmikroskopie in Verbindung gebracht, um den für die Dehnungsrate bestimmenden Mechanismus zu charakterisieren. Bei Temperaturen über 1500°C wurde ein Erholungsmechanismus durch Versetzungsklettern erhalten, der eine Aktivierungsenergie von ungefähr 510 kJ/mol entsprechend der Kationendiffusion hat.

Des tests à vitesse de déformation constante ont été réalisés sur des monocristaux de ZrO_2 cubique stabilisés par 9·4 mol% Y_2O_3, dans une atmosphère d'argon, jusqu'à la température de 1750°C. Les cristaux étaient orientés selon la direction ⟨112⟩ afin d'avoir un glissement {001} ⟨110⟩ facile. Les résultats mécaniques ont été corrélés avec des observations en microscopie électronique par transmission, afin de caractériser le mécanisme contrôlant la vitesse de déformation. A des températures supérieures à 1500°C, un mécanisme de réparation par montée des dislocations a été obtenu avec une énergie d'activation d'environ 510 kJ/mol, correspondant à la diffusion de cations.

1 Introduction

Zirconia-based ceramics show excellent properties of strength and toughness at low temperatures because of stress-induced martensitic transformation of the tetragonal to the monoclinic phase.[1,2] When stabilized with Y_2O_3, this alloy shows attractive mechanical properties at high temperatures ($T > 0{\cdot}5T_M$, where T_M is the melting temperature, about 2700°C), superplasticity of fine-grained polycrystals[3,4] and potent hardening either by solid solution[5,6] or precipitation.[7] In the latter case, the hardening is possible because of the high stability of the tetragonal particles against aging, which is due to the special microstructure of the ZrO_2–Y_2O_3 system, formed by 'colonies' containing two 90° twin-related variants.[7]

In the authors' previous work,[5,6,8–12] the high-temperature plastic deformation of Y_2O_3-stabilized cubic ZrO_2 single crystals up to 1500°C has been studied. Detailed microstructural observations were performed.[9–11] A transition in the rate-controlling mechanism was found around 1450°C in creep,[8] dislocation climb being the recovery mechanism proposed above this temperature. However, the temperature range studied was too small to obtain definite conclusions about this mechanism.

In this work the temperature range has been extended to 1750°C where diffusion processes are more important. Macroscopic results have been correlated with transmission electron microscopy

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(TEM) observations, in order to obtain information about the rate-controlling mechanism. These results have been compared with diffusion data to check the deformation–diffusion relations.

2 Experimental Procedure

Materials and experimental techniques are similar to those used in the authors' previous work. Fully stabilized cubic ZrO_2 single crystals (supplied by Ceres Corp., North Billerica, MA, USA) containing 9·4 mol% Y_2O_3, optically transparent and grown by skull melting were used in this study. Crystals were oriented by the Laue X-ray back-reflection technique and then cut into parallelepipeds of $6 \times 3 \times 3$ mm in size for compression tests. The long axis (the loading axis) was parallel to the $\langle 112 \rangle$ direction, while the lateral faces were parallel to $\{111\}$ and $\{110\}$ planes. This orientation provided a Schmid factor of 0·47 for the easy $\{001\}$ $\langle 110 \rangle$ slip system.

High-temperature mechanical tests were carried out at a constant strain rate in an Instron machine equipped with a furnace with tungsten heating elements working in an argon atmosphere at 1 atm pressure. The temperature of the tests ranged from 1450°C to 1750°C, and the cross-head speed from 5 mm/min (corresponding to an initial strain rate of $1{\cdot}4 \times 10^{-5}\,s^{-1}$) to 20 mm/min. Pads of polycrystalline SiC were inserted between the sample and the tungsten punching rams to avoid reactions. Above 1750°C, strong indentation between the samples and SiC pads was observed, preventing mechanical tests. Recorded data, sample elongation versus time, were analysed as engineering stress σ–engineering strain ε curves.

After test completion, the power was switched off and the temperature decreased quickly, quenching the specimen microstructure. For example, the temperature decreased from 1700°C to 1100°C in 60 s; it was below 700°C after 3 min. After tests in argon, the material was darkened. This effect has been associated to the reduction of the Zr^{4+} ions to Zr^{3+}.[13]

Foils for transmission electron microscopy were cut from deformed samples quasi-parallel to the glide plane, and thinned to electron transparency by standard methods (mechanical polish and ion thinning). Observations were made using an Hitachi H800-2 transmission electron microscope operating at 200 kV (Microscopy Service, University of Seville, Spain).

Damage by electron irradiation appeared after some time of observations in the TEM. Small loops formed on dislocations segments, a phenomenon which seems faster at 1200°C or 1600°C than at 1400°C.

3 Results and Discussion

3.1 Mechanical behaviour

σ–ε curves are shown in Fig. 1 for different temperatures. Curves obtained at lower temperatures on the same material but deformed in air are also shown.[6] A yield drop can be observed at higher temperatures, which tends to disappear when the temperature increases. This drop has been associated to the activation of secondary slip systems (namely $\{100\}$ $\langle 011 \rangle$ and $\{111\}$ $\langle 101 \rangle$).[9,10]

The steady-state deformation regime at constant stress is reached after $\simeq 2\%$ strain with constant stresses (Fig. 1), due to inhomogeneous deformation of the samples; they were skewed over the $\{001\}$ plane along the $\langle 011 \rangle$ direction, with a very small increase in the sample cross-section.

Results in air and argon are close, as can be observed in Fig. 2, which shows the flow stress as a function of the temperature. An independence in the mechanical behaviour with the oxygen partial pressure (P_{O_2}) was found in the creep of c-ZrO_2 single crystals (between 0·21 and 10^{-5} atm at

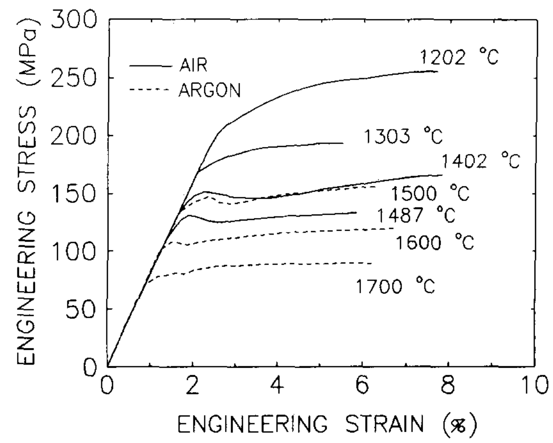


Fig. 1. Engineering strain versus engineering stress curves for Y-FSZ 9·4 mol% deformed in argon atmosphere. Curves obtained in air are also shown (from Ref. 6). The initial strain rate was $1{\cdot}4 \times 10^{-5}\,s^{-1}$.

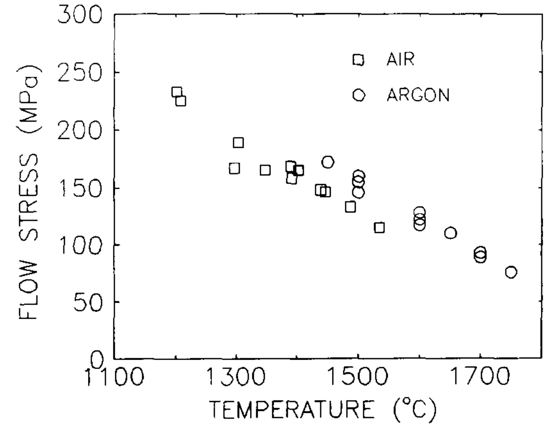


Fig. 2. Values of the flow stress at different temperatures measured for Y-FSZ 9·4 mol% in argon and air atmospheres at 0·03 strain. The initial strain rate was $1{\cdot}4 \times 10^{-5}\,s^{-1}$.

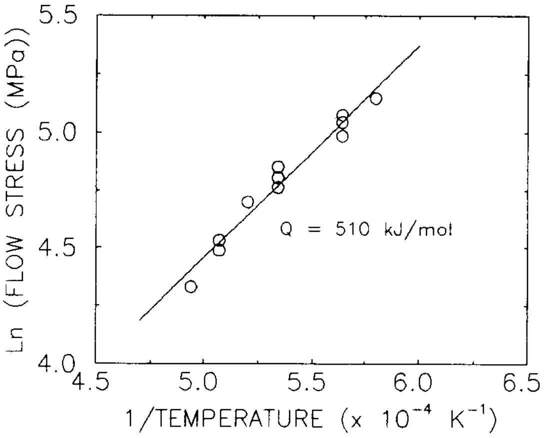


Fig. 3. Fit of the log of the flow stress with the inverse of the temperature. An activation energy of 510 kJ/mol was determined from the slope, with a stress exponent of 6·3.

1300–1400°C)[8] and polycrystals (between 0·21 and 10^{-9} atm).[14] The creep experiments are more accurate in the determination of the P_{O_2} dependency because the same sample is used. The small scatter observed in the flow stress between air and argon (Fig. 2) can be due to the fact that different testing machines were used in the argon and air experiments.

Changes of strain rate and temperature have been performed in steady-state regimes to obtain the stress sensitivity n and the activation energy of the process Q, according to the high-temperature plastic deformation equation:[15]

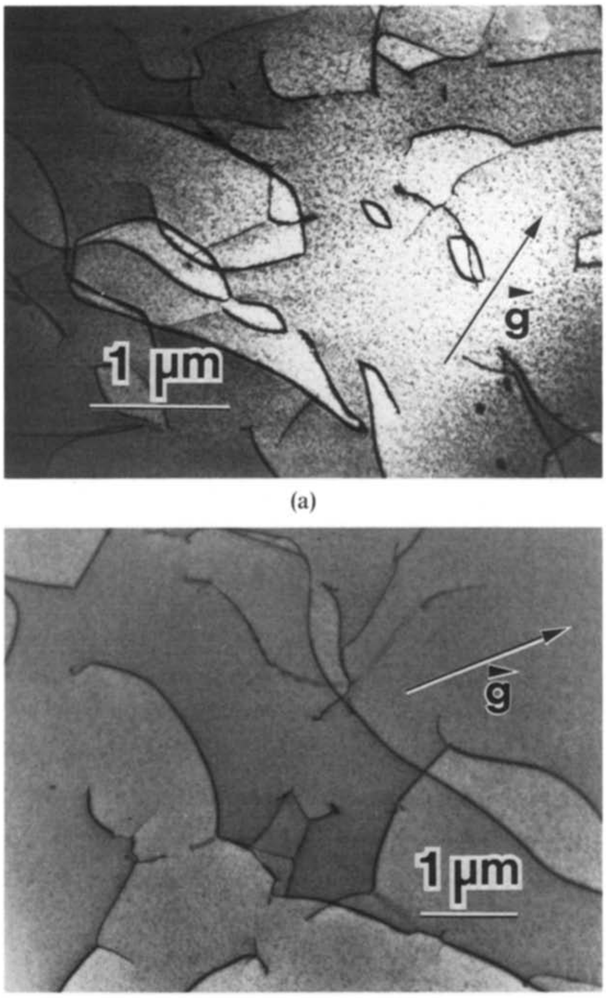
$$\dot{\varepsilon} = A \cdot \sigma^n \cdot \exp(-Q/kT) \qquad (1)$$

An average value of 6·3 + 1·0 was found for the stress exponent; with this value, the activation energy value determined from changes in the temperature on the same test was 570 ± 80 kJ/mol. A fit of the flow stresses measured on the different samples with the temperature (Fig. 3) gave a value of 510 ± 30 kJ/mol. These activation energies are close to those reported in the literature (520 to 550 kJ/mol) for the diffusion-controlled deformation in ZrO_2–Y_2O_3 polycrystals with a large range of yttria concentrations (from 2 to 25 mol% corresponding to crystals from tetragonal to cubic phases[3,4,14,16]), and on the creep of 9·4 mol% Y_2O_3–ZrO_2 single crystals at temperatures higher than 1450°C (580 kJ/mol).[8]

3.2 Dislocation substructure

Stereo pairs obtained with the diffraction vector **g** = (220) were used to study the three-dimensional nature of the dislocation structures. Standard **g.b** analysis was carried out to determine Burgers vectors of dislocations.

Very different dislocation structures in the deformed samples were found depending on the temperature of the test (Fig. 4). Below 1450°C, the dislocation density was high ($\rho \simeq 10^{13}\,\mathrm{m}^{-2}$).[5] Dislocations were very curved (Fig. 4(a)), belonging especially to the primary slip plane, with extensive reaction between them. Significant cross-slip on {111} planes occurred, as observed by stereo pairs.



(a)

(b)

Fig. 4. TEM micrographs of dislocation substructures in Y-FSZ 9·4 mol% samples deformed (a) at 1500°C in air, and (b) at 1600°C in argon atmosphere ({001} plane, g = (220)).

Conversely, at higher temperatures ($T > 1600$°C), the dislocation density was much lower ($\rho \simeq 10^9\,\mathrm{m}^{-2}$). Dislocations were especially straight, forming polygonal structures with segments along the ⟨101⟩ and ⟨011⟩ directions (Fig. 4(b)). For dislocations in the {001} plane, **b** was of the type ⟨110⟩ (edge character), but for the other dislocations, the other four ⟨110⟩ Burgers vectors were also present (edge and mixed character), indicating that different slip systems have been activated. No screw dislocations were found.

Stereo pairs (Fig. 5) showed that many dislocations were perpendicular to the {001} primary slip plane, indicating that significant structure recovery by dislocation climb occurred at the higher temperatures. No loops were observed, indicating that diffusion is fast enough to anneal the loops at these temperatures. A similar dislocation structure was observed in the creep of c-ZrO_2 single crystals at temperatures higher than 1450°C,[8] where the

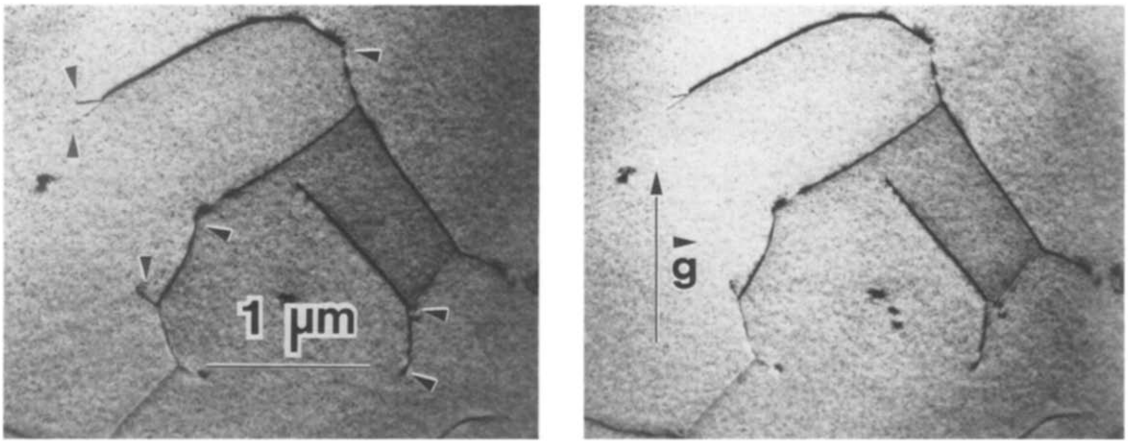


Fig. 5. Stereo pair of transmission electron micrographs of dislocation substructure in Y-FSZ 9·4 mol% sample deformed at 1700°C in argon atmosphere, showing extensive climb of dislocations (arrows) ({001} plane, **g** = (220)).

steady-state strain rates were a factor 10 lower than the values used in this work.

However, a cell structure formed by dislocation arrays in subgrain boundaries (typical of the high-temperature steady-state deformation in metals and ceramics[15]) was not observed. A pseudo-tridimensional distribution of dislocations (of about 50 mm in diameter) was observed by X-ray topography in c-ZrO_2 single crystals deformed at 1400°C.[9]

3.3 Discussion

Values of about 6 in the stress exponent have been ascribed to a rate-controlling mechanism by dislocation climb in different ceramic materials,[15,17] which is the slowest process in relation to dislocation glide. An increase in the stress exponent is found when the temperature decreases, corresponding to a change in the deformation mechanism. In c-ZrO_2 single crystals the n exponent increases from about 6 at temperatures higher than 1500°C to about 12 at 1200°C.[6]

TEM observations confirm an extensive climb of dislocations at temperatures higher than 1500°C. In this case, the climb is controlled by the diffusion of the slowest ionic species in the crystal. In the ZrO_2–Y_2O_3 system, yttrium and zirconium are the slowest ones, with very similar diffusivities between them[18,19] and about ten times smaller than the oxygen diffusivity.[20] Under these conditions, the energy of the process can be ascribed to the cation diffusion in the bulk of the material.

Two independent measurements of diffusion coefficients have been performed in the ZrO_2–Y_2O_3 system,[18,19] with a factor 10 of difference between them. The more recent results[19] have been obtained on crystals with the same origin and yttria content as the present samples. The activation energies for zirconium and yttrium are very similar between them, 480 and 450 kJ/mol, respectively (Fig. 6). Also, an analysis of the data from high-temperature deformation creep in c-ZrO_2 polycrystals, from the annealing studies of prismatic dislocation loops in c-ZrO_2 single crystals and from the interdiffusion measurements, treated as a single data set, showed that they could be fitted by an effective diffusion coefficient with an activation energy of 490 kJ/mol.[8] These energies, ascribed to cation diffusion, are very close to the present Q value of 570 ± 80 kJ/mol.

A diffusion coefficient cannot be directly deduced from the power law (eqn (1)) because it is too empirical, the dimensionless constant being unknown. However, assuming that eqn (1) can be written as:[15]

$$\dot{\varepsilon} = B\frac{\sigma^n}{T}D^1$$

where D^1 is the diffusivity of the slowest species, D^1 can be obtained by computation over temperature taking $D^1 = 2{\cdot}0 \times 10^{-17}$ m²/s at the highest temperature of the tests, 1750°C.[19] The result is shown in Fig. 6. The important point is that the data above 1400°C fit well as a straight line, but it shows a change in the rate-controlling mechanism below this temperature. TEM observations indicate that extensive cross-slip

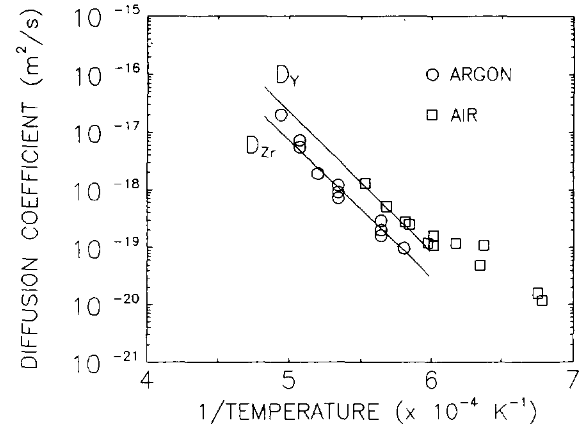


Fig. 6. Comparison of diffusion coefficients for yttrium (D_Y) and zirconium (D_{Zr}) in c-ZrO_2 obtained from tracer diffusion measurements[19] with values deduced from high-temperature steady-state deformation, taking $D = 2{\cdot}0 \times 10^{-17}$ m²/s at 1750°C.

occurred during deformation at temperatures below about 1400°C.[5,8]

These features allow it to be concluded that, at temperatures above 1500°C, the deformation of c-ZrO_2 single crystals is controlled by recovery of the dislocation structure through climb via cation diffusion. The independence of the steady state from oxygen activity implies that the equilibrium concentration of the minority point defects which controls the cation diffusion is not sensitive to P_{O_2} because their concentrations are fixed by the oxygen vacancy concentration through the Y_2O_3 doping.

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