JOURNAL OF MATERIALS SCIENCE 19 (1984) 2639–2642

Viscous creep deformation of polycrystalline $CaTiO_3$ at elevated temperatures

HISAO YAMADA
University of Utah, Department of Materials Science and Engineering, Salt Lake City, Utah 84112, USA

Creep deformation of polycrystalline $CaTiO_3$ has been investigated in air at temperatures between 1100 and 1200° C and stresses between 4 and 13 MPa. The results indicate that the creep deformation of this material can be described by a threshold process with associated activation energy of 200 kcal mol^{-1} (836.8 kJ mol^{-1}). It is tentatively concluded that creep deformation of polycrystalline $CaTiO_3$ within the ranges of experimental parameters investigated is rate-controlled by interfacial defect creation and/or annihiliation at grain boundaries.

1. Introduction

While $BaTiO_3$ and $SrTiO_3$ have been the subjects of intensive studies, $CaTiO_3$ has received comparatively little attention. Although some progress has been made in identifying the majority ionic defects and their associated electronic defects by electrical conductivity measurements [1–4], little information is available on the minority ionic defects the motion of which controls diffusion and mass transport, which are important in processes such as sintering, grain growth, thermal grooving and particle coarsening.

To date the characteristics of minority ionic defects have been studied primarily by measurements of ionic diffusivity and shrinkage kinetics during the initial and intermediate stages of sintering. Since the effects of doping and the dependencies of oxygen partial pressure have been observed to be similar in both sintering and diffusional creep [5–10], the diffusional creep of a dense polycrystalline solid may be used more effectively to investigate the minority ionic defects in $CaTiO_3$ than is possible in the sintering of a non-ideal powder compact. Hence in the present study viscous creep deformation of a dense polycrystalline $CaTiO_3$ has been investigated at elevated temperatures.

2. Experimental details

Disc-shaped specimens (4.13 cm diameter, 0.76 cm thick) with densities over 99% theoretical were obtained with grain sizes of 3.1 μm after hot-pressing $CaTiO_3$ powder* at temperatures between 1100 and 1500° C. Rectangular bar specimens with a cross-section of 0.20×0.50 cm were cut from the hot-pressed discs and all four sides of the specimens were ground and polished to 0.3 μm finish. Grain sizes were determined from standard linear intercept averages multiplied by 1.5 before and after creep testing to confirm that no grain growth was occurring at temperatures of interest here.

Dead-load, four-point-bending creep tests were conducted in air at temperatures between 1100 and 1200° C. The experimental test apparatus has been described in detail by Hollenberg and Gordon [8]. Stresses and strains were calculated from standard visco-elastic relations originally derived by Hollenberg *et al.* [11]. All the data presented in this paper represent those observed during steady state creep conditions which were easily achieved at the test temperatures. The major variables of stress, temperature and grain size were investigated systematically. Stress and temperature dependencies were determined by conducting

---

*Powders from TAM ceramic, Inc. Lot Number 129.

0022–2461/84 $03.00 + .12

single specimen tests in which the variable to be studied was changed in stepwise fashion (e.g. stress) while holding other variables (e.g. temperature) constant.

3. Results and discussion

Steady state creep deformation may be represented phenomenologically by either a power law process or a threshold process. In the power law process creep rate ($\dot{\epsilon}$) is given by

$$\dot{\epsilon} = K\sigma^n d^{-m} \exp(-Q/RT) \qquad (1)$$

where σ, d and T are the stress, the grain size and the temperature, respectively. Four constants K, n, m and Q can be determined experimentally. On the other hand, in the threshold process creep rate is given by

$$\dot{\epsilon} = \begin{cases} K'(\sigma - \sigma_0)\, d^{-m'} \exp(-Q'/RT) & \text{for } \sigma > \sigma_0 \\ 0 & \text{for } \sigma \leqslant \sigma_0 \end{cases} \qquad (2)$$

where σ_0 is the threshold stress which can be determined experimentally together with other constants K', m' and Q'. In the following experimental results will be discussed from the viewpoints of the power law process and the threshold process. Significances of experimentally determined values of n, m and Q will also be discussed in the light of various modellings of creep deformation.

Creep rates for specimens with grain sizes of 3.1 and 10.5 μm are plotted in both logarithmic and linear scales in Figs. 1 and 2. The stress exponents, n, and the threshold stresses, σ_0, were calculated using a method of least squares and are indicated in parentheses for temperatures of 1100, 1150 and 1200° C in the figures. Although it is difficult from figures to distinguish the difference between the power law process and the threshold process because of the similarity of the curves $\dot{\epsilon} \propto \sigma^{n>1}$ and $\dot{\epsilon} \propto (\sigma - \sigma_0)$ at low values of σ, it seems that the threshold process represents the experimental data better than the power law process because the stress exponents less than unity are observed for the specimens with grain sizes of 10.5 and 12.6 μm at 1100° C, which cannot be accounted for by any creep deformation mechanisms. In addition it seems inconceivable that the stress exponents have such a strong temperature dependence as indicated in Fig. 1.

Crossland [12] reviewed creep data on metals and observed that the threshold stress varies sys-

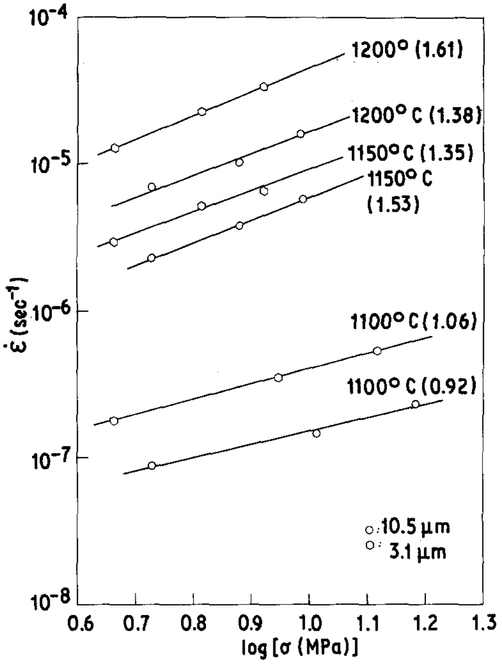

Figure 1 Logarithmic strain rate–stress relationships for creep deformation of polycrystalline CaTiO$_3$ with grain sizes of 3.1 and 10.5 μm. The numbers in parentheses after temperatures indicate the stress exponents, n.

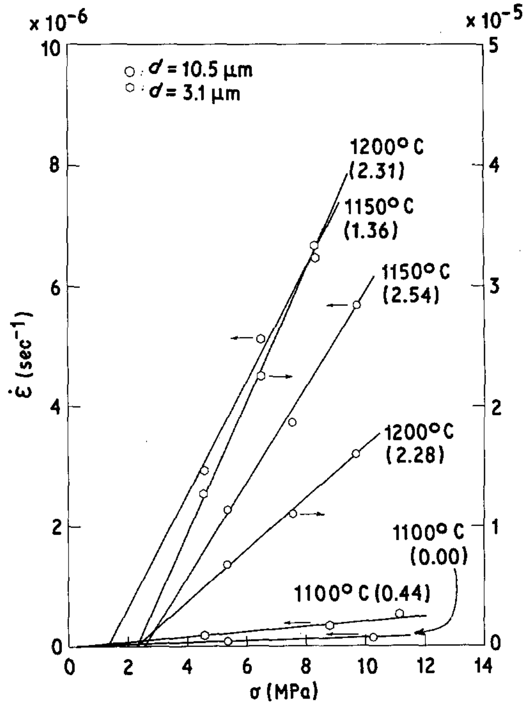

Figure 2 Linear strain rate–stress relationships for creep deformation of polycrystalline CaTiO$_3$ with grain sizes of 3.1 and 10.5 μm. The numbers in parentheses after temperature indicate the threshold stresses in MPa.

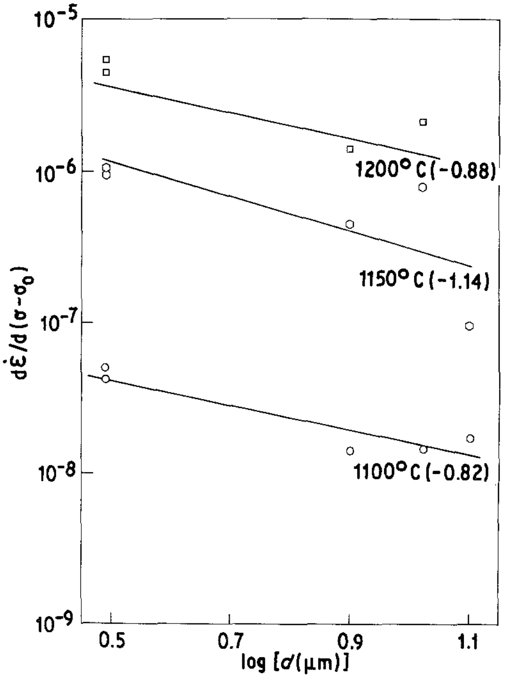

Figure 3 Effect of grain size on the diffusional creep of polycrystalline $CaTiO_3$. The slopes $d\varepsilon/d(\sigma - \sigma_0)$ (sec^{-1} MPa^{-1}) are plotted as a function of grain size in μm.

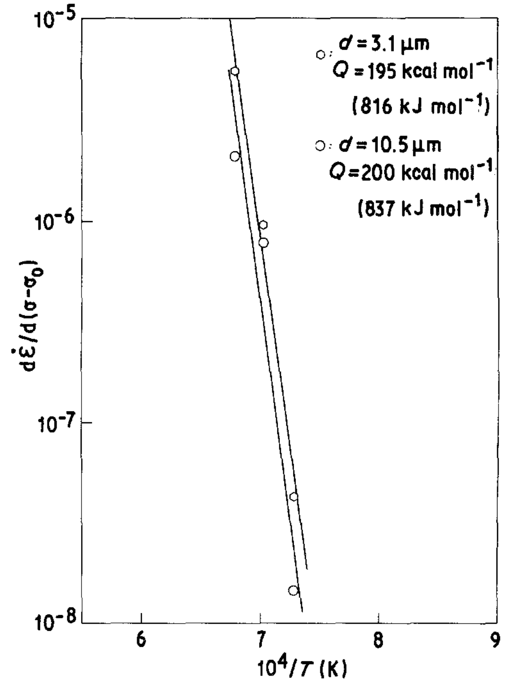

Figure 4 Effect of temperature on the diffusional creep of polycrystalline $CaTiO_3$. The slopes, $d\dot{\varepsilon}/d(\sigma - \sigma_0)$ (sec^{-1} MPa^{-1}) are plotted as a function of $1/T$.

tematically with temperature and grain size and obeys the empirical law:

$$\sigma_0 = \frac{A}{d} \exp\left(\frac{U}{kT}\right) \tag{3}$$

where A and U are constants. The threshold stresses given in Fig. 2 indicate that no such empirical law can describe the dependence of threshold stress on temperature and grain size for the polycrystalline specimens of $CaTiO_3$ in the ranges of temperature and grain size investigated in this study.

It is interesting to note that the stress exponent slightly larger than unity was also reported for polycrystalline alumina and silicon nitride [13, 14]. Although Heuer *et al.* [15] have attempted to explain slightly nonviscous behaviours by invoking nonviscous grain-boundary sliding, no definitive proof has been presented to date.

In Fig. 3 the effect of grain size on the steady state creep deformation of polycrystalline $CaTiO_3$ is presented. In the figure the slopes, $d\dot{\epsilon}/d(\sigma - \sigma_0)$, calculated by the linear intercept method in the unit of $sec^{-1}\,MPa^{-1}$ are plotted as a function of grain size. The grain size exponents, m', are calculated to be 0.82, 1.14 and 0.88 at temperatures of 1100, 1150 and 1200° C, respectively. From the m' values obtained the rate-controlling mechanism in polycrystalline $CaTiO_3$ in the ranges of temperature, grain size and stress investigated is tentatively identified to be interfacial defect reactions.

The effect of temperature on the steady state creep deformation of polycrystalline $CaTiO_3$ is presented in Fig. 4. From Arrhenius plots of the slopes, $d\dot{\epsilon}/d(\sigma - \sigma_0)$, activation energies of creep deformation are determined to be 195 and 200 kcal mol^{-1} (836.8 kJ mol^{-1}) for the polycrystalline $CaTiO_3$ specimens with grain sizes of 3.1 and 10.5 μm, respectively. Although no diffusion coefficient of oxygen ions for $CaTiO_3$ has been reported to the knowledge of the present author, the activation energy for the diffusion of oxygen ions is expected to be similar to that of $SrTiO_3$ (26 kcal mol^{-1}, 108.78 kJ mol^{-1}) [16]. Hence it is expected that the activation energy for the motion of the least mobile cationic defects is several times higher than that for the motion of anionic defects (i.e. oxygen vacancies). This is consistent with the observations reported by Rhodes and Kingery [17] who investigated the self diffusion of cations in $SrTiO_3$ and observed that self diffusion coefficients for both strontium and titanium ions are several orders of magnitudes lower than that for oxygen ions. They also reported nonhomogeneous kinetics with enhanced diffusion in dislocation pipes, which might have some significant implication on the viscous creep deformation observed in polycrystalline $CaTiO_3$.

4. Conclusion

Viscous creep deformation has been observed for polycrystalline $CaTiO_3$ at temperatures between 1100 and 1200° C and stresses between 4 and 13 MPa. The stress dependence of creep rates seems to be best described by a threshold process rather than a power law process. Based on the observed grain size dependence, it is tentatively concluded that creep deformation of polycrystalline $CaTiO_3$ is rate-controlled by interfacial defect creation and/or annihilation at grain boundaries. Activation energy for creep deformation has been determined to be about 200 kcal mol^{-1} (836.8 kJ mol^{-1}) which is roughly eight times higher than that for the motion of oxygen ions.

Acknowledgements

The author would like to express his appreciation to Professor R. S. Gordon for many lively discussions during the course of this work. This work was supported by the University of Utah Research Committee.

References

1. W. L. GEORGE and R. E. GRACE, *J. Phys. Chem. Solids* **30** (1969) 881, 889.
2. U. BALACHANDRAN, B. ODEKIRK and N. G. EROR, *J. Solid State Chem.* **41** (1982) 185.
3. *Idem, J. Mater. Sci.* **17** (1982) 1656.
4. *Idem, ibid.* **17** (1982) 1795.
5. R. D. BAGLEY, I. B. CUTLER and D. L. JOHNSON, *J. Amer. Ceram. Soc.* **53** (1970) 136.
6. W. RAJA RAO and I. B. CUTLER, *ibid.* **56** (1973) 588.
7. J. R. KESKI and I. B. CUTLER, *ibid.* **48** (1965) 653; **51** (1968) 440.
8. G. W. HOLLENBERG and R. S. GORDON, *ibid.* **56** (1973) 140.
9. P. A. LESSING and R. S. GORDON, *J. Mater. Sci.* **12** (1977) 2291.
10. Y. IKUMA and R. S. GORDON, *J. Amer. Ceram. Soc.* **66** (1983) 139.
11. G. W. HOLLENBERG, G. R. TERWILLIGER and R. S. GORDON, *ibid.* **54** (1971) 196.
12. I. G. CROSSLAND, in "Physical Metallurgy of Reactor Fuel Elements", edited by J. E. Harris and E. C. Sykes (The Metals Society, London, England 1975) p. 66.
13. S. UD DIN and P. S. NICHOLSON, *J. Mater. Sci.* **10** (1975) 1375.
14. *Idem, J. Amer. Ceram. Soc.* **58** (1975) 500.
15. A. H. HEUER, R. M. CANNON and N. J. TIGHE, Plastic Deformation in Fine Grained Ceramics, in "Ultrafine-Grained Ceramics", edited by J. Burke and V. Weiss (Syracuse University Press, Syracuse, New York, 1970) p. 339.
16. A. E. PALADINO, L. G. RUBIN and J. S. WAUGH, *J. Phys. Chem. Solids* **26** (1965) 391.
17. W. H. RHODES and W. D. KINGERY, *J. Amer. Ceram. Soc.* **49** (1966) 521.

Received 19 July
and accepted 29 November 1983