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Creep in nanocrystalline zirconia

Santonu Ghosh[1] and Atul H. Chokshi*

Department of Materials Engineering, Indian Institute of Science, Bangalore 560 012, India

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Grain boundary sliding remains a dominant deformation process during creep in both nanocrystalline and submicron-grained zirconia. The level of segregation of Y to grain boundaries is reduced by a factor of ~2 in nanocrystals. However, a scaling relationship for compression creep was valid in a 3 mol.% yttria-stabilized tetragonal zirconia with grain sizes in the range of ~65–400 nm, indicating the same deformation mechanism over this range of grain sizes.

Keywords: Nano; Creep; Zirconia; Segregation; Grain boundary sliding

The high-temperature deformation characteristics of superplastic materials can be expressed as [1]:

$$\dot{\varepsilon} = \frac{ADGb}{kT}\left(\frac{b}{d}\right)^{p}\left(\frac{\sigma}{G}\right)^{n}, \quad (1)$$

where $\dot{\varepsilon}$ is the steady-state strain rate, A is a dimensionless constant, D is the appropriate diffusion coefficient, G is the shear modulus, b is the magnitude of the Burgers vector, k is Boltzmann's constant, d is the grain size, and p and n are constants termed the inverse grain size and stress exponent, respectively. The diffusion coefficient is given as $D = D_0 \exp(-Q/RT)$, where D_0 is a frequency factor, Q is the appropriate activation energy, and R is the gas constant.

As shown by Herring [2] for sintering, the scaling relationship offers a convenient means for examining variations in time scale via a change in a length scale. For Coble diffusion creep [3] involving transport along grain boundaries, $n = 1$, $p = 3$ and $Q = Q_{gb}$ (the activation energy for grain boundary diffusion). Thus, for a scaling relationship based on grain sizes to be valid, all creep data over a range of grain sizes should fall on a single line in a plot of $\dot{\varepsilon}d^p$ vs. ϕ.

Experiments over a wide range of experimental conditions have revealed a range of transitions in the creep behavior of zirconia, which are sensitive to impurity content and grain size [4–10]. Although most investigations attribute superplastic creep to grain boundary sliding (GBS), two different rate-controlling mechanisms have been proposed: interface-controlled Coble diffusion creep (Lifshitz sliding) or GBS (Rachinger sliding) with a grain size-dependent threshold stress [4–15].

In an interesting approach, following Jamnik and Raj [16], Guiterrez-Mora et al. [17] noted that grain boundary segregation will cause changes in the local electric potential, leading to a reduction in strain rate in a nano-3 mol.% yttria-stabilized tetragonal zirconia (n-3YTZ). In the limit of very fine grain sizes, the level of segregation may vary inversely with grain size [18], so that changes in the grain size can also influence the local electric potential. The analysis [17], and its correction for very fine grain sizes [19], suggests that changes in grain boundary chemistry can influence creep in zirconia at very fine grain sizes [11].

There have been very few studies on creep in nanocrystalline zirconia [20–28] due to the difficulty in making such samples dense. Inspection of the limited data on creep in nano-zirconia, Supplementary Fig. S1, reveals considerable variation in the data under nominally similar conditions; the reported stress exponents range from $n \approx 1.4$–3. Furthermore, the expected scaling relationship in conventional materials with $d > 0.3$ μm is reportedly not valid in the nanocrystalline range, with the nanosamples exhibited higher creep strength than expected [25,28]. The observed strengthening

* Corresponding author. Tel.: +91 8022932684; e-mail: achokshi@materials.iisc.ernet.in

[1] Current address: Element Six Ltd., Harwell Science Park, Oxfordshire, UK.

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was attributed to the influence of grain boundary segregation in nano-zirconia.

The above brief description demonstrates a need to consider three important interrelated issues: (i) Is the scaling relationship for creep valid in the nanocrystalline regime? (ii) Is there a change in grain boundary segregation with a decrease in grain size? (iii) Is there change in deformation mechanism in n-3YTZ?

High-purity 3YTZ powder was obtained from Tosoh Corporation, Japan. The powder was cold compacted and sinter-forged using a two-stage process. Parallelepiped specimens of n-3YTZ with nominal dimensions of 4.5 mm × 2.5 mm × 2.5 mm were cut from the sinter-forged disks and only specimens with relative density greater than ~98% were used for the creep experiments.

Linear intercept grain sizes were measured from the micrographs captured using a scanning electron microscope (Sirion XL 30 FE SEM), for 500–700 grains. Dense compacts were annealed at temperatures ranging from 1423 to 1773 K for up to 10 h to obtain grain sizes from 65 to 380 nm. Samples with grain sizes of $\leqslant$120 or >120 nm are hereinafter referred to as n-3YTZ and c-3YTZ, respectively.

High-temperature creep experiments were carried out under constant compressive stresses from 20 to 200 MPa, at 1373–1423 K. A few experiments were also carried out under constant crosshead velocity. Selected samples were polished prior to testing in order to characterize the GBS. The specimens were cooled rapidly under load from the testing temperature to avoid changes in surface topography that may influence GBS measurements.

To characterize segregation, samples with a grain size of either 65 and 310 nm were quenched from a high temperature, polished and examined using a Tecnai F30 analytical transmission electron microscope, operating at 300 kV. The chemical analysis of grain boundaries and the bulk was performed in scanning transmission mode using a probe size of ~2 nm. The grain boundaries were tilted to near edge-on and energy-dispersive X-ray spectroscopy scans were carried out at more than 10 points each, across five different grain boundaries.

GBS measurements were carried out by atomic force microscopy (Nanosurf easy scan 2). Selected samples were polished to 0.25 μm and tested to a strain of 20% at 80 MPa and temperatures of 1373, 1398 and 1423 K. After deformation, the relative vertical displacements between adjacent grains were measured at about 200 boundaries. The strain due to GBS was calculated as [15,29–31] $\varepsilon_{gbs} = \phi(\bar{v}/\bar{L}_f)(1+\varepsilon_f)$, where ϕ (=1.4) is a constant [29], $\bar{v}$ is the average value of the vertical component of the GBS vector, and $\bar{L}_f$ is the final grain size after deformation to a final engineering strain ε_f. To account for possible errors due to polishing as well as surface changes due to heating to the test temperature, a blank run was performed on a sample taken to the test temperature and cooled down without application of a load.

The coarse-grained (Fig. 1a) and nanograined (Fig. 1b) samples exhibited a microstructure similar to that in conventional fully dense 3YTZ samples, with equiaxed grains; the grains remained equiaxed after creep. There was no evidence of any amorphous grain

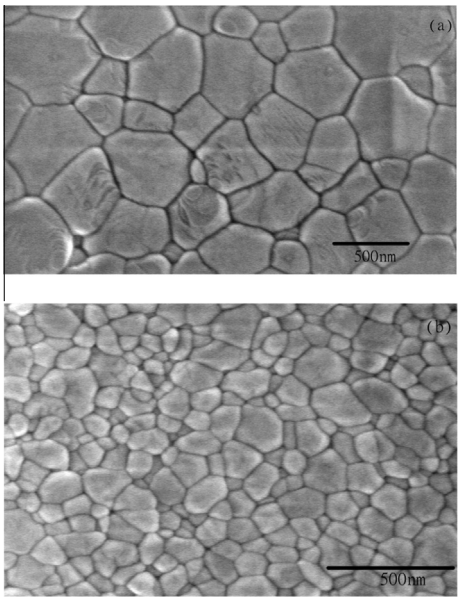

Figure 1. Microstructures of the specimens used in this study with grain sizes of (a) 310 nm and (b) 83 nm.

boundary zone from high-resolution microscopy. The experimental data obtained on segregation are shown in Figure 2a and b in terms of the variation in the Y/Zr ratio with position across a grain boundary for the c- and n-3YTZ samples, respectively. The experimental measurements revealed that the segregation enrichment ratio $(Y/Zr)_{gb}/(Y/Zr)_{bulk}$ is between 2.1 and 2.4 for c-3YTZ and between 1.2 and 1.4 for n-3YTZ. An earlier study noted that the segregation ratio was ~2.4 and ~2.7 for high- and low-purity zirconia, respectively [32]. Note that a decrease in grain size by a factor of

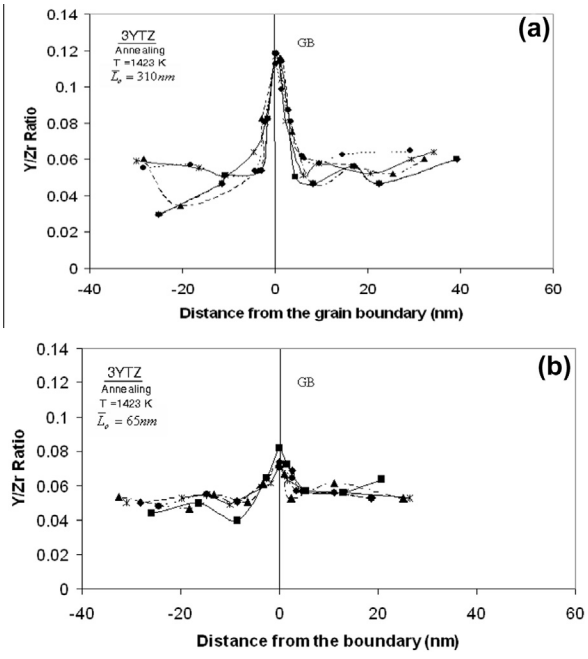

Figure 2. Variation in the ratio of (Y/Zr) across grain boundaries in (a) c-3YTZ (a) and (b) n-3YTZ.