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Original Article

Influence of grain boundary sliding on diffusion in yttria doped zirconia

Santonu Ghosh[a,*], Sathya Swaroop[b,c], Peter Fielitz[b], Guenter Borchardt[b], Atul H. Chokshi[a]

[a] *Department of Materials Engineering, Indian Institute of Science, Bangalore, Karnataka 560012, India*
[b] *Institut fuer Metallurgie, Technische Universitaet Clausthal, 38678 Clausthal - Zellerfeld, Germany*
[c] *School of Science and Humanities, VIT University, Vellore 632 014, India*

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Abstract

Grain boundary sliding during high temperature deformation can lead to stress concentrations and an enhancement of diffusion in mobile boundaries. Experiments were conducted on a fine grained 3 mol% yttria stabilized tetragonal zirconia, under conditions associated with superplastic flow involving grain boundary sliding. Tracer diffusion studies under creep conditions and without load indicate that there is no enhancement in either the lattice or grain boundary diffusivities. The experimental creep data are consistent with an interface controlled diffusion creep mechanism.

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

1. Introduction

It is well known that grain boundaries play an important role in many processes such as precipitation, grain growth, oxidation, creep, superplasticity, and cavitation failure; these processes are frequently controlled by diffusional mass transport.[1,2]

The movement of adjacent grains perpendicular to their mutual interface and along the interface relates to grain boundary migration and sliding, respectively.[3,4] There have been many studies dealing with grain boundary migration, and the influence of vacancies and diffusion in such processes[2,3]; some studies suggest that grain boundary diffusion is enhanced by several orders of magnitude in processes involving diffusion-induced grain boundary migration.[5,6]

Creep in an important deformation process in high temperature structural applications of materials; the creep rate $\dot{\varepsilon}$ can be expressed as:

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

where A is a dimensionless constant, D is the diffusion coefficient, G is the shear modulus, b is the magnitude of the Burgers vector, k is Boltzmann's constant, T is the absolute temperature, d is the grain size, σ is the imposed stress, and p and n are constants termed as the inverse grain size exponent and stress exponent, respectively. The diffusion coefficient can be expressed as $D = D_0 \exp(-Q/RT)$, where D_0 is the pre-exponential term, Q is the appropriate activation energy and R is the gas constant.

A comparison of the experimental data with the theoretical creep models requires the diffusion coefficient D. Most models implicitly assume that the diffusion coefficient during deformation is identical to that determined from tracer studies on materials with stationary boundaries. Clearly, such a comparison between the theory and experiments will not be valid if the diffusivity is higher in mobile boundaries during high temperature deformation compared to static conditions without any load.

Superplastic flow with large elongations to failure is associated typically with $n \sim p \sim 2$ during tests at high temperature in fine grained materials.[7] Fine grains tend to grow rapidly at high temperatures, and it is now recognized that GBS associated with superplastic flow enhances grain growth at high temperatures.[8,9] Nieh and Wadsworth[10] attributed dynamic grain growth in 3YTZ to enhanced diffusion. Thus, it is clear that dynamic microstructural processes associated with deformation can significantly alter grain boundary kinetics at high temperatures.

The possible influence of GBS on diffusion is also of considerable significance for nanomaterials and ultrafine grained materials as GBS is implicated in several studies on their deformation.[4,11,12]

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* Corresponding author. Tel.: +91 80 2293 2684; fax: +91 80 2360 0472.
E-mail address: santonu@materials.iisc.ernet.in (S. Ghosh).

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We propose to use an experimental approach for critically examining the influence of GBS on diffusion by conducting diffusion measurements on specimens deforming superplastically together with experiments on specimens exposed to the same thermal history without any load.

2. Experimental material and procedure

High purity 3YTZ powder from Tosoh Corporation, Japan, with a total impurity content ($Al_2O_3 + SiO_2$) <0.01 wt%, was cold compacted under a pressure of 40 MPa and sintered in air at 1723 K for 2 h. Compression creep specimens with nominal dimensions of 3 × 3 × 5 mm were cut out from the disk and density of these specimens was measured using Archimedes' principle. Only specimens with a density >99% of the theoretical value of 6.08 g cm^{-3} were used for this study. These specimens were annealed further at 1873 K for 6 h to obtain a larger grain size. Grain size measurements were carried out from SEM (Sirion, XL30) micrographs using a linear intercept method, on polished specimens that were thermally etched at 1673 K for 1 h. The mean liner intercept grain size was obtained from more than 500 measurements to reduce the error to <5% at the 95% confidence level. Atomic force microscopy (nanosurf) was used to examine changes in the topology of polished surfaces before and after creep deformation.

Following earlier studies, diffusion measurements involved using Hf which has a similar ionic radius and same valency as Zr; a thin layer of HfO_2 was pulse-laser deposited on to a polished surface of a 3YTZ specimen.[13,14]. Based on an earlier measurement of Hf lattice diffusion, it was concluded that heating at a rate of 22 K/min in a creep furnace environment and allowing 15 min for stabilization will not have a significant effect on diffusion measurements at testing temperatures of up to 1623 K.

The diffusivity measurements were carried out using a Cameca IMS 3f secondary ion mass spectrometer (SIMS) with a depth resolution less than 3 nm. All the measurements were carried out using a primary beam of O^- ions with an energy of 15 keV and a current of ~150 nA. A crater of dimensions ~250 μm × 250 μm was created by rastering the beam for depth profiling, and the crater depth from a blank run was calibrated with a profilometer to convert the depth profiling times to distances. More details of the experimental procedures are presented elsewhere.[13,14]

Stress jump compression creep experiments were conducted at 1598 and 1623 K, to characterize the stress dependence of creep. Constant stress compressive creep experiments were carried out at 1598 and 1623 K and stresses of 20 and 50 MPa to strains of 5% and 10%, for specimens that were coated with the tracer. An experiment was also conducted without stress at 1623 K for the longest time used in the creep study.

3. Experimental results

The initial mean linear intercept grain size of the annealed samples was 0.90 ± 0.05 μm, and the initially equiaxed grain shape and grain size did not change under the present creep experiments.

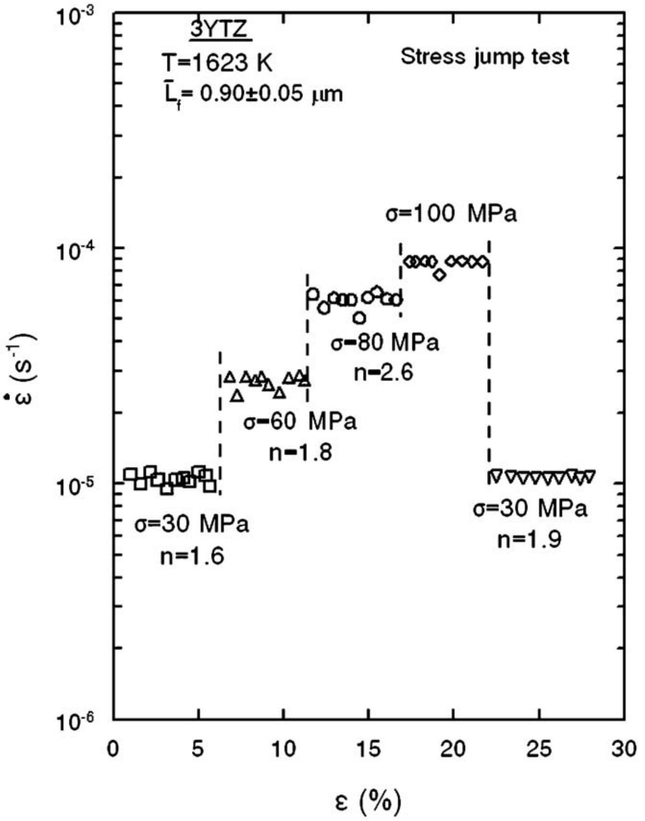

Fig. 1. Variation in strain rate with strain for a stress jump experiment at 1623 K.

3.1. Creep data

Fig. 1 shows the variation in strain rate with strain during stress jump tests at 1623 K. It is clear that deformation occurred by steady state creep under all conditions. It is to be noted that the strain rate was essentially identical at the end of the first segment and last segment of the stress jump test, at the same stress; this is consistent with the absence of any change in the grain size.

The variation in steady state strain rate with stress is illustrated on a logarithmic scale in Fig. 2 for tests at 1598 and 1623 K. It is clear that the data exhibit a stress exponent of $n \sim 2$ over the entire range of stress used. The vertical arrows depict the stresses used for the present constant stress experiments to characterize diffusion. Predictions from a Coble diffusion creep model[15] are also shown, and discussed later. Experimental observations of polished surfaces by atomic force microscopy revealed evidence for grain boundary sliding, in a manner similar to earlier reports.[16,17]

3.2. Diffusion measurements

Hafnia coated parallelepiped compression specimens were characterized by SIMS depth profiling. The specimens were coated with carbon to avoid charging. Fig. 3 is the concentration profile of the specimen deformed at 1598 K to a strain of 10% under a constant compressive stress of 20 MPa. The ^{177}Hf was taken as a tracer and the concentration of the tracer was

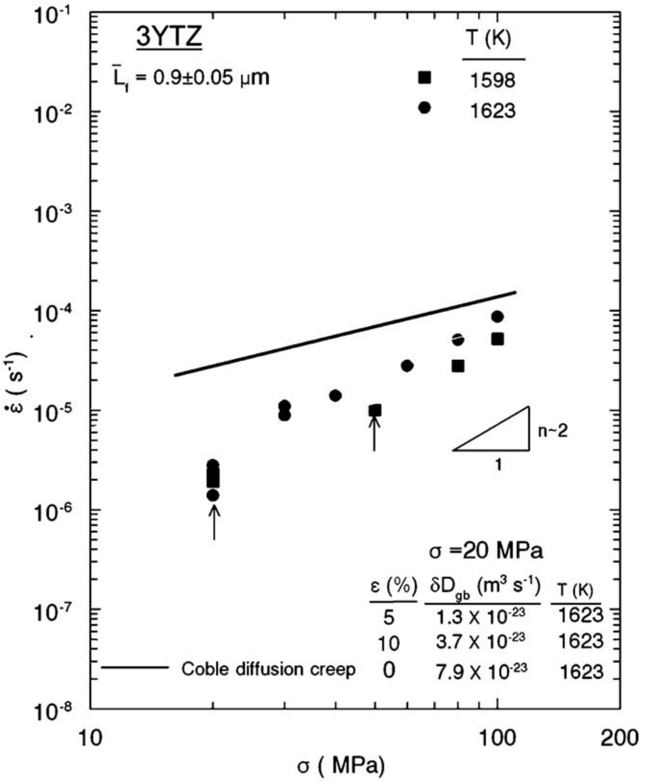

Fig. 2. Variation in steady state strain rate with stress for tests at 1598 and 1623 K, together with predictions of the Coble diffusion creep model.

normalized with the concentration of ^{96}Zr and plotted as a function of depth; the depth resolution of the SIMS was 3 nm. The concentration of ^{96}Zr remained constant from the surface to the interior.

These profiles were used to calculate the lattice and grain boundary diffusivities. The data in Fig. 3 suggest that there are two different regimes: an initial region and a tail region corresponding to lattice and grain boundary diffusion, respectively.

Fig. 3b shows the concentration vs depth^2 (y^2) plot from which the lattice diffusivity is calculated using the expressions given by Fischer.[18] Fig. 3c is the corresponding plot of concentration vs depth$^{6/5}$, from which the grain boundary diffusion coefficient is obtained using the analysis by Whipple[19]; the slope of the tail part of the curve was used for this purpose. The lattice diffusivity (D_l) and grain boundary diffusivity (D_{gb}) were calculated using the standard expressions relating the variations in concentrations with depth.[13,14]

The experimental data obtained from such an analysis are summarized in Table 1, and are also shown in Fig. 4a and b in terms of the variation with inverse temperature in the lattice and grain boundary diffusion coefficients, respectively. Assuming that Hf is a tracer for Zr, the value of segregation factor s[13,14] was taken tentatively as unity. Also shown in Fig. 4a and b are some data reported earlier for lattice and grain boundary diffusion coefficients in yttria stabilized tetragonal zirconia.[16,17,21] Inspection of the data reveals that the present measurements yield somewhat higher values of the diffusion coefficients.

In general, diffusivity data of elements which are transported by minority defects in oxides show a much larger scatter, even for nominally identical materials, than the diffusivity data of the elements transported by majority defects. In yttria doped zirconias, the scatter in the cation diffusivity data is therefore much larger than in the oxygen diffusivity data. Further, this effect is even more pronounced for grain boundary diffusion than for bulk diffusion—probably because of the propagation of errors in the calculation of the grain boundary diffusivity and variations in grain boundary concentrations of impurities. If one therefore accepts a scatter of about one order of magnitude (although the errors in the individual measurements are substantially smaller), the present experimental data suggest that there is no significant enhancement in the diffusion coefficient because of GBS, as the data with and without stress are essentially identical within the typical experimental errors between different studies.

4. Discussion

Superplastic flow in many metals and ceramics is associated with a stress exponent of $n \sim 2$ and a retention of an equiaxed grain size.[7] The present experimental conditions, with $n = 2$ and observations of AFM surface offsets, are clearly favourable for critically examining the influence of GBS on diffusion.

4.1. Diffusion measurements

After creep deformation, the specimen surface roughness increased because of GBS. AFM measurements yielded a mean root square roughness value of ∼20–30 nm, and a vertical displacement of <100 nm after creep testing, both of which are substantially lesser than the lattice penetration of the Hf tracer. Hence, the surface roughness is not expected to significantly influence the measurements of the lattice and grain boundary diffusivity on the deformed specimens.

The present study indicates that the lattice and grain boundary diffusivities were not significantly influenced by GBS, as the diffusion data from creep tested samples were essentially identical to those on specimens without any load at $T = 1598$ and 1623 K, Fig. 4a and b. The use of hafnia as a tracer for the diffusivity measurements is reasonable, because the only data available with ^{96}Zr tracer yielded essentially identical lattice diffusion coefficient as Hf,[20] as noted in Fig. 4a.

In oxide ceramics, high temperature plastic deformation must involve diffusional transport of both the cations and anions in the appropriate ratio. For ZrO_2, it is well known that anion diffusion is very rapid through the lattice and along grain boundaries, so that creep will be controlled by cation diffusion.[13]

Inspection of Fig. 4 also indicates that the current values of cation diffusion coefficients are somewhat higher than those reported in the earlier studies. The main difference between the studies is the use of different furnaces: for conventional diffusion annealing, the specimens were placed inside an alumina tube, whereas for creep studies the specimens were placed inside a split furnace without an alumina tube enclosure. There may also be other possible causes for the difference, e.g. different sources for the HfO_2 tracer and 3YTZ specimens. It is important to note that minority carrier mediated diffusion in oxides may show a

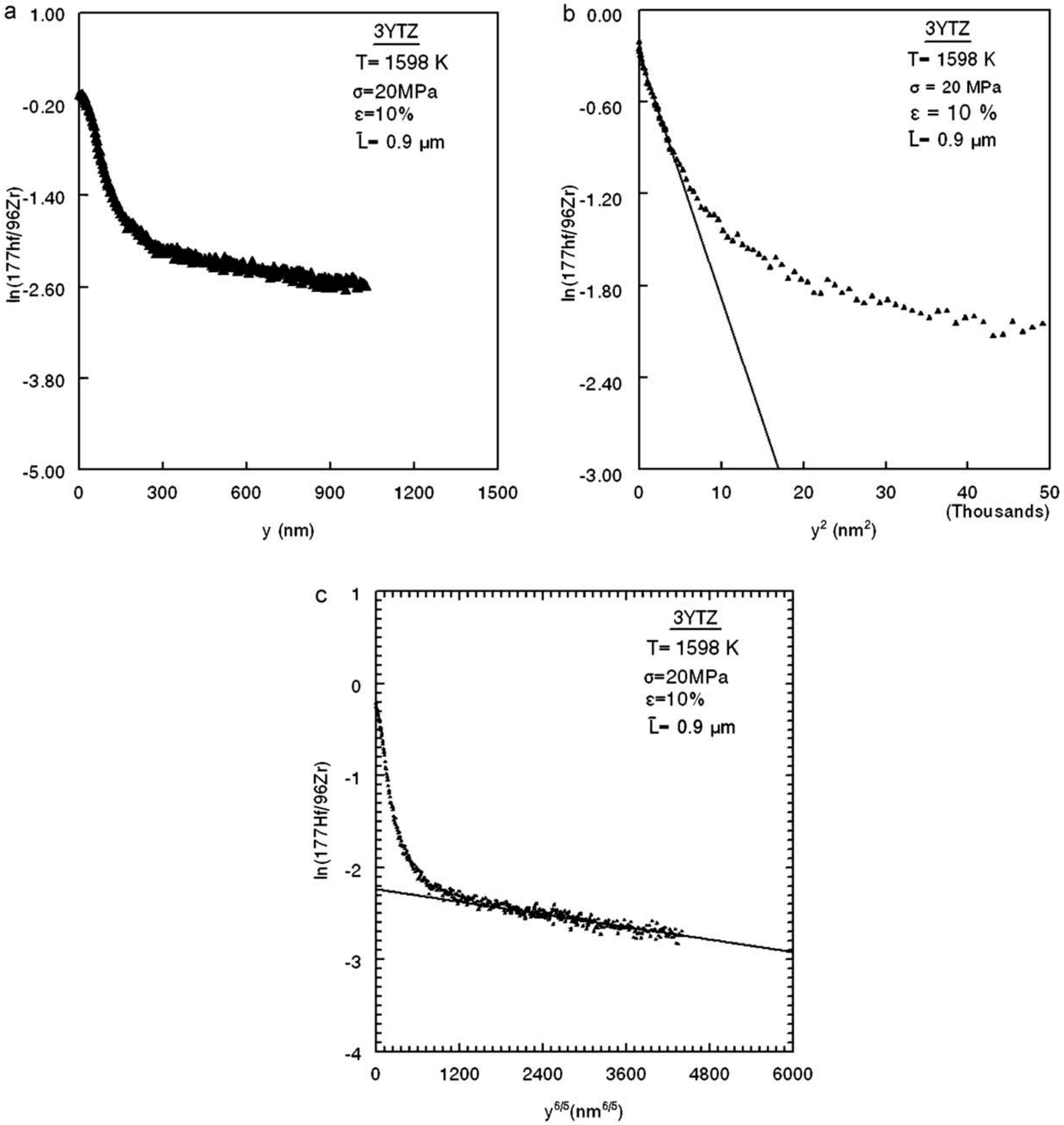

Fig. 3. (a) Typical tracer profile of a specimen after creep testing at $\sigma = 20$ MPa, $T = 1598$ K and $\varepsilon = 10\%$. (b) and (c) Tracer profiles replotted for calculating the lattice diffusion (b) and grain boundary diffusion (c) coefficients.

Table 1
Experimental data for Hf diffusion in zirconia.

Annealing temperature (K)	Applied stress (MPa)	Strain (%)	Annealing time (s)	D_l (m^2 s^{-1})	δD_{gb} (m^3 s^{-1})
1598	20	10	65,980	$3.0 \pm 0.81 \times 10^{-19}$	$2.6 \pm 2 \times 10^{-23}$
1598	20	10	65,980	$2.0 \pm 1.1 \times 10^{-19}$	$2.4 \pm 1.6 \times 10^{-23}$
1598	50	10	11,980	$6.3 \pm 2.0 \times 10^{-19}$	$2.4 \pm 2.0 \times 10^{-23}$
1598	50	10	11,980	$2.4 \pm 0.8 \times 10^{-19}$	$1.0 \pm 0.97 \times 10^{-23}$
1623	20	5	31,070	$1.3 \pm 1.0 \times 10^{-19}$	$1.3 \pm 1.2 \times 10^{-23}$
1623	20	10	60,210	$1.5 \pm 0.85 \times 10^{-19}$	$3.7 \pm 1.1 \times 10^{-23}$
1623	0	0	72,000	$9.0 \pm 3.1 \times 10^{-20}$	$7.9 \pm 4.1 \times 10^{-23}$

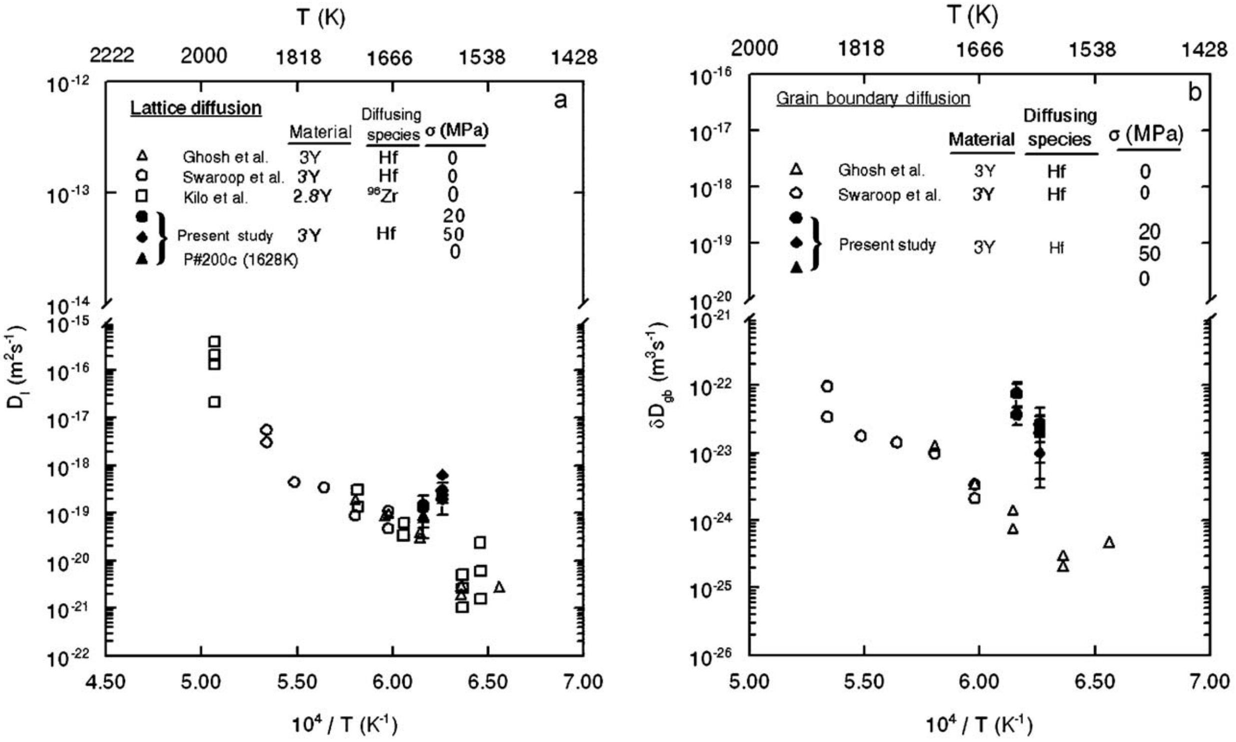

Fig. 4. Variation with inverse temperature in the lattice (a) and grain boundary (b) diffusion coefficients.

scatter of one order of magnitude, and it is possible that the present data fall within this broad range.

4.2. Implications for creep mechanisms

There have been several studies on 3YTZ showing an extended $n \sim 2$ region, with possible transition to $n \sim 3$ at low stresses and $n \sim 1$ at high stress.[21–24] Superplastic flow in 3YTZ has been attributed variously to grain boundary sliding, interface controlled diffusion creep and grain boundary sliding with a threshold stress.[21–25] Grain boundary sliding requires accommodation by either diffusion transport or dislocation activity[4]; in the present context, GBS associated with diffusion transport is identified with Coble creep whereas that associated with intragranular dislocation activity is termed GBS as an independent process. It is important to note that grain boundary sliding as an independent process should lead to strain rates that are higher than those predicted by Coble diffusion creep,[15] and this approach has been considered in superplasticity of metallic alloys.[7] Therefore, the theoretical curve for diffusion creep can provide guidance on the validity of some mechanisms.

The Coble creep rate[15,17,23] was evaluated for the present experimental conditions using $T = 1623$ K, the spatial grain size $d = 1.74\ \bar{L}$, $b = 0.36$ nm, and the experimental value of $\delta D_{gb} = 7.9 \pm 1.1 \times 10^{-23}\ \mathrm{m^3 s^{-1}}$, and the results are shown in Fig. 2. The experimental strain rates are somewhat slower than those anticipated from Coble diffusion creep. There have been several different models proposed for interface controlled diffusion creep, but regardless of the details the above approach suggests that the experimental results are consistent with the sequential operation of an interface controlled Coble diffusion process.[23] It is also clear that any model based on GBS occurring as an independent process would lead to creep rates that are faster than the diffusion creep rates, which would make them inconsistent with the current experimental results.

The present experimental results and analysis demonstrate clearly that the implicit assumption of a stress and GBS-independent diffusion is valid, so that the form of Eq. (1) is suitable even under conditions where grain boundaries are mobile.

5. Summary and conclusions

Creep, grain boundary sliding and tracer diffusion measurements were conducted in a superplastic 3 mol% yttria stabilized tetragonal zirconia. Detailed SIMS measurements of diffusion profiles obtained without load and under creep conditions reveal that GBS does not significantly influence diffusion. Furthermore, the experimental data are consistent with an interface controlled Coble diffusion creep process.

Acknowledgments

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