Creep in TiO$_2$ doped Zirconia: Implications for high strain rate superplasticity

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Abstract In ceramics, dopants offer the possibility of higher creep rates by enhancing diffusion. The present study examines the potential for high strain rate superplasticity in a TiO$_2$ doped zirconia, by conducting creep experiments together with microstructural characterization. It is shown that both pure and doped zirconia exhibit transitions in creep behaviour from Coble diffusion creep with $n \approx 1$ to an interface controlled process with $n \approx 2$. Doping with TiO$_2$ enhances the creep rate by over an order of magnitude. There is evidence of substantial grain boundary sliding, consistent with diffusion creep.

1. Introduction
Superplasticity refers to the ability of some fine grained polycrystalline materials to exhibit large elongations to failure [1]. The process is well established in metallic alloys, and it is being utilized to form components with complex shapes. It is now recognized that even nominally brittle intermetallic compounds and ceramics can exhibit large ductility under some conditions. A 3 mol% yttria stabilized tetragonal zirconia (3YTZ) has become a standard material for examining different aspects of superplasticity in ceramics [1-4]. Experimental data reveal that superplasticity occurs in fine grained materials tested at high temperatures. The superplastic strain rate is given as

$$
\dot{\varepsilon} \propto D d^{-p} \sigma^n
$$

where $D$ is the diffusion coefficient, $d$ is the grain size, $\sigma$ is the stress and $p$ and $n$ are constants termed the inverse grain size and stress exponent, respectively. For typical superplastic conditions, $n \approx p \approx 2$. The diffusion coefficient can be expressed as $D = D_0 \exp(-Q/RT)$, where $D_0$ is the pre-exponential term, $Q$ is the activation energy for the rate controlling process, $R$ is the gas constant and $T$ is the absolute temperature.

Conventional superplastic Ti and Al alloys with grain sizes of $\sim 10 \mu$m exhibit superplasticity at relatively slow strain rates of $\sim 10^{-4}$ s$^{-1}$ [1]. For economic viability, it is desirable to displace optimum superplasticity to higher strain rates. Equation (1) suggests that it is possible to obtain high strain rate superplasticity by refining the grain size, and this is a popular approach in metallic alloys where a refinement in grain size from $\sim 10$ to $\sim 1 \mu$m leads to an enhancement in strain rate from $\sim 10^{-4}$ to $>10^{-2}$ s$^{-1}$ [1].

In contrast to metallic alloys where superplasticity requires a grain size of $< 10 \mu$m, superplasticity in ceramics requires a finer grain size of $< 1 \mu$m. Further refinement in grain size to $< 0.1 \mu$m is possible, but difficult. Equation (1) also suggests that an increase in temperature can lead
to an increase in strain rate, by enhancing D. However, experimental data on superplastic zirconia reveals that an increase in testing temperature to 1823 K leads to drastic grain growth [5], so that initial grain sizes of ~0.3 µm increase rapidly to values > 1 µm. These results suggest that it is not possible to sustain superplasticity at higher temperatures in nominally single phase ceramics. Kim et al. [6] have used the strategy of multiphase alloying to limit grain growth at higher temperatures to obtain high strain rate superplasticity in zirconia-spinel composites.

In contrast to metallic alloys, where diffusion is controlled by the thermal concentration and migration of defects, diffusion in ceramics can also be modified by doping. Experimental data in 3YTZ indicate that there are many transitions in stress exponents from ~7 at high stresses (related to intragranular dislocation creep) to ~1 and ~2 and ~3 with a decrease in stress corresponding to Coble diffusion creep, and interface controlled diffusion creep [7]. These transitions are sensitive to impurity content as well as concentrations of dopants [1-3,7-9]. Experiments have shown that elements such as Al, Si, Ti and Ge influence both the flow stress and the transitions in creep behavior [8-13]. A recent detailed study has shown that silica additions do not influence the diffusion coefficients, but they retard the transition from Coble creep to interface controlled creep and possibly enhance ductility by limiting concurrent cavitation [14]. Sakuma and co-workers have shown that Ti and Ge either individually or together also enhance ductility, and these have been attributed to changes in bonding [10,11,13]. However, the influence of Ti additions on deformation mechanisms has not yet been examined.

We report below some experimental results on pure 3YTZ and TiO₂ doped 3YTZ, and demonstrate that TiO₂ addition enhances diffusion giving rise to the possibility of high strain rate superplasticity in such materials.

2. Experimental Materials and Procedure

Pure 3YTZ powders were obtained from Tosoh corporation in Japan. A wet-chemistry approach was utilized to dope 3YTZ powders with TiO₂; precursor of TiO₂ was formed by the hydrolysis of Titanium n-Butoxide [15]. Based on earlier promising results by Sakuma, we produced a composition of 3YTZ doped with 4.8 wt% TiO₂. Dense compacts of pure 3YTZ and TiO₂ doped 3YTZ were prepared by cold compaction and sintering at 1723 K for 2 hours. A range of grain sizes between ~0.6 and 1.4 µm were obtained by annealing sintered samples at various temperatures for different times. Parallelepiped specimens with nominal dimensions of 3x3x5 mm were machined for compression testing; only samples with densities >99% were used for the creep study. X-ray diffraction was used to determine the crystalline phases present in the materials, and to also calculate the theoretical densities.

Constant load and load change experiments were conducted for evaluating the creep characteristics. Selected deformed specimens were examined after creep testing for changes in the grain size and shape. Surface offsets at grain boundaries, indicative of grain boundary sliding, were measured using AFM data.

3. Experimental Results and Discussion

Fig 1: XRD patterns for annealed (a) 3YTZ (b) 3YTZ – 4.8 wt% TiO₂
Figures 1a and 1b are x-ray data obtained from pure 3YTZ and TiO$_2$-doped 3YTZ: both materials are largely tetragonal, with small \{200\} and \{311\} cubic zirconia peaks in annealed specimens with coarse grain sizes. There was no evidence of any separate TiO$_2$ peaks in the doped material, indicating that all the TiO$_2$ was dissolved in the 3YTZ. All specimens exhibited an equiaxed grain shape.

The variation in creep rate with strain is depicted in Fig. 2 for the TiO$_2$-doped specimens tested at either a constant load or by the load change method. There is almost no primary region, and most of the data correspond to steady state creep. There are very small transients accompanying load changes. These results suggest that there no significant internal microstructural changes, consistent with experimental observations on selected deformed specimens of the retention in an equiaxed grain shape and no grain growth.

Figure 3 is a logarithmic plot of the variation in strain rate with stress for the pure and the doped specimens with a grain size of ~0.7 to 1.0µm. It is clear that the data from load change tests are consistent with those from individual constant load tests. Furthermore, Fig. 3 depicts transitions in stress exponents from $n \approx 1$ to $n \approx 2$ with a decrease in stress, for both materials. Comparison of the data indicates also that TiO$_2$ doping enhances the creep rates by over an order of magnitude and reduces the stress for a transition from $n \approx 1$ to $n \approx 2$.

Earlier detailed studies on pure and SiO$_2$-doped 3YTZ [7,14] indicate that the $n \approx 1$ region is related to Coble diffusion creep which leads to the following creep rate $\dot{e}_{CO}$:

$$\dot{e}_{CO} = \frac{33 \delta D_{gb} G}{kT} \left( \frac{\sigma}{G} \right)^{2/3}$$

where $\delta$ is the grain boundary width, $D_{gb}$ is the grain boundary diffusion coefficient, $G$ is the shear modulus, $b$ is the magnitude of the Burgers vector and $k$ is Boltzmann’s constant. Experimental data show that $p=3$ when $n=1$, consistent with Coble diffusion creep. For a constant stress and temperature, eqn. 2 suggests that an increase in creep rate is related to an increase in $D_{gb}$. Thus, the present experimental data indicate that titania doping enhances grain boundary diffusion in 3YTZ, offering the potential for high strain rate superplasticity.

![Fig 2: Strain rate vs strain curves for 3YTZ - 4.8 wt% TiO$_2$](image)

![Fig 3: Variation of strain with stress for 3YTZ and 3YTZ - 4.8 wt% TiO$_2$ showing n~ 2 → 1](image)

![Fig 4: AFM image of deformed 3YTZ- 4.8 wt% TiO$_2$ and surface profile showing vertical offsets.](image)
It is recognized that diffusion creep must involve GBS to maintain specimen coherency, and this is referred to as Lifshitz sliding [18, 19], and measurements of sliding should yield high values for the GBS contribution. Figure 4 shows the surface topology of a deformed TiO$_2$ doped specimen; the offsets along grain boundaries are recorded, as shown on the right had side of Fig. 4. Such measurements of offsets along many boundaries can be used to calculate the GBS contribution to creep, following procedures described by Langdon. The experimental results yield a value of the GBS contribution to creep of $\geq 50\%$, which is consistent with Coble diffusion creep.

Coble creep and Lifshitz sliding are expected to lead to an elongation of grains along the tensile axis [16, 17]. However, the grains retained their equiaxed shapes in the present study. It is possible to account for this observation by referring to a model for diffusion creep developed by Lee [18], which involves grain switching and the retention of an equiaxed grain shape. It has also been pointed out that grain growth will also lead to grain switching which enables the retention of an equiaxed grain shape [19].

The transition from $n=1$ to $n=2$ at lower stresses is consistent with the operation of an interface controlled diffusion creep process, involving grain boundary sources and sinks that do not operate perfectly. The segregation of TiO$_2$ to grain boundaries, reported elsewhere [20], is likely to modify the efficiency of grain boundaries, and this can lead to a decrease in the stress for a transition from Coble diffusion creep to interface controlled Coble diffusion creep.

4. Summary and Conclusions

Compression creep experiments on pure and TiO$_2$-doped zirconia reveal a transition in stress exponents from $n=1$ at high stresses to $n=2$ at low stresses. The data are consistent with a transition from Coble diffusion creep to an interface controlled process at lower stresses. Titania doping enhances the creep rate by one order of magnitude, indicating that the dopant enhances grain boundary diffusion. There is considerable grain boundary sliding, consistent with Coble diffusion creep.

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