

Analysis of mass transport in the diffusional creep of polycrystalline MgO-FeO-Fe₂O₃ solid solutions

R. S. GORDON, J. D. HODGE

Division of Materials Science and Engineering, University of Utah, Salt Lake City, Utah, USA

An analysis of mass transport in the diffusional creep of iron-doped, polycrystalline MgO was conducted. Creep regimes in which magnesium grain boundary, oxygen grain boundary, and magnesium-lattice diffusion were rate-controlling were identified. An analytical procedure was developed for the estimation of the diffusion constants for these three processes.

1. Introduction

Recently [1] an analysis was presented for mass transport in the diffusional creep of polycrystalline ionic solids. In that treatment several limiting creep situations were suggested for the creep of polycrystalline MgO doped with iron. In this paper, actual strain rate-grain size data taken in the viscous creep regime at 1300 to 1400°C will be presented which can be used to separate the various contributions of cation lattice and grain-boundary diffusion, as well as anion grain-boundary diffusion to the creep of polycrystalline MgO-FeO-Fe₂O₃ (magnesiowüstite) solid solutions over a range of compositions (0.05 to 5.3 cation % iron)* and grain sizes† (8 to 98 μm).

2. Experimental

For details concerning the experimental aspects and the evidence for viscous creep behaviour the reader is referred to extensive discussions given elsewhere [2-4].

3. General creep equation

In the mass transport analysis for the diffusional creep of magnesiowüstite, the general creep equation‡, neglecting impurity terms, is as follows [1]:

$$\text{*Cation \% iron} = \left(\frac{\text{moles iron}}{\text{moles magnesium} + \text{moles iron}} \right) 100.$$

†Grain sizes in this paper are linear intercept averages multiplied by the factor 1.5 [5].

‡The numerical constants in Equation 1 are those of the combined analysis of Raj and Ashby [6] and are only slightly different from those in the generally accepted Nabarro-Herring and Coble creep equations [1].

$$\dot{\epsilon} = \left[\frac{44\Omega_v\sigma}{kT(GS)^3} \right] \frac{[(GS/\pi)D_{Mg}^l + \delta_{Mg}D_{Mg}^b]}{\left[1 + \frac{(GS/\pi)D_{Mg}^l + \delta_{Mg}D_{Mg}^b}{(GS/\pi)D_O^l + \delta_O D_O^b} \right]} \quad (1)$$

in which

- $\dot{\epsilon}$ = strain rate,
- Ω_v = MgO molecular volume (1.86×10^{-23} cm³),
- σ = stress,
- k = Boltzmann's constant,
- T = absolute temperature,
- GS = grain size,
- D_{Mg}^l, D_O^l = magnesium and oxygen lattice diffusion coefficients, respectively,
- D_{Mg}^b, D_O^b = magnesium and oxygen grain-boundary diffusion coefficients, respectively,
- δ_{Mg}, δ_O = effective grain-boundary thicknesses, respectively, for magnesium and oxygen boundary diffusion.

In MgO, pure and doped with iron, it has been shown that $(GS/\pi)D_O^l \ll \delta_O D_O^b$ for grain sizes $\gtrsim 400$ μm and at temperatures $\leq 1400^\circ\text{C}$ [1]. Consequently,

TABLE I Transition between magnesium boundary and lattice diffusion (1300°C)

Cation % Fe	$D_{Mg^1}(cm^2 sec^{-1})$ [2, 4]	$\delta_{Mg}D_{Mg^b}(cm^2 sec^{-1})$ [2, 3]	Transition grain size (μm)
0.05	$(3.3 \pm 0.6) \times 10^{-13}$	$(1.5 \pm 0.6) \times 10^{-16}$	16 ± 8

$$\dot{\epsilon} = \left[\frac{44\Omega_v\sigma}{kT(GS)^3} \right] \frac{[(GS/\pi)D_{Mg^1} + \delta_{Mg}D_{Mg^b}]}{\left[1 + \frac{(GS/\pi)D_{Mg^1} + \delta_{Mg}D_{Mg^b}}{\delta_O D_O^b} \right]}. \quad (2)$$

4. Coble creep limit

Let us now examine several interesting limits for Equation 2. In the limit of very small grain sizes and low magnesium lattice diffusivities, $(GS/\pi)D_{Mg^1} \ll \delta_{Mg}D_{Mg^b}$ and Equation 2 can be simplified to

$$\dot{\epsilon} = \left[\frac{44\Omega_v\sigma}{kT(GS)^3} \right] \left[\frac{[\delta_{Mg}D_{Mg^b}]}{1 + \frac{\delta_{Mg}D_{Mg^b}}{\delta_O D_O^b}} \right]. \quad (3)$$

In this limit, Coble creep should be observed ($\dot{\epsilon} \propto (GS)^{-3}$). Since $\delta_O D_O^b$ is expected to be large in magnesiowüstite [1], $\delta_{Mg}D_{Mg^b} \ll \delta_O D_O^b$. Thus

$$\dot{\epsilon} = \frac{44\Omega_v\sigma\delta_{Mg}D_{Mg^b}}{kT(GS)^3}. \quad (4)$$

Coble creep has been reported [2, 3] in magnesiowüstite for iron concentrations ≤ 0.27 cation %, grain sizes between 6 and 23 μm , and temperatures $\leq 1300^\circ C$.

For large values of $\delta_O D_O^b$ the transition between Coble creep controlled by magnesium grain-boundary diffusion and Nabarro-Herring creep controlled by magnesium lattice diffusion is defined by Equation 5, i.e.

$$\frac{(GS)}{\pi} D_{Mg^1} = \delta_{Mg}D_{Mg^b}. \quad (5)$$

Nabarro-Herring creep has been reported in MgO doped with 0.05 cation % iron at $1400^\circ C$ [2, 4] for grain sizes over $\sim 23 \mu m$. In Table I values for $\delta_{Mg}D_{Mg^b}$ and D_{Mg^1} are listed at $1300^\circ C$. D_{Mg^1} was calculated from creep data extrapolated from $1400^\circ C$ using an activation energy of 117 kcal mol⁻¹. * Using these values the transition grain size at $1300^\circ C$ was calculated, from Equation 5, to be $\sim 16 \pm 8 \mu m$. This grain size should decrease as the temperature is raised above $1300^\circ C$ and as the iron dopant level is increased. These predictions are in accord with

*An activation energy of 117 kcal mol⁻¹ was identified as that corresponding to Nabarro-Herring creep in magnesiowüstite [4].

experiment in that at higher temperatures and for higher iron concentrations, creep is controlled either by magnesium lattice or oxygen grain-boundary diffusion or both [4] in this grain size regime ($\geq 15 \mu m$). In addition, at $1300^\circ C$ for 0.05% specimens, Coble creep was observed [2, 3] up to $\sim 23 \mu m$, which is in reasonable accord with the calculated transition grain size in Table I.

5. Nabarro-Herring creep limit

At larger grain sizes, higher iron concentrations, and higher temperatures, $(GS/\pi)D_{Mg^1} \gg \delta_{Mg}D_{Mg^b}$ and Equation [2] reduces to

$$\dot{\epsilon} = \left[\frac{14\Omega_v\sigma}{kT(GS)^2} \right] \left[\frac{[D_{Mg^1}]}{1 + \frac{(GS/\pi)D_{Mg^1}}{\delta_O D_O^b}} \right]. \quad (6)$$

When $\delta_O D_O^b \gg (GS/\pi)D_{Mg^1}$, then

$$\dot{\epsilon} = \frac{14\Omega_v\sigma D_{Mg^1}}{kT(GS)^2}. \quad (7)$$

Equation 7 is, of course, the Nabarro-Herring relation corresponding to creep controlled by magnesium lattice diffusion. This behaviour (i.e. $\dot{\epsilon} \propto (GS)^{-m}$; $m = 2$) has been reported at $1400^\circ C$ for creep specimens tested in oxygen at the 0.05% dopant level [2]. Oxidizing ($P_{O_2} = 0.86$ atm) creep data at $1350^\circ C$ are presented in Fig. 1 for the 0.53% dopant level. These data indicate reasonably good agreement with the Nabarro-Herring creep equation (i.e. $m = 1.94$; $m = 2$ theoretical value). The value of D_{Mg^1} ($2.3 \times 10^{-12} cm^2 sec^{-1}$) which is computed from these data is in reasonable agreement with that predicted from magnesium tracer diffusion [7].

6. Mixed Coble and Nabarro-Herring creep

If, however, $(GS/\pi)D_{Mg^1} \approx \delta_O D_O^b$, then the general expression (Equation 6) must be used and a mixed grain-size dependence (i.e. $2 < m < 3$) should result. In Fig. 1, oxidizing ($P_{O_2} = 0.86$ atm) creep data at $1350^\circ C$ are plotted for specimens doped with 2.65 cation % iron. A least squares analysis of these data resulted in a grain size exponent (m) of 2.38. In order to estimate values of D_{Mg^1} and $\delta_O D_O^b$ at this concentration,

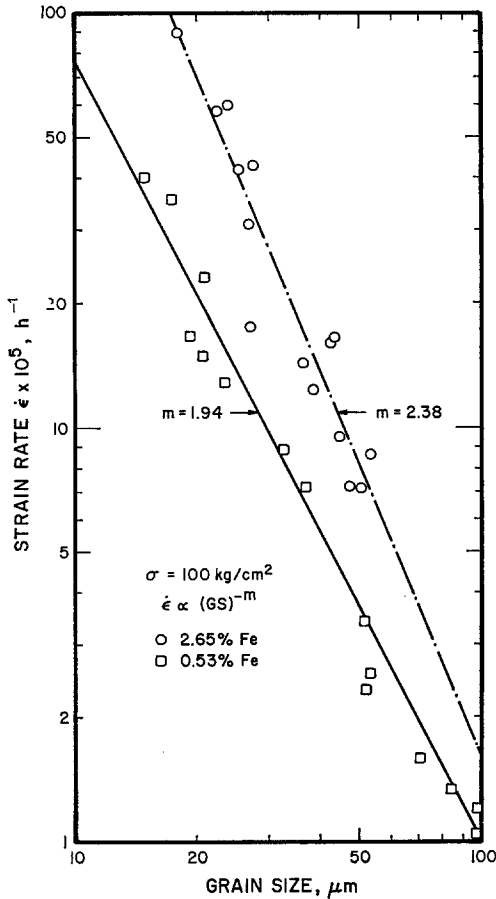


Figure 1 Effect of grain size on creep rate in oxidizing atmospheres at 1350°C.

Equation 6 must be arranged into the following form:

$$\dot{\epsilon}(GS)^2 = -\frac{(GS)^3 D_{Mg}^1}{\pi \delta_O D_O^b} \dot{\epsilon} + \frac{14\Omega_v \sigma}{kT} D_{Mg}^1 \quad (7)$$

Thus a plot of $\dot{\epsilon}(GS)^2$ versus $\dot{\epsilon}(GS)^3$ should result in a straight line with a slope (M) and an intercept (B) given by the following equations:

$$M = -\frac{D_{Mg}^1}{\pi \delta_O D_O^b} \quad (8)$$

$$B = \frac{14\Omega_v \sigma D_{Mg}^1}{kT} \quad (9)$$

D_{Mg}^1 and $\delta_O D_O^b$ can then be evaluated from these two relations.*

*Johnson [8] has suggested a procedure similar to this for the evaluation of cation lattice and anion boundary contributions to the sintering of ionic compounds.

Usually in creep experiments the normal scatter in strain-rate size data ($\sim 20\%$) precludes a plot of the foregoing type using raw creep data because the functions $\dot{\epsilon}(GS)^2$ and $\dot{\epsilon}(GS)^3$ are extremely sensitive to small changes in the grain size. Therefore, an alternative procedure has been used to construct this plot which involves fitting the creep data first to a relation of the type

$$\dot{\epsilon} = K(GS)^{-m} \quad (10)$$

For the creep data at the 2.65% dopant level a least squares analysis has resulted in a line with $m = 2.38$ (Fig. 1). Using this least squares fit, arbitrary values of $\dot{\epsilon}$ for various grain sizes were generated. From these computations, values of $\dot{\epsilon}(GS)^2$ and $\dot{\epsilon}(GS)^3$ were computed and plotted in Fig. 2. A linear least squares analysis of these values resulted in the following values (99% confidence limits) for the slope and the intercept.

$$M = -0.02648 \pm 0.00530 \mu\text{m}^{-1}$$

$$B = 0.16441 \pm 0.03288 \mu\text{m}^2 \text{h}^{-1}$$

From these values we calculate D_{Mg}^1 and $\delta_O D_O^b$ at 1350°C to be $9.0 (\pm 1.8) \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ and $1.6 (\pm 0.3) \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$. These values are reasonable when compared with magnesium tracer values [7] and estimates of oxygen grain-boundary diffusion [2, 4]. It is noted that if either the Nabarro-Herring or Coble creep equations were used separately to calculate values of D_{Mg}^1 and $\delta_O D_O^b$ from the data, significant *underestimates* of these quantities would result. When these values of D_{Mg}^1 and $\delta_O D_O^b$ are substituted into Equation 8, a line is generated which essentially duplicates the least squares line in Fig. 1. Thus Equation 10 is a good approximation and indicates that the transition between the Nabarro-Herring and Coble creep regimes is not sharp but extends over a range of grain sizes.

Having estimated values of D_{Mg}^1 and $\delta_O D_O^b$ for MgO doped with 2.65 cation % Fe, we can now estimate the grain size at which we could expect equal contributions of magnesium lattice and oxygen grain-boundary diffusion, i.e.

$$GS \approx \frac{(\delta_O D_O^b) \pi}{D_{Mg}^1} \quad (11)$$

$$\approx 57 \pm 11 \mu\text{m}.$$

If, as a first approximation, we assume $\delta_O D_O^b$ is nearly independent of iron concentration in the

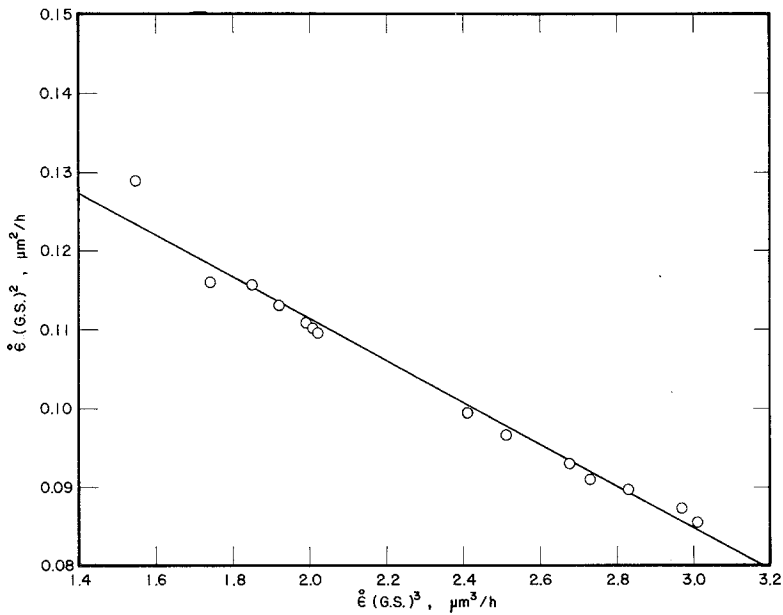


Figure 2 Analytical plot for the determination of D_{Mg}^1 and $\delta_O D_O^b$.

range between 0.53 and 5.3 cation %, we can estimate the transition grain size in an oxygen atmosphere for successively increasing iron concentrations from computed values of D_{Mg}^1 . These computations are summarized in Table II.

TABLE II Transition between magnesium lattice and oxygen grain-boundary diffusion (1350°C)

Cation % Fe	D_{Mg}^1 (cm ² sec ⁻¹)	$\delta_O D_O^b$ (cm ⁸ sec ⁻¹)	Transition grain size (μ m)
0.53	2.3×10^{-12}	$\sim 1.6 \times 10^{-14*}$	~ 220
2.65	9.0×10^{-12}	1.6×10^{-14}	57
5.3	$\sim 18 \times 10^{-12*}$	$\sim 1.6 \times 10^{-14*}$	~ 30

*Estimated values

Thus it is apparent that for dopant levels $\leq 0.53\%$ Nabarro-Herring creep should only be observed since the practical upper experimental limit for the grain size is $\sim 100 \mu$ m (i.e. viscous creep rates become immeasurably slow at these and larger grain sizes). However, as the iron concentration increases, the relative contribution of oxygen grain-boundary diffusion should increase since the transition grain size is lowered well within the experimental range. It should be noted that as the temperature is increased over 1350°, the transition grain sizes will decrease since the activation energy for extrinsic mag-

nesium lattice diffusion ($\sim 117 \text{ kcal mol}^{-1}$) is higher than oxygen grain-boundary diffusion ($\leq 81 \text{ kcal mol}^{-1}$) in magnesiowüstite [4].

7. Summary

In summary, it has been shown that a generalized diffusional creep equation which takes into account mass transport of anions and cations over both lattice and grain-boundary paths can be used to describe the creep of polycrystalline MgO-FeO-Fe₂O₃ solid solutions. Using appropriate limits of the general equation, estimates have been made of the diffusion coefficients for magnesium grain boundary, oxygen grain boundary, and magnesium lattice diffusion. This type of analysis should, in principle, be applicable to other systems and ceramic processes (e.g. sintering, thermal grooving) in which anions and cations diffuse over more than one path.

Acknowledgements

The authors acknowledge the assistance of R. T. Tremper and R. A. Giddings in the collection of some of the data. D. Lynn Johnson is acknowledged for suggesting the method of analysis in computing values of D_{Mg}^1 and $\delta_O D_O^b$. The authors are also grateful for helpful discussions with P. Lessing. This research was supported by the Atomic Energy Commission under Contract AT(11-1)-1591.

References

1. R. S. GORDON, *J. Amer. Ceram. Soc.* **56** (1973) 147.
2. G. R. TERWILLIGER, H. K. BOWEN and R. S. GORDON, *J. Amer. Ceram. Soc.* **53** (1970) 241.
3. R. S. GORDON and G. R. TERWILLIGER, *J. Amer. Ceram. Soc.* **55** (1972) 450.
4. (a) R. T. TREMPER, R. A. GIDDINGS, J. D. HODGE and R. S. GORDON, *J. Amer. Ceram. Soc.* **57** (1974) 421.
(b) R. T. TREMPER, Ph.D. Thesis, University of Utah 1971.
5. D. D. MARCHANT and R. S. GORDON, *J. Amer. Ceram. Soc.* **55** (1972) 19.
6. R. RAJ and M. F. ASHBY, *Trans. AIME* **2** (1971) 1113.
7. B. J. WUENSCH, W. C. STEELE and T. VASILOS, *J. Chem. Phys.* **58** (1973) 5258.
8. D. LYNN JOHNSON, private communication.

Received 29 April and accepted 2 July 1974.