

High temperature creep of ultrafine-grained Fe-doped MgO polycrystals

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Creep deformation in ultrafine-grained (0.1 to 1 μm) Fe-doped magnesia polycrystals is studied in compression, at temperatures of 700 to 1050° C, and constant loads of 50 to 140 MPa. The stress exponent observed to be nearly unity and the strong grain size sensitivity ($\dot{\epsilon} \sim d^{-2.85}$) suggest that diffusional creep mechanisms dominate the deformation. In the grain size range of the present study the grain boundary diffusion contribution is significantly more important than lattice diffusion. Magnesium is tentatively identified as the rate-controlling species along grain boundaries from an analysis of the diffusivities inferred from the present work and from other authors for Fe-doped magnesia.

1. Introduction

The mechanical properties of fully dense, fine-grained magnesia polycrystals have been of interest for a long time [1–9]. In many creep experiments published on MgO polycrystals, viscous deformation has been reported for materials at small grain size ($\lesssim 30 \mu\text{m}$) [1–4, 6, 8, 9]. In most of these works, the experimental data fall in a grain size range which is controlled by Nabarro–Herring creep, and up to now evidence was found only once for a creep controlled solely by grain boundary diffusion [6]. However, in ultrafine-grained ceramics, the possibility should exist for observing a predominant grain boundary creep behaviour.

Experiments at very small grain sizes are complicated by problems associated with specimen fabrication and grain growth during test. An ultrafine-grained ($\sim 0.1 \mu\text{m}$), almost fully dense (91%) MgO has been produced by reactive hot-pressing. This paper deals with the role of grain boundary diffusion on the deformation of these ceramics in a grain size range of 0.1 to 1 μm . A further paper will be concerned with the microstructure and grain boundary sliding. The creep rate due to the vacancy stress-directed diffusion between grain boundaries at elevated tempera-

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tures is usually written for a metal as [10]

$$\dot{\epsilon} = \frac{14\Omega}{kTd^2} \left[D_1 + \frac{\pi\delta D_b}{d} \right] \sigma \quad (1)$$

where $\dot{\epsilon}$ is the compressive creep rate under the applied compressive stress σ , D_1 and D_b are the lattice and grain boundary diffusivities, δ is the width of the grain boundary region in which enhanced grain boundary diffusion occurs, d is the grain size, Ω the atomic volume and kT has its usual meaning.

For ceramics like MgO, several possible mass transport mechanisms dependent on nature and concentration of dopants can occur [11]: intrinsic/extrinsic isolated vacancy diffusion, or vacancy pair diffusion. In the case of isolated vacancy diffusion, both ions must of course diffuse and Equation 1 becomes [12]

$$\dot{\epsilon} = \frac{14\Omega_C\sigma}{kTd^2} D_{\text{complex}} \quad (2)$$

with

$$\frac{1}{D_{\text{complex}}} = \frac{1}{[D_1^{\text{Mg}} + \pi\delta^{\text{Mg}} D_b^{\text{Mg}}/d]} + \frac{1}{[D_1^{\text{O}} + \pi\delta^{\text{O}} D_b^{\text{O}}/d]}$$

where Ω_C is the MgO molecular volume, and the superscripts refer to cations and anions. In the case of a vacancy pair diffusion, Equation 1 remains relevant but D_1 and D_b are now lattice and grain boundary vacancy pair diffusivities and Ω must be taken as Ω_C .

Passemore *et al.* [2] were the first to study the deformation of fully dense MgO as a function of temperature, stress, and grain size for grain sizes from 2 to 20 μm . They found the observed creep rate versus grain size dependence is described by an exponent -2.5 for grain sizes between 5 and 20 μm , leaving unclear whether lattice or grain boundary diffusion is the rate-controlling mechanism in this experiment. This work led to further investigations in the search for diffusional creep in fully dense magnesia and Terwilliger *et al.* [6] reported Coble creep for Fe-doped MgO (0.05 to 0.25% Fe cations) with grain sizes between 5 and 14 μm at 1300°C. However, it cannot be concluded definitively which ionic species controls the boundary diffusion process.

In the work reported here, we show that diffusional creep is predominant over the range of temperatures (700 to 1050°C) stresses (50 to 140 MPa) and grain sizes (0.1 to 1 μm) studied, and that our results are consistent with the grain boundary controlled creep behaviour as found by Terwilliger *et al.* [6].

2. Experimental procedure

2.1. Specimen fabrication

Ultrafine-grained polycrystalline MgO is produced by reactive hot-pressing during the dehydroxylation of magnesium hydroxide powder at temperature 900°C and pressure 110 MPa for 15 min. All as-pressed specimens (Specimens A) have an average grain size of 0.1 μm , as determined by both the X-ray line broadening method and electron microscope characterization [13]. All specimens are >91% dense and doped with 0.5% Fe cations. In order to determine the grain size effect on creep rate, larger grained specimens have been obtained by annealing at 900°C for 2 h (Specimen B), and at 1100°C for 6 h (Specimens C).

Electron microscopical observations will be described in a further paper. They show mainly the localization of some porosity at triple points and the lack of dislocations in most of the grains with size < 3 μm .

In order to keep porosity and grain size as stable as possible during tests, the samples are

always crept below the hot-pressing or sintering temperature. With these precautions the density of samples, determined before and after creep using a hydrostatic weighing technique, remains nearly constant during creep tests.

2.2. Creep testing

For the creep tests, samples are cut from the pressed discs into $2 \times 2 \times 5 \text{ mm}^3$ parallelepipeds parallel to the pressing direction. Compression creep tests are conducted in air throughout the temperature range 700 to 1050°C, using constant load equipment described elsewhere [14]. Stresses up to 160 MPa are transmitted to the sample by alumina rods and sapphire discs which prevent indentation. The strain is measured by a sapphire probe which activates an LVDT and is continuously recorded.

The stress dependence of creep rate is determined both by the differential and the conventional method, i.e. either by stress jumps on the same sample, or by comparing several samples at different stresses. Creep activation energies are obtained both from the Dorn technique, and from $\log \dot{\epsilon}$ versus T^{-1} plots.

3. Results

(a) Specimens A have been allowed to creep between 700 to 860°C at a stress of 140 MPa, as reported earlier [13]. After several ten hour periods the quasi-steady state strain rate levels out in the range 10^{-8} to 10^{-7} sec^{-1} . The stress exponent, as obtained from differential tests ($\Delta\sigma \approx 0.13\sigma$) is found to be nearly unity over the whole temperature range. The apparent activation energy, about 36 kcal mole $^{-1}$ as determined from a $\log \dot{\epsilon}$ versus T^{-1} plot (Fig. 1) is surprisingly low in comparison with the usual values in MgO (from 50 kcal mole $^{-1}$ to 120 kcal mole $^{-1}$).

In order to confirm this value, and to investigate the grain size dependence, larger grained specimens, Specimens B and C have been also tested.

(b) Specimens B with 0.2 μm grain size, have been allowed to creep at 730 to 860°C and 140 MPa. Representative examples of creep curves are presented in Fig. 2. They are quite similar to the ones obtained for Specimens A. After a long initial period, a quasi-steady state is achieved. However, due to a larger initial grain size (by a factor 2), quasi-steady state creep rates are lower. The ap-

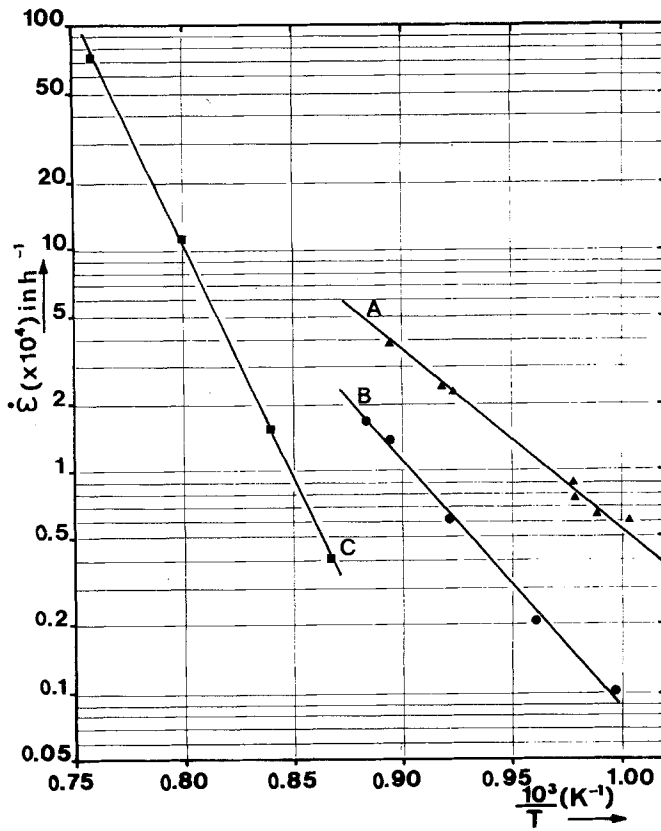


Figure 1 Log creep rate versus T^{-1} , showing the apparent activation energies for: (a) $\sigma = 140 \text{ MPa}$, initial grain size = $0.1 \mu\text{m}$ (line A). (b) $\sigma = 140 \text{ MPa}$, initial grain size = $0.2 \mu\text{m}$ (line B). (c) $\sigma = 100 \text{ MPa}$, initial grain size = $1 \mu\text{m}$ (line C).

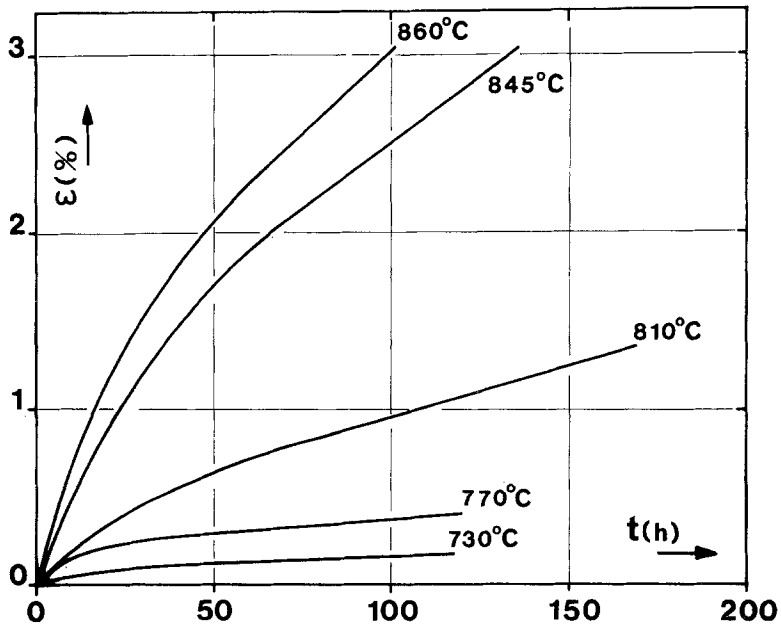


Figure 2 Creep curves at $\sigma = 140 \text{ MPa}$, initial grain size = $0.2 \mu\text{m}$.

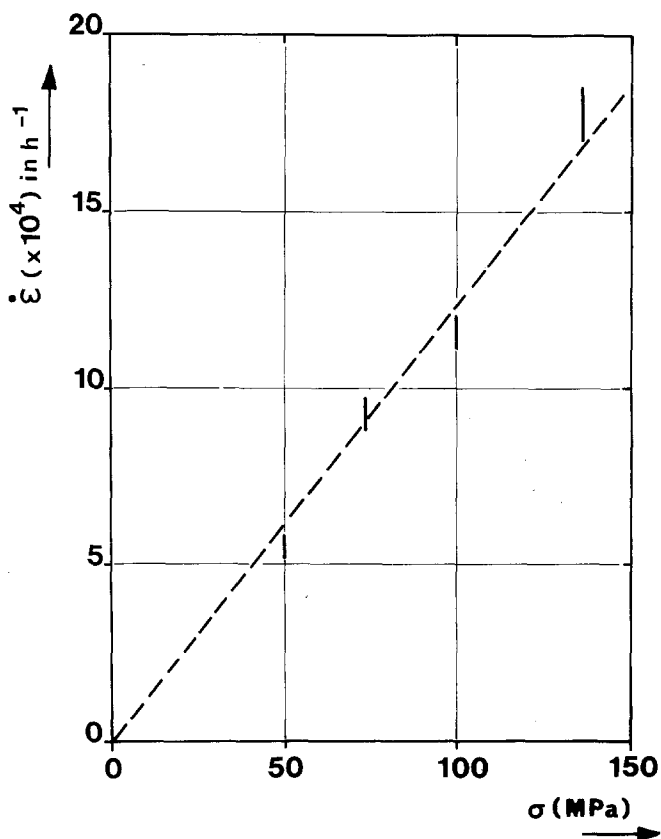


Figure 3 Creep rate versus stress curve at 977° C and grain size = 1 μ m.

parent activation energy, obtained from a $\log \dot{\epsilon}$ versus T^{-1} plot, (Fig. 1) is found to be 54 kcal mole⁻¹.

The difference between these two apparent energies for otherwise quite comparable samples can only be ascribed to some microstructural feature, i.e. the grain size. If a slight grain growth does occur during tests at the highest temperatures, then apparent rates are correspondingly lowered, and so is the apparent energy. Now the smaller the initial size, the larger this effect should be, as is observed (Fig. 1).

In order to avoid grain growth problems creep activation energies were redetermined using the Dorn technique, i.e. performing the temperature changes on a single creep sample. In this case, grain sizes remain nearly constant during the temperature change (ΔT small, comparison of short-time creep rates). With this technique, more consistent results are found for Specimens A, $\Delta H_{\text{creep}} = 87 \pm 17$ kcal mole⁻¹, and for specimens B, $\Delta H_{\text{creep}} = 88 \pm 16$ kcal mole⁻¹.

(c) A third series of specimens, Specimens C of grain size 1 μ m, has also been allowed to creep at 880 to 1050° C and 100 MPa.

After a much shorter period than above, generally less than five hours, quasi-steady creep rates are obtained in the range 10^{-7} to 10^{-5} sec⁻¹.

The stress dependence is determined from isothermal tests at 977° C and stresses in the range 50 to 140 MPa. Plotting $\log \dot{\epsilon}$ versus $\log \sigma$ gives a stress exponent $n = 1.1$. Further confirmation is obtained on a linear scale which yields a straight line passing through the origin (Fig. 3). This shows clearly, together with the results on Specimens A, that viscous creep is predominant in MgO over the whole range 700 to 1050° C, 50 to 140 MPa, and 0.1 to 1 μ m.

The creep activation energy for 1 μ m size is found to be $\Delta H_{\text{creep}} = 90$ kcal mole⁻¹ from a simple $\log \dot{\epsilon}$ versus T^{-1} plot (Fig. 1). This value is quite comparable with those observed by the Dorn technique on 0.1 μ m and 0.2 μ m samples and with the one reported by Passmore *et al.* [2] for 3 μ m, showing that here no grain growth affects the measurement.

Finally the grain size dependence can be determined from the slope of a log-log plot of $\dot{\epsilon}/\sigma$ versus grain size at 730° C. The data for 1 μ m samples are measured for temperatures of 880° C

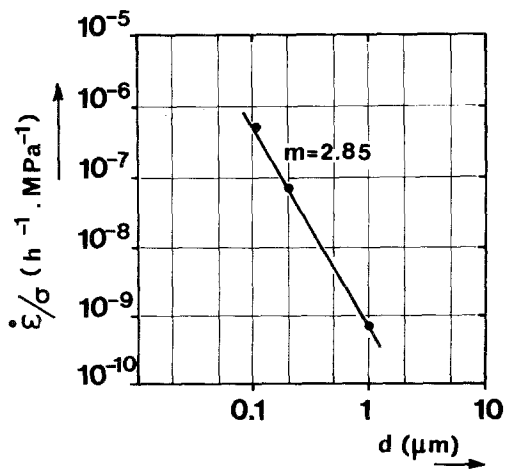


Figure 4 Log $\dot{\epsilon}/\sigma$ - log grain size) curve at 730° C.

and above, so that values extrapolated from Fig. 1 to 730° C have been used. A straight line with a slope $m = -2.85$, describes the data reasonably (Fig. 4).

4. Discussion

As suggested by the value near unity found for the stress exponent for submicron as well as micron sized grains, diffusional creep must be the prevailing mechanism in these ultrafine-grained magnesia. The grain size exponent, -2.85 , on the other hand (see in Fig. 4) suggests Coble creep ($\dot{\epsilon} \sim d^{-3}$) makes a significant contribution to the total creep strain. However, the deviation of this non-integer exponent from 3 might be indicative of a slight contribution of lattice diffusion also, for it is obtained from data taken over a decade in grain size.

Since the nature of the controlling diffusing species is not yet definitively stated, it is of interest to attempt to determine the rate-controlling diffusivities. Following the analysis of Cannon *et al.* in Al_2O_3 [15], controlling diffusivities are inferred from our data by assuming Equation 1 is applicable with either lattice or

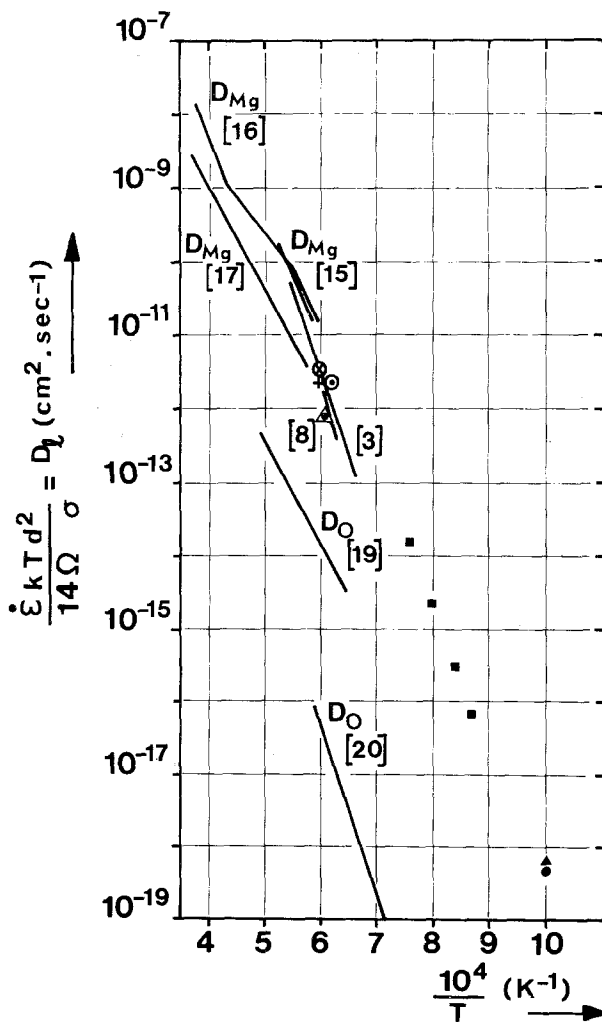


Figure 5 Comparison of apparent lattice diffusivities from this work and from [3, 4, 6, 9], with tracer diffusivities from [16-18, 20] and with loop shrinkage measurements from [21]. This work: 0.5% Fe cation-doped MgO; \blacktriangle 0.1 μm ; \bullet 0.2 μm ; \blacksquare 1 μm ; in air. [6]: 0.05% Fe cation-doped MgO; \times 15 to 30 μm ; in air. 0.5% Fe cation-doped MgO; $+$ 19 μm ; in air. [3, 4]: 99.9% MgO; line 20 μm ; in air. 0.55% Fe cation-doped MgO; \circ 20 μm ; in air. [9] 0.05% Fe cation-doped MgO; \blacktriangle 30 μm ; in $\text{PO}_2 = 0.86$ atm. 0.53% Fe cation-doped MgO; \odot > 15 μm ; in $\text{PO}_2 = 0.86$ atm. 0.53% Fe cation-doped MgO; line 35 μm ; in $\text{PO}_2 = 1$ atm.

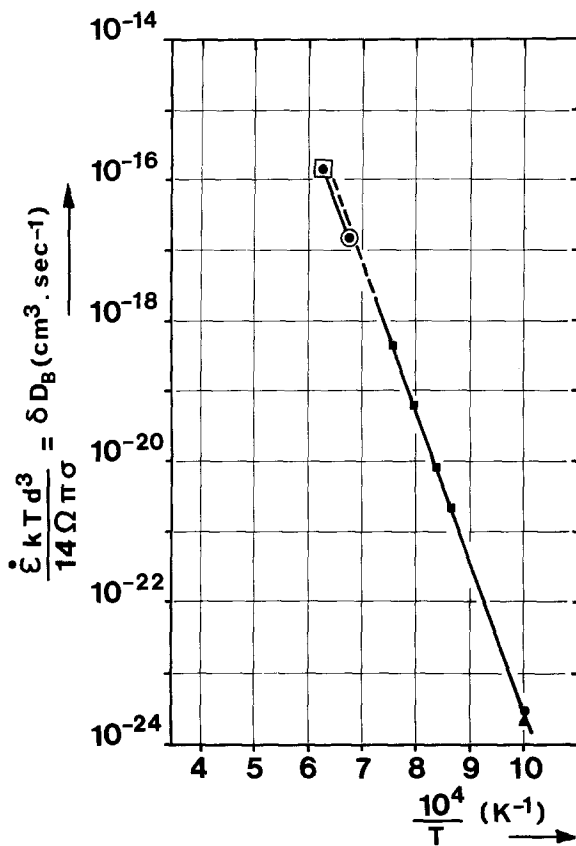


Figure 6 Apparent boundary diffusivity-widths from this work and from [6, 8, 12]. This work: 0.5% Fe cation-doped MgO; \blacktriangle 0.1 μm ; \bullet 0.2 μm ; \blacksquare 1 μm ; in air. [8, 12]: 0.05% Fe cation-doped MgO; \circ 7 to 9 μm ; in air. [6]: 0.05% Fe cation-doped MgO; \square 5 to 14 μm ; in air.

boundary diffusion prevalent. The obtained lattice diffusivities are plotted versus T^{-1} in Fig. 5, while the boundary ones are shown in Fig. 6. Again, it can be noted that our data points fall along a unique straight line in a much better fit when boundary diffusion applies; moreover they agree reasonably well with data from other authors obtained for sizes below 15 μm in this case.

Although direct diffusivity measurements are not available for comparison with each possible type of isolated vacancy it is possible to set a scale of diffusivities from the knowledge of the nature of lattice versus boundary creep diffusion.

Firstly, it is clear that lattice diffusion by oxygen vacancies makes a negligible contribution to mass transport kinetics, since creep diffusivities, as reported in Fig. 5 for grain sizes below 30 μm from different authors, are several magnitudes higher than measured oxygen diffusivities, as it has been previously noted by Gordon [15]. Now lattice diffusion is supported by a number of creep data* for sizes in the range 10 to 30 μm , where a

grain size dependence closer to 2 than to 3 is found (Passemore *et al.* [2]: -2.5 from 5 to 20 μm ; Terwilliger *et al.* [6]: -2 from 15 to 30 μm ; Tremper *et al.* [9]: -1.95 from 10 to 30 μm). Therefore, from the expression of D_{complex}^{-1} given in Equation 2 where D_1^{O} has been made negligible, the only possibility consistent with the above statement is

$$\frac{\pi \delta D_b^{\text{Mg}}}{d} \ll D_1^{\text{Mg}} \ll \frac{\pi \delta D_b^{\text{O}}}{d}.$$

At the other end of the size range 10 to 0.1 μm , the grain size dependence is found, on the contrary, to be closer to 3 than to 2 (Terwilliger *et al.* [6]: -3 from 10 to 4 μm , this work: -2.85 from 1 to 0.1 μm) in favour of boundary diffusion control. Referring back to Equation 2, with respect to the above inequality for the boundary-width diffusivities, it is seen that it has to be

$$\frac{\pi \delta D_b^{\text{O}}}{d} \gg \frac{\pi \delta D_b^{\text{Mg}}}{d} \gg D_1^{\text{Mg}}.$$

*Creep data for Fe-doped magnesia with dopant level \lesssim 0.5% Fe cations are only quoted here, and the same applies in Figs. 5 and 6.

So that the consistent scale of diffusivities should be

$$D_1^O \ll D_1^{Mg} \ll \frac{\pi \delta D_b^{Mg}}{d} \ll \frac{\pi \delta D_b^O}{d}$$

at least for Fe³⁺-doped magnesia, and 10 μm > d ≥ 0.1 μm.

Considering now this work, it follows from above that both ions are transported through grain boundaries, the magnesium grain boundary diffusion being rate controlling. This result is quite complementary with electron micrograph observations done in our laboratory on 1 μm grains. These show that some boundary opening up and some porosity redistribution around the grains along boundaries, are the major features after creep straining.

The apparent magnesium grain boundary diffusivity can be estimated from our creep data. The plot in Fig. 6 gives

$$\delta D_b^{Mg} = 3.4 \times 10^{-3} \exp \frac{-96 \text{ kcal mole}^{-1}}{kT} \quad (\text{cm}^3 \text{sec}^{-1}). \quad (3)$$

Although no direct measurement of δD_B is available, this expression can be compared to a similar creep diffusivity inferred from Gordon *et al.* [8]

$$\delta D_b^{Mg} = 1.5 \times 10^{-1} \exp \frac{-108 \text{ kcal mole}^{-1}}{kT} \quad (\text{cm}^3 \text{sec}^{-1}) \quad (4)$$

for 0.05% Fe-doped MgO allowed to creep in air at 1200 to 1300°C and 7 to 9 and 5 to 14 μm grain size. These two results give similar diffusivities in the observed creep conditions by a balance between the activation energies and the pre-exponential factors; but because of the larger range in the investigated temperatures, we think that our Equation 3 is more reliable, although good precision on activation energies cannot be claimed (compare, for example, with the value near 90 kcal mole⁻¹ measured by differential tests in Part 3).

It is generally recognized that activation energy for boundary diffusion must be equal to or slightly less than that for lattice diffusion. The activation energy of 96 kcal mole⁻¹ found here for mag-

nesium boundary diffusivity is lower than the average value of 120 kcal mole⁻¹ found in other creep studies by Trember *et al.* [9] for the magnesium sublattice.

All creep results discussed here are for doped MgO, so that cation lattice diffusivity should be extrinsic. Consistently, all the energies above creep activation energy are higher than that reported for magnesium tracer diffusion in MgO [16–18]. It is generally suggested that high activation energy in an oxide which is doped with a transition metal probably results from a contribution of temperature dependence from both the Fe³⁺/Fe²⁺ ratio and the solubility of the dopant [9, 19]. However, it can be noted that Tagai *et al.* [3, 4] found also a high activation energy of 104 kcal mole⁻¹ for both a 0.55% Fe cation-doped and a much purer MgO, and Tremper *et al.* [9] reported a high activation energy of ≈ 117 kcal mole⁻¹ in a large range of dopant levels. Furthermore, the apparent boundary diffusivity deduced here is close to the one inferred from the creep studies of Gordon *et al.* [8] for a 0.05% Fe cation-doped MgO. Therefore δD_b appears to be insensitive to dopant levels.

This remark raises the question of a possible change in the basic diffusion mechanism for creep in doped materials from isolated vacancy diffusion to vacancy pair diffusion, as it has been suggested in Al³⁺-doped MgO [11], where the creep activation energy of 120 kcal mole⁻¹ is correlated with lattice vacancy pair diffusion. In this case our 96 kcal mole⁻¹ would represent the energy of the boundary vacancy pair diffusion, again smaller than the lattice value.

Acknowledgements

The financial support of CNRS is acknowledged. J. Crampton is grateful for helpful discussions with Drs R. M. Cannon and A. H. Heuer. We should also like to thank Dr A. Risbet for his assistance at the start of the project and Professor A. C. D. Chaklader for providing us with the samples.

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Received 28 February and accepted 26 May 1978.