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Creep behavior of nanocrystalline monoclinic ZrO_2

Michael J. Roddy[1], W. Roger Cannon*, Ganish Skandan[2], H. Hahn[3]

Ceramic and Materials Engineering, Rutgers University, 607 Taylor Road, Piscataway, NJ 08854-8065, USA

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Abstract

Creep of nanocrystalline monoclinic zirconia, grain sizes of 75, 125, 175 nm were tested at 950 and 1000 °C. Dynamic grain growth occurred during creep but results were corrected for grain growth. Creep behavior followed an $n=1.7$ and $p=3$ behavior. It is proposed that grain boundary sliding is an active mechanism and results fit with Coble creep behavior. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Because of the destructive tetragonal to monoclinic phase transformation at 1170 °C, sintering of monoclinic zirconia must occur below that temperature and hence only one study of creep of monoclinic zirconia has been reported in the literature;[1] however, in this case grain growth was rapid and no correction for grain growth was made. In the current study creep of nanocrystalline monoclinic zirconia is reported. Because of lack of data on monoclinic zirconia, the creep behavior is compared with nanocrystalline yttria stabilized zirconia polycrystals (Y-SZP). Although a several creep studies on nanocrystalline ZrO_2 have been reported,[1–5] Gutierrez-Mora et al.[4] contend that in these studies densification rates dominated the kinetics. We add an additional argument. Even if sintering rates were not dominant, stress dependencies at low stresses may be influenced by the sintering stress. The strain rate for a porous solid is given by[6]

$$\dot{\varepsilon}_z = \frac{\Sigma}{3K} + \frac{\sigma_z}{\eta_e} \tag{1}$$

where $\dot{\varepsilon}_z$ is the measured strain rate, Σ is the sintering stress, K is the bulk viscosity (sintering viscosity), σ_z is the applied stress and η_e is the creep viscosity. The second term, when corrected for porosity, is usually taken as the creep rate of porous solid. Σ is of the order of magnitude of 5–10 MPa in nanocrystalline ceramics.

The Gutierrez-Mora[4] study presented a stress dependence but no grain size dependence. The study found $n=1.4$ behavior in the equation

$$\dot{\varepsilon} = A\frac{Gb}{kT}\left(\frac{b}{d}\right)^p\left(\frac{\sigma}{G}\right)^n D \tag{2}$$

where $\dot{\varepsilon}$ is the creep rate, A is a constant, G is the shear modulus, k is the Bolzmann constant, T is the absolute temperature, b is the Burgers vector, d is the grain diameter, σ is the stress, and D is the self diffusion coefficient. With $n=1.4$, the creep behavior might be Coble creep and yet Coble creep has also been observed in micron-crystalline ZrO_2, $d\sim 1$ μm, at moderately high stresses.[7] It is not clear how the same mechanism might operate both for the micron-crystalline and the nanocrystalline ZrO_2, especially when other mechanisms operate in between. The operating mechanisms are described as a function of stress. At the highest stress a $n\approx 1$ region is observed for micron-crystalline ZrO_2. We

* Corresponding author. Tel.: +1-732-445-4718; fax: +1-732-445-8148.

E-mail address: cannon@alumina.rutgers.edu (W.R. Cannon).

[1] Now at Procter and Gamble Co, Este Process Technology Center, Cincinnati, Ohio, USA.

[2] Now at Nanopowder Enterprises Inc., 120 Centenial Avenue, Piscataway, NJ 08854-3908, USA.

[3] Now at Darmstadt University of Technology, Petersenstrasse 23, D-64287, Darmstadt, Germany.

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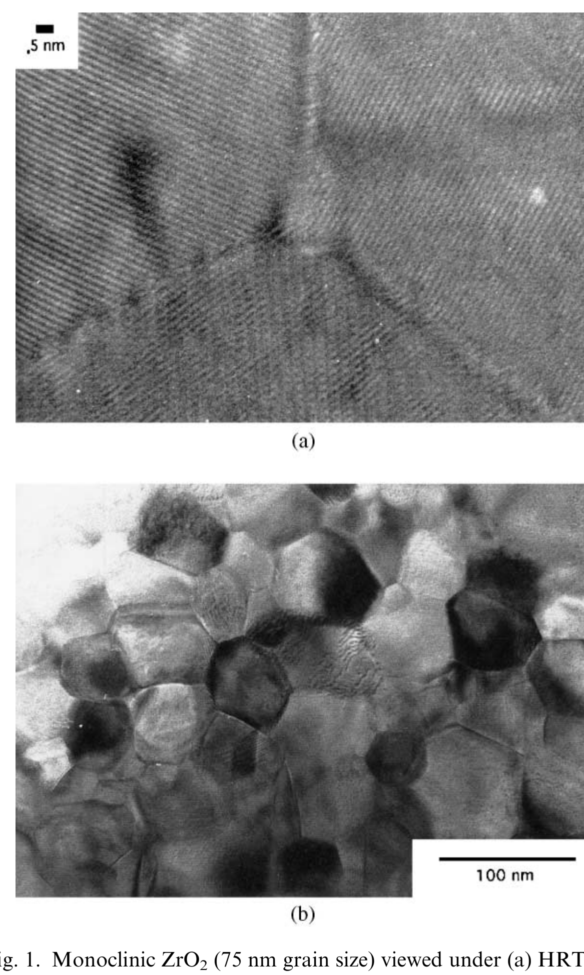
will designate this as Region III. As the stress is decreased there is a transition to the $n \sim 2$ superplastic region (Region II). At still lower stress in studies of high purity submicron ZrO_2 there is a further transition to $n > 2$ due either to a threshold stress, σ_o [8] or an $n = 3$ region (Region I).[9] At even lower stresses there are indications of a transition to $n < 2$ (Region 0).[8] The transitions between each of these regions depend on stress, grain size and temperature. Experimentally the stress for the transitions from region I to region II and the stress for the transition from region II to region III both increase with decreasing grain size and decreasing temperature.[8,9] It is estimated based on the threshold stress theory that for $d = 40$–60 nm and at a low temperature $T = 1100$ °C, $\sigma_o = 190$–270 MPa,[4] compared to $\sigma_0 = \sim 30$ MPa at $d = 500$ nm and $T = 1350$ °C. On this basis Gutierrez-Mora justified nanocrystalline ZrO_2 tested between 69 and 211 MPa as being in region 0.

For less pure ZrO_2 the $n = 2$, superplastic region extends to lower stress. It is believed that an amorphous grain boundary phase in the lower purity ZrO_2 eliminates or shifts the transition stress to a lower value.



(b)

Fig. 1. Monoclinic ZrO_2 (75 nm grain size) viewed under (a) HRTEM and (b) TEM.

In this paper creep of dense nanocrystalline, monoclinic ZrO_2 without any stabilizing additives, Y, Ce, Mg or Ca tested at 1000 °C is described. This complicates the comparison with other ZrO_2 creep results since most investigators have studied Y-SZP. Even though earlier investigators[10] contended that Y content had no on effect the creep rate, and zirconium ion self diffusion coefficient, D_{Zr} were not sensitive to yttria concentrations,[11] more recently a clear Y concentration dependence was found for creep[12] and diffusion.[13] As a consequence in this study the creep rate of 2.5Y-SZP of similar grain size was measured for comparison.

The lack of yttria had another effect. It resulted in rapid grain growth and so that grain growth studies were performed on these specimens. The test temperature was also much lower than in previous studies since tests must be below 1170 °C to avoid phase transformations.

1.1. Experimental

Sintering of the monoclinic ZrO_2 was performed under high vacuum to 975 °C as described in Ref. 14. Final densities exceeded 99% of theoretical. The as-sintered grain size was 75 nm and was annealed at 1000 °C to grow grains to three sizes: 75, 125 and 175 nm. The 2.5Y-TZP specimens were prepared by sinter-forging partially sintered specimens containing Tosoh TZ 2.5Y Powder at 60 MPa and 1200 °C for 20 min to 99+% density at a grain size $d = 165$ nm.

The impurity concentration of the dense monoclinic ZrO_2 was 0.04 wt.% Al_2O_3, 0.08 wt.% SiO_2, 0.08 wt.% Fe_2O_3 and 0.1% other impurities (Emission Spectoscopy Luvak, Boston, MA). Jimenez-Melendo et al.[8] found 0.1 wt.% to divide high purity Y SZP from less pure Y SZP. Taking into account the approximately six times higher grain boundary surface area, however, the monoclinic ZrO_2 may be considered high purity. TEM revealed an occasional triple point phase. HRTEM was not successful in imaging any siliceous grain boundaries though triple points phases were observed (Fig. 1a).

X-ray peak broadening was used to determine the average grain size of some monoclinic ZrO_2 (Siemens, Diffrak, Bohn, Germany). Grain sizes were also directly measured from SEM, and TEM micrographs using the line intercept technique in accordance with ASTM standard E 112–88. The average grain diameter, d_{ave}, was calculated from the average line intercept length, l_{ave} by $d_{ave} = 1.56$ (l_{ave}). (Fig. 1b). In all cases at least 330 grains were measured to determine the average grain size. There was good agreement between the X-ray and the line intercept method. The average apparent aspect ratio was measured from micrographs by directly measuring the longest axis of each grain and dividing by the length of the axis orthogonal to the longest axis and found to be 1.2 both before and after creep. The fast grain growth rates are presumably able to restore the equi-axed nature of the grain shape even under Coble creep conditions.

Constant load-compressive creep tests were performed on 2×3 mm specimens. Each creep rate data point resulted from a single specimen.

2. Results

Creep rate vs. time curves for monoclinic ZrO_2 in Fig. 2 show that steady state creep rates were never reached. The observed primary results from rapid grain growth in monoclinic ZrO_2. For this reason both static and dynamic grain growth were measured. Static grain growth was measured on specimens under no load placed in the furnace near specimens under load (dynamic grain growth). Fig. 3(b) shows the stress dependence of dynamic grain growth. Assuming a third power grain growth behavior kinetic constants for the monoclinic zirconia were found to be almost four orders of magnitude faster than those for Y-SZP extrapolated from high temperature (Fig. 3a and b).

To avoid prejudicing ourselves by assuming a grain size dependence for correcting the creep rates in determining the stress dependence, creep rates extrapolated to zero time were used (Fig. 2). Because of dynamic grain growth it was impossible to extract creep rates at a constant microstructure except at zero time. Once the grain size dependence was determined, then the grain size corrections were made to be sure there are no other contributions to primary creep. The results are shown by the open circles in Fig. 2. The normalized creep rate still decays with time, however the decay in the strain rate is less than a factor of 2.

Fig. 4 shows the stress dependence for monoclinic ZrO_2 at 950 and 1000 °C for three different grain sizes and the results for 2.5 Y-SZP with $d=165$ nm. In monoclinic ZrO_2 the stress exponent was $n \cong 1.7$ for all grain sizes. There is some evidence of a lower stress exponent at low stresses at 950 °C. The stress exponent for 2.5Y-SZP was $n=2.3$ and also some evidence of a lower stress exponent at low stresses but the creep rate agreed in magnitude with the monoclinic ZrO_2 of similar grain size.

The grain size dependence shown in Fig. 5 is $p \cong 3$. The datum points shown in Fig. 5 are taken from the

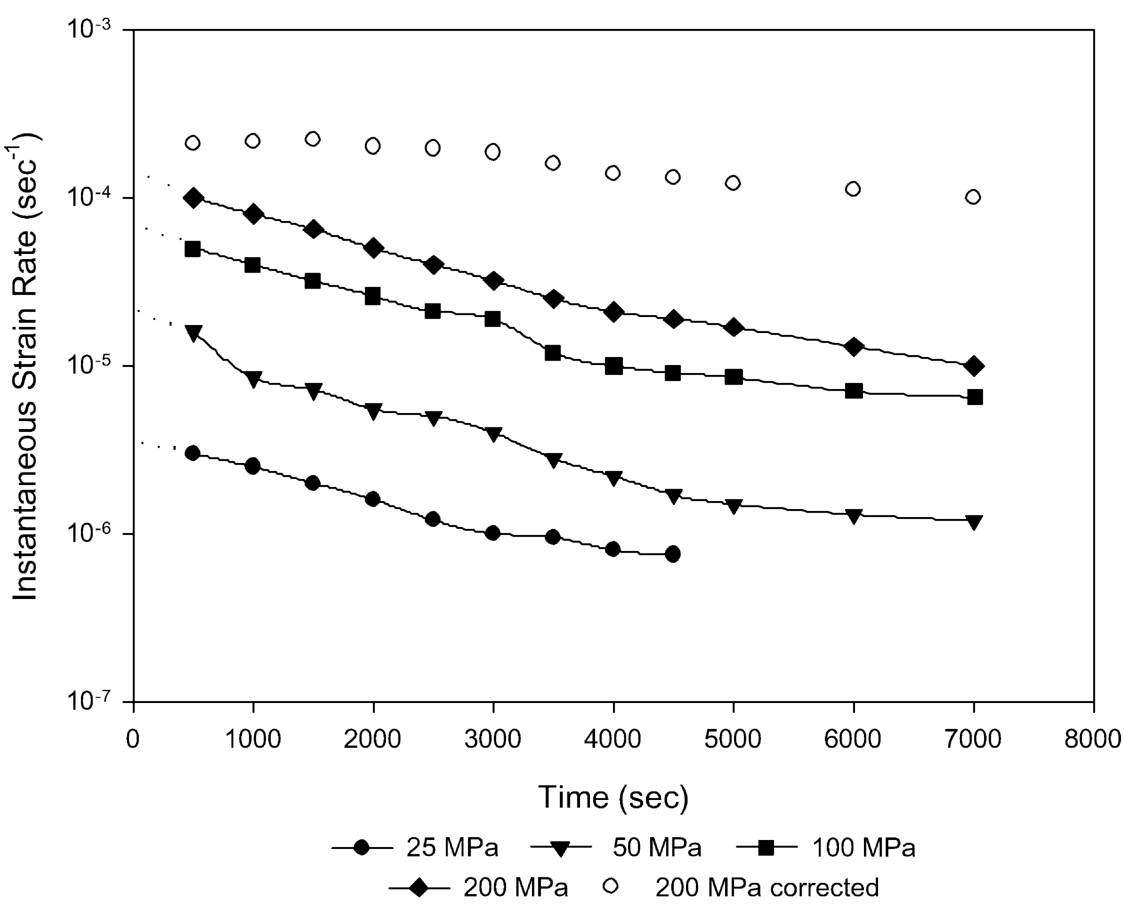


Fig. 2. Instantaneous strain rates vs. time. The dotted line indicates the extrapolation to zero time. Open circles are corrected for grain growth with $p=3$ and correct for constant load through $\dot{\varepsilon}^{\sigma} = \dot{\varepsilon}^{\sigma_o}(\exp\varepsilon)^n$.

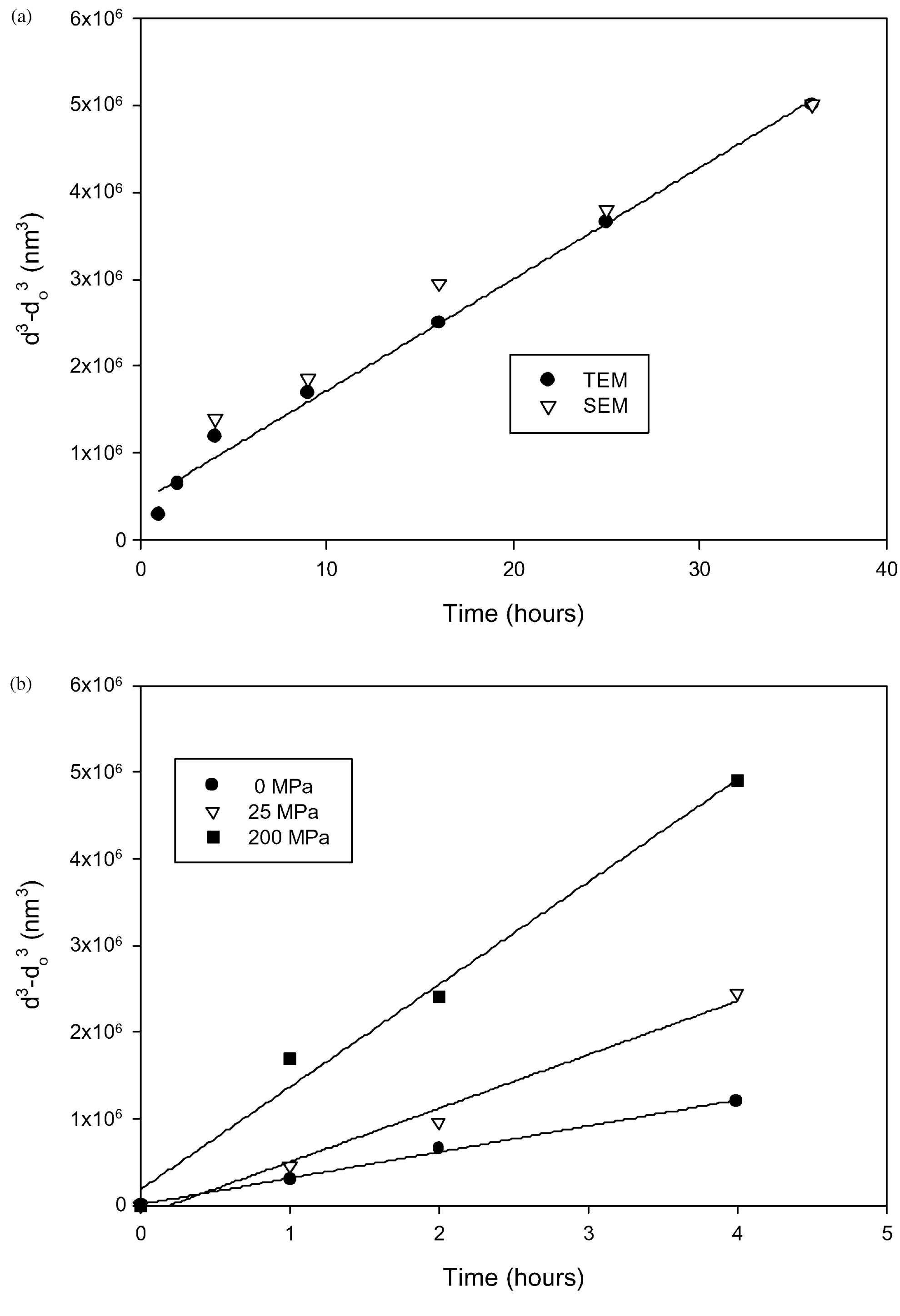


Fig. 3. Grain growth results plotted assuming a third power rate behavior for (a) static grain growth and (b) dynamic grain growth.

least square lines drawn through the data of Fig. 4. The activation energy based on the 950 and 1000 °C results is $Q_c \cong 330$–360 kJ/mol. Commonly reported activation energies in Y-SZP are between 500 and 600 kJ/mol.

3. Discussion

The measured stress exponent $n = 1.7$ lies between $n = 1$ for Coble creep or Nabarro–Herring creep and $n = 2$ for superplastic creep, however, the grain size

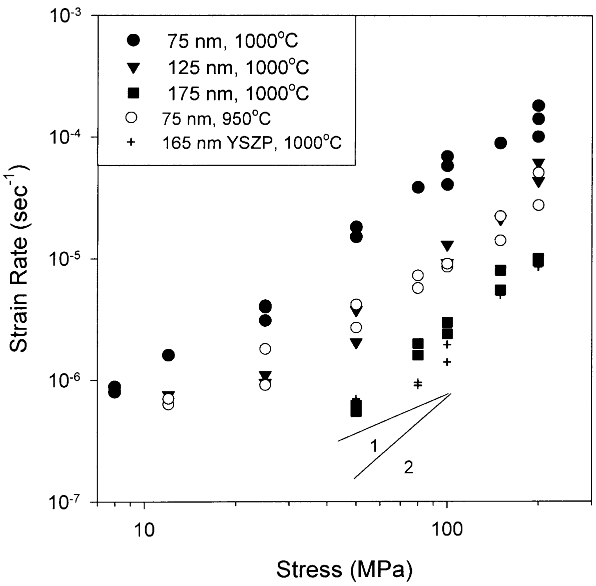


Fig. 4. Stress dependence of monoclinic ZrO_2 of 75, 125 and 175 nm at 1000 °C and 75 nm at 950 °C. The stress dependence of fully dense Y-SZP with a 165 nm grain size at 1000 °C. The stress exponent for the monoclinic ZrO_2 was $n=1.7$ and for the Y-SZP was $n=2.3$. The activation energy for the monoclinic ZrO_2 was 330–360 kJ/mol.

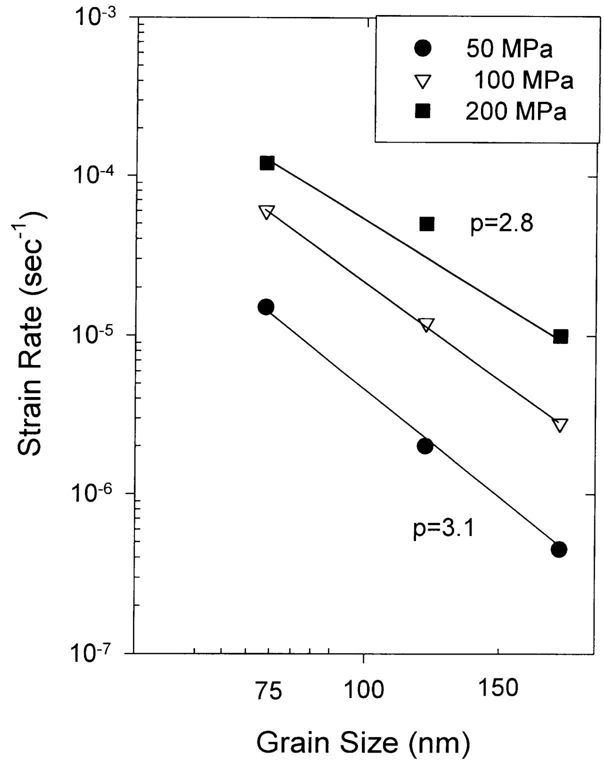


Fig. 5. Grain size dependence of the creep rate. Datum points were taken from the least square fit of Fig. 2.

exponent, p, lies closer to $p=3$ for Coble creep than superplastic or Nabarro-Herring creep. For such a fine grain size Nabarro–Herring creep is unlikely. Although we cannot absolutely distinguish between Coble creep and superplastic creep, we compared the magnitude of the creep rate with Y-SZP measured at higher temperatures and grain sizes with monoclinic zirconia without yttria. The comparison was made using values of the grain boundary diffusion coefficient, δD_{Zr}^{gb}, based on the Coble equation:

$$\dot{\varepsilon} = \frac{33\delta D_{Zr}^{gb}\sigma}{kTd^3} \quad (3)$$

Results are shown in Fig. 6. The current results are also compared with measured δD_{Zr}^{gb} from Sakka et al.[15] and Oishi et al.[11] Because of the much lower temperature of the current study on monoclinic ZrO_2 (Roddy), it is difficult to compare results but the calculated diffusion coefficient from this study lies approximately on line with δD_{Zr}^{gb} whereas the results of Gutierrez-Mora et al.[4] lie several orders of magnitude below this joining dotted line. The suggestion of Gutierrez-Mora et al.[4] that their data lies in region 0 is consistent with the lower creep rate. Because of the intervening regions between regions 0 and III, region 0 rates must be lower than region III rates. In each region the rates are lower than the extension of the region of higher stress immediately above it. Gutierrez-Mora et al.[4] contend that grain boundary sliding is not operative in region 0 and they support this contention with the observation that cavitation was observed. In our study cavitation was not observed after compressive strains of 20%, either by TEM or by density measurements. The grains continued to form sharp apexes with each other and grain separation was not evident. The physical appearance of grain boundaries and triple points in the samples remained constant for deformed samples as observed by HRTEM. Dynamic grain growth would suggest that grain boundary sliding occurred. It is well known that yttria segregates to the grain boundaries and it may be that the presence of yttria in the specimens of Gutierrez-Mora inhibited the movement of grain boundary dislocations. On the other hand, the creep rates of the 2.5 Y-SZP shown in Fig. 5 are on the order of magnitude of those of the monoclinic ZrO_2 but the stress exponent is higher than the monoclinic ZrO_2 without yttria. Unfortunately neither the impurity level nor the grain size dependence of the 2.5Y-SZP specimens is known. In fact, it may be that the 2.5Y-SZP exhibits superplastic creep of region II because of a viscous second phase in the grain boundaries. It must be emphasized that these comparisons are somewhat difficult since increased yttria has been found to decrease creep rates of single crystalline zirconia with additions of yttria between 9.5 and 21 mol% according to an inverse cubic relationship. The fact that 2.5% yttria did not reduce the creep rate significantly below that of high purity zirconia is not well understood and must be further studied.

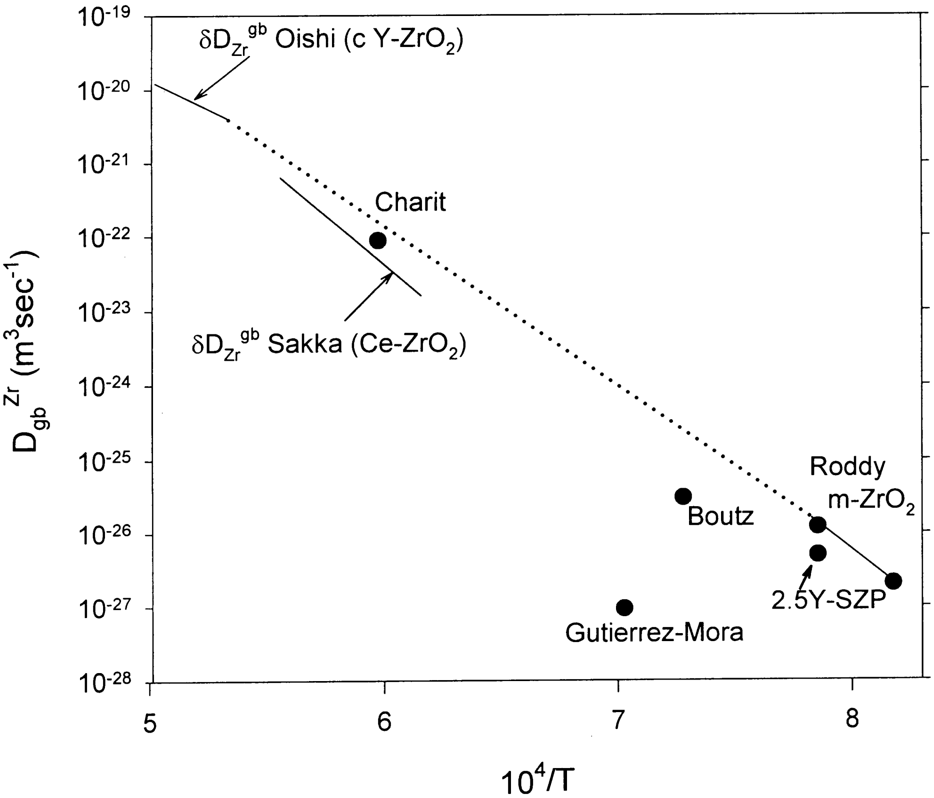


Fig. 6. A comparison of measured grain boundary diffusion coefficients, δD_{Zr}^{gb}, with grain boundary diffusion coefficients calculated from the Coble equation for Charit[7] Gutierrez-Mora[4] and Roddy (current results).

4. Conclusion

The creep behavior of the nanocrystalline monoclinic ZrO_2 tested in this study is consistent with Coble creep but superplastic creep cannot be ruled out. The creep behavior appears to be different from that of nanocrystalline Y-SZP studied by Gutierrez-Mora et al. whose creep rate was slower and exhibited cavitation.

Acknowledgements

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