

Diffusional Creep of Polycrystalline Mn-Zn Ferrite

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Four-point bending creep of polycrystalline Mn-Zn ferrite was studied at temperatures between 1100° and 1400°C. Deformation mechanisms were inferred on the basis of current creep theories. At grain sizes between 15 and 80 μm , 'Coble creep' was observed, which was considered to be controlled by oxygen grain-boundary diffusion. Apparent oxygen grain-boundary diffusivity was calculated and the activation energy was 52 kcal/mol. At grain sizes larger than 80 μm and at higher stresses, 'Nabarro creep' controlled by dislocation climb process was observed, in which the steady-state creep rate was independent of grain size. Apparent oxygen lattice diffusivities were obtained, which showed different activation energies according to temperature range: 39 kcal/mol at temperatures between 1100° and 1300°C, 92 kcal/mol at temperatures between 1300° and 1400°C.

KEY WORDS: Diffusional creep/ Mn-Zn ferrite/ Coble creep/ Nabarro creep/ Oxygen grain boundary diffusion/ Oxygen lattice diffusion/

1. INTRODUCTION

Polycrystalline materials deform by lattice and grain-boundary diffusion of constituent atoms or ions, dislocation movement, and grain-boundary sliding. In ionic polycrystals, plastic deformation at elevated temperatures is controlled principally by ion diffusion through lattice or along grain-boundary. And analysis of high-temperature creep behaviors of ionic polycrystals can give us the information of lattice and/or grain-boundary diffusion. It is the purpose of this study to obtain the information of ion diffusion in Mn-Zn ferrite through creep testing.

2. EXPERIMENTAL PROCEDURES

Mixtures of MnCO_3 , ZnO and Fe_2O_3 powders in a molar ratio 1:1:2 were calcined in air at a temperature between 850° and 1100°C for 2 h, and then crushed and ball-milled for 16 to 48 h with a stainless steel pot and balls. The calcined powders were hot-pressed at 1250°C and 200 kg/cm² for 30 min, followed by annealing in N_2 on various conditions (1350° to 1430°C, 5 to 7 h) to release residual stresses in hot-pressed bodies and to obtain specimens with various grain sizes (~ 15 to ~ 1000 μm). The specimens of smaller grain size had uniformly distributed grains and flat grain-boundaries, while those of larger size ($> \sim 300$ μm) had some irregularities in grain size distribution and in grain-boundary shape. The densities of obtained Mn-Zn

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ferrite polycrystals were higher than 98% of theoretical.

Creep deformation (strain) rate, $\dot{\epsilon}$, were measured in air by four-point bending technique¹⁾ with rectangular beams ($\sim 3.5 \times 6 \times 65 \text{ mm}^3$) cut from the hot-pressed billets. Load and support members (rod, knife-edges) were made of sintered alumina. Stress, σ , and strain, ϵ , were calculated from load, deflection, dimensions of specimen and knife-edges, and stress exponent ($n: \dot{\epsilon} \propto \sigma^n$).²⁾ The stress exponents were obtained from creep curves (deflection *vs* time) measured at various load levels.

Creep testing was conducted at a temperature between 1100° and 1400°C and at a stress between 5 and 200 kg/cm². For Mn-Zn ferrite, it was confirmed by pre-examination that the spinel phase was stable in air at the temperatures tested. Grain growth during creep testing was not observed.

3. RESULTS AND DISCUSSIONS

On all deformation conditions (stresses and temperatures mentioned above), the steady-state creep region ($\dot{\epsilon} = \text{constant}$) was observed immediately after applying load. The steady-state creep rate has been found to be expressed as a function of stress (σ), grain size (d) of specimen and temperature, *i.e.* $\dot{\epsilon} \propto \sigma^n d^m \exp(-E/RT)/T$, where n and m are stress- and grain size-exponent, respectively.³⁾ Stress dependence

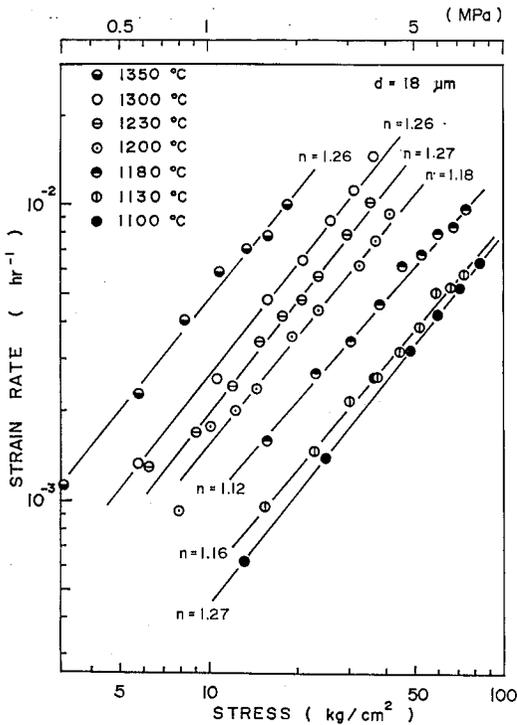


Fig. 1. Stress dependence of strain rate for hot-pressed Mn-Zn ferrite (grain size; $d=18 \mu\text{m}$). (n : stress exponent, $\dot{\epsilon} \propto \sigma^n$)

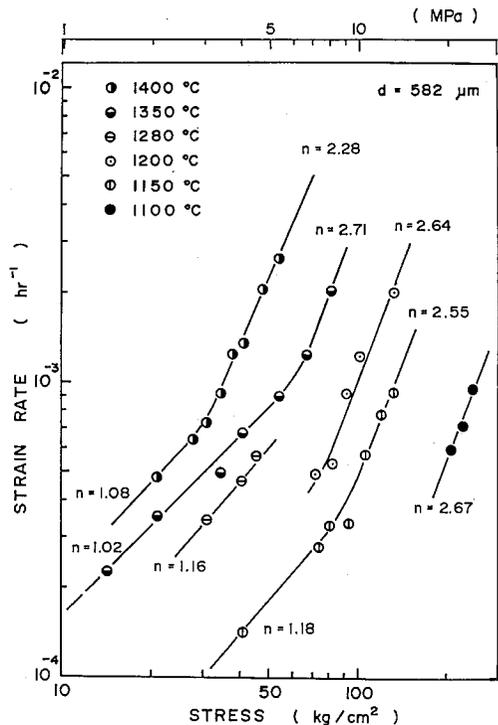


Fig. 2. Stress dependence of strain rate for hot-pressed Mn-Zn ferrite (grain size; $d=582 \mu\text{m}$).

of strain rate for two grain sizes is shown in Figs. 1 and 2. At a small grain size of $18\ \mu\text{m}$ (Fig. 1), stress exponent was nearly unity at any temperature between 1100° and 1400°C , showing 'viscous diffusional creep'. The viscous creep was observed at grain sizes between about 15 and $80\ \mu\text{m}$ in the same temperature range. For coarser-grained specimens, different stress dependence was found as shown in Fig. 2. At lower stresses, the relation was the same as that for the finer-grained ones, but the stress exponent increased to approximately 3 at higher stresses at any test temperature. (In Figs. 1 and 2, stresses and strains were calculated as $n=1$ for convenience. True stress and strain values can be obtained by taking account of n , since σ and ϵ are the functions of n .²⁾) This type of 'non-viscous' behavior appeared for grain sizes between 80 and $1000\ \mu\text{m}$.

In each of the two regions of viscous (smaller grain size) and non-viscous (larger grain size) creep, grain size dependence of strain rate is shown in Fig. 3. The strain rates in the viscous region (at $\sigma=30\ \text{kg/cm}^2$, $T=1473^\circ\text{K}$ and 1623°K) were highly dependent on grain size ($m \approx -3$), whereas those in the non-viscous region ($\sigma=80\ \text{kg/cm}^2$, $T=1473^\circ\text{K}$) were almost independent of grain size.

From these results, it was suggested that the creep deformation at grain sizes between 15 and $80\ \mu\text{m}$ were characterized by 'Coble creep' ($\dot{\epsilon} \propto \sigma/d^3$), which was controlled by grain-boundary diffusion of constituent ion. On the assumption that cations diffuse more rapidly through lattice in the ferrite, oxygen ion was thought to be rate-controlling species for Mn-Zn ferrite polycrystals of grain size smaller than

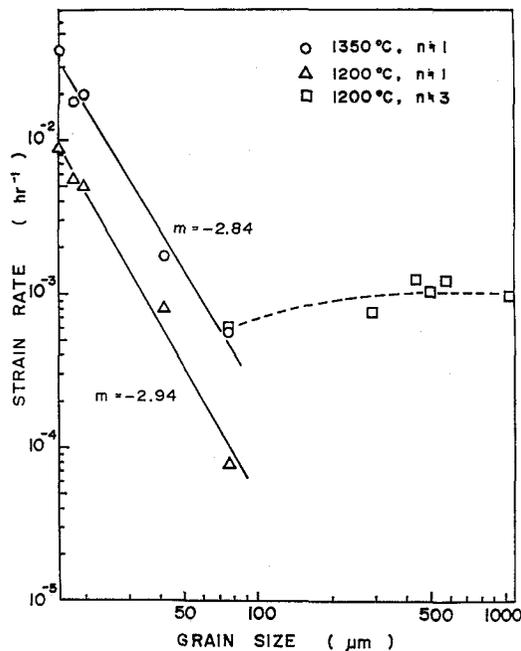


Fig. 3. Grain size dependence of strain rate for hot-pressed Mn-Zn ferrite at $\sigma=30\ \text{kg/cm}^2$ for viscous creep ($n \approx 1$) and at $\sigma=80\ \text{kg/cm}^2$ for non-viscous creep ($n \approx 3$). (m : grain size exponent, $\dot{\epsilon} \propto d^m$)

80 μm at stresses and temperatures tested. Applying the current creep theory for ionic polycrystals,³⁾ oxygen grain-boundary diffusion coefficient, D_0^b , was calculated approximately from the following relation:

$$\delta D_0^b = \frac{d^3 k T \dot{\epsilon}}{14\pi\sigma(\Omega/4)} \quad (1)$$

where δ is the width of grain-boundary region (not evaluated), $\dot{\epsilon}$ is the steady-state creep (strain) rate under a constant stress, σ , and temperature, T , d is the grain size, and Ω is the 'molecular' volume of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Temperature dependence of calculated values (at $\sigma=30 \text{ kg/cm}^2$) is shown in Fig. 4. The least squares fit gave δD_0^b as follows:

$$\delta D_0^b = 4.21 \times 10^{-6} \exp\left(\frac{-51800 \pm 2100 \text{ cal/mol}}{RT}\right) \text{ cm}^3/\text{sec.}$$

δD_0^b in Ni-Zn ferrite obtained from creep testing⁴⁾ is also shown in Fig. 4. It is seen from the figure that the diffusivities were in the same order, but the activation energy of D_0^b in Mn-Zn ferrite was lower in comparison with that of grain growth in Mn-Zn ferrite in which diffusion through grain-boundary was considered to be the rate-determining step.⁵⁾

At grain sizes larger than 80 μm , it was suggested that 'Nabarro creep' ($\dot{\epsilon} \propto \sigma^3$) was prevailing, which was controlled by dislocation climb process. Oxygen ion being slower diffusing species through lattice in the ferrite, oxygen lattice diffusion co-

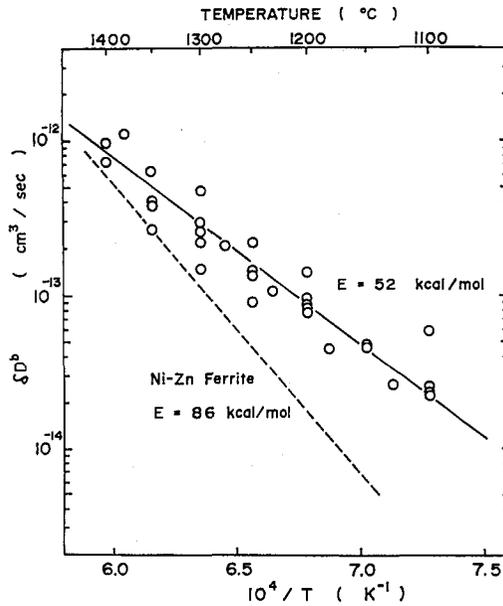


Fig. 4. Apparent grain-boundary diffusivity of oxygen ion in Mn-Zn ferrite, calculated from Eq. (1) for grain sizes between 15 and 80 μm (solid line). Broken line is that for Ni-Zn ferrite with grain sizes between 15 and 30 μm .⁴⁾

efficient, D_0^l , can be calculated from 'Nabarro-Weertman's equation'.⁶⁾

$$D_0^l = \frac{10b^2G^2kT\dot{\epsilon}}{\pi\beta^2\sigma^3(Q/4)} \quad (2)$$

where b is Burgers vector ($=\frac{1}{2}\langle 110 \rangle$ in spinel), β is the constant (≈ 1), and G is the shear modulus. Elastic modulus was measured at elevated temperatures (up to $\sim 800^\circ\text{C}$) by resonance technique and the values obtained were extrapolated to those at temperatures creep-tested. In Fig. 5, calculated diffusion coefficients (at $\sigma=80$ kg/cm²) are plotted against $1/T$ and the least squares fit led to the following expressions different according to temperature range.

$$D_0^l = 1.40 \times 10^{-5} \exp\left(\frac{-39300 \pm 2800 \text{ cal/mol}}{RT}\right) \quad \text{cm}^2/\text{sec}$$

between 1100° and 1300°C ,

$$D_0^l = 2.48 \times 10^2 \exp\left(\frac{-91700 \pm 15900 \text{ cal/mol}}{RT}\right) \quad \text{cm}^2/\text{sec.}$$

between 1300° and 1400°C .

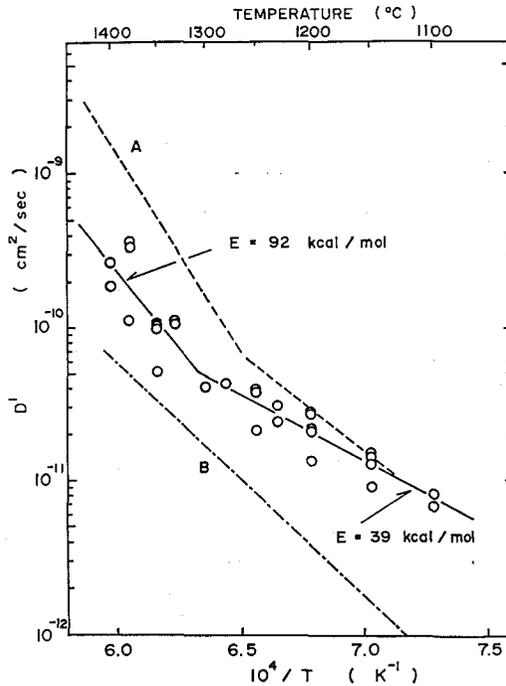


Fig. 5. Apparent lattice diffusion coefficient of oxygen ion in Mn-Zn ferrite, calculated from Eq. (2) for grain sizes between 80 and 1000 μm (solid line).

A (broken line): Apparent diffusion coefficient of oxygen ion in Ni-Zn ferrite for grain sizes between 80 and 120 μm obtained through creep testing.⁴⁾ $E=116$ kcal/mol at higher temperatures, $E=59$ kcal/mol at lower temperatures.

B (chain line): Oxygen tracer diffusion coefficient in single crystal of Fe-rich Ni ferrite.⁷⁾ $E=61$ kcal/mol.

The activation energy at lower temperatures is thought to be related to migration energy of oxygen defect (vacancy). Although the data were scattered and the temperature range was limited, the higher value of activation energy at higher temperatures may include both energies of migration and of formation of oxygen vacancy due to oxygen dissociation or vaporization of ZnO. Oxygen lattice diffusion coefficients in Ni ferrite (single crystal, measured by ^{18}O tracer experiment⁷⁾) and in Ni-Zn ferrite (polycrystal, measured by creep testing⁴⁾) are also shown by line B and A in Fig. 5, respectively. Lattice diffusion coefficients of cation (Fe) in Mn-Zn ferrite single crystal (annealed in air) and polycrystal (sintered in air) measured by ^{59}Fe tracer has reported by S. Ogawa and Y. Nakagawa,⁸⁾ showing values about 2 orders of magnitude higher than D_0^l obtained here (*e.g.* 5×10^{-9} at 1200°C and 2×10^{-9} at 1100°C for D_{Fe}^l). These higher values of D_{Fe}^l may support that the creep in non-viscous region was rate-controlled by oxygen lattice diffusion in Mn-Zn ferrite.

Specimens after creep testing were slightly surface-polished on the tensile side, and etched by dil. H_2SO_4 at $\sim 100^\circ\text{C}$, followed by optical microscopic or SEM examination. There were no evidences of grain growth and micro-cracking, but etch pits showing the presence of dislocations^{9,10)} were observed especially in coarse-grained specimens. Fig. 6 shows the etch pits on the surface of a coarse-grained specimen ($d=390 \mu\text{m}$) after non-viscous creep deformation. The density of etch pit was, though different considerably among grains in a specimen, roughly averaged $\sim 2 \times 10^6 \text{ cm}^{-2}$ in a sample with $460 \mu\text{m}$ grain size after creep testing at 80 kg/cm^2 and 1280°C . On the other hand, the pit densities in finer-grained ones were lower ($\sim 1/10$) and the average distance of pits was comparable to the grain size, which was consistent with the difference of deformation mechanism between finer- and coarser-grained Mn-Zn ferrite.

At small grain sizes, the stress exponents slightly larger than unity (Fig. 1) may suggest the contribution of grain-boundary sliding due to the flat grain-boundary rather than that of dislocation climb, while the exponents slightly smaller than 3 at large grain sizes (Fig. 2) may be due to the contribution of the usual diffusion mass trans-

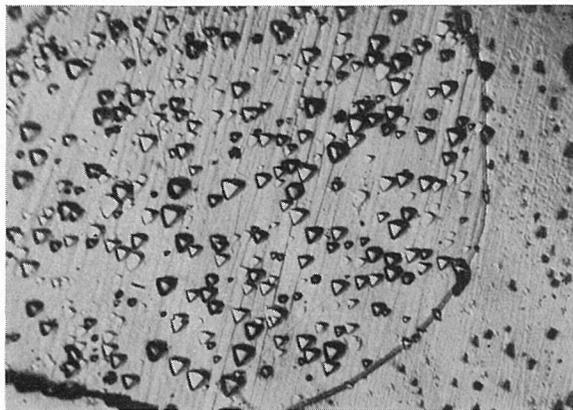


Fig. 6. Etch pits on the tensile surface of a coarse-grained specimen (grain size; $d=390 \mu\text{m}$) after creep testing.

port, between boundaries (Coble or Nabarro-Herring creep). Therefore, the calculated values of diffusivities both through lattice and along grain-boundary (Figs. 4 and 5) may be somewhat overestimated.

Consistent with the prediction of the creep theory, it was suggested from these results that, with increasing grain size, reduced the contribution of grain-boundary to diffusion as sources and sinks for vacancies and as diffusion path, and instead, dislocations in grains were acting as sources and sinks for vacancies.

4. SUMMARY

For polycrystalline Mn-Zn ferrite with an average grain size between 15 and 1000 μm , four-point bending creep testing was conducted at a stress between 5 and 200 kg/cm^2 and at a temperature between 1100° and 1400°C. Controlling mechanisms of creep deformation were inferred from stress- and grain size- dependence of steady-state creep rate. For grain sizes smaller than about 80 μm , Coble creep ($\dot{\epsilon} \propto \sigma/d^3$) was observed, which was thought to be controlled by oxygen grain-boundary diffusion. The product of oxygen grain-boundary diffusion coefficient (D_0^b) and grain-boundary width (δ) was estimated as $\delta D_0^b = 4.21 \times 10^{-6} \exp(-51800 \pm 2100/RT) \text{ cm}^3/\text{sec}$. At grain sizes larger than 80 μm and at higher stresses, non-viscous creep ($\dot{\epsilon} \propto \sigma^n$) was observed, in which the stress exponents (n) were approximately 3, suggesting Nabarro creep controlled by dislocation climb. Oxygen lattice diffusion coefficients were obtained as follows, according to test temperature range: $D_0^l = 1.40 \times 10^{-5} \exp(-39300 \pm 2800/RT) \text{ cm}^2/\text{sec}$ between 1100° and 1300°C, $D_0^l = 2.48 \times 10^2 \exp(-91700 \pm 15900/RT) \text{ cm}^2/\text{sec}$ between 1300° and 1400°C.

REFERENCES

- (1) T. Nishikawa, H. Nakajima, T. Ishida, and K. Umeya, *Yogyo-Kyokai-Shi*, **79**, 209 (1971).
- (2) G. W. Hollenberg, G. R. Terwilliger, and R. S. Gordon, *J. Amer. Ceram. Soc.*, **54**, 196 (1971).
- (3) For example, (a) P. A. Lessing and R. S. Gordon, in "Deformation of Ceramic Materials", ed. by R. C. Bradt and R. E. Tressler, Plenum Press, New York, 1975, p. 271 (b) R. M. Cannon and R. L. Coble, in "Deformation of Ceramic Materials", ed. by R. C. Bradt and R. E. Tressler, Plenum Press, New York, 1975, p. 61.
- (4) T. Nishikawa, Y. Okamoto, T. Nakagawa, and H. Kimura, *Yogyo-Kyokai-Shi*, **87**, 529 (1979).
- (5) T. Iimura, in "Ferrites", Proceedings of the International Conference 1970, ed. by Y. Hoshino, S. Iida and M. Sugimoto, The University of Tokyo Press, Tokyo, 1971, p. 128.
- (6) J. Weertman, *Trans. ASM*, **61**, 681 (1968).
- (7) H. M. O'Bryan, Jr. and F. D. DiMarcello, *J. Amer. Ceram. Soc.*, **53**, 413 (1970).
- (8) S. Ogawa and Y. Nakagawa, *J. Phys. Soc. Japan*, **23**, 179 (1967).
- (9) M. Mizushima, *Japan. J. Appl. Phys.*, **7**, 893 (1968).
- (10) S. Kawado, *Japan. J. Appl. Phys.*, **9**, 24 (1970).