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Diffusional flow and hot-pressing: a study on MgO

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Magnesium oxide powder is hot-pressed at temperatures between 1200 and 1400°C and at stresses up to 22.4 MN m^{-2}. Theoretical values of the hot-pressing rate are calculated for grain-boundary and volume-diffusion mechanisms. The observed rates are shown to be linearly proportional to the applied stress and to be consistent with the volume-diffusion mechanism. A value of $D_L = 0.3 \exp(-4.9 \times 10^5/RT)$ m^2 sec^{-1} is obtained for the lattice diffusion coefficient, where R is in J mol^{-1} K^{-1}.

1. Introduction

The hot-pressing of ceramic powders is commonly used for the manufacture of fine-grain dense material without recourse to additives Frequent utilization of the technique has not, however, been accompanied by a complete understanding of the mechanisms resulting in densification.

Mackenzie and Shuttleworth [1] considered the powder to behave as viscous spheres acted on by a hydrostatic stress. The hot-pressing rate is proportional to the applied stress and a term was included to account for the stress magnification at the sphere contacts. It is now known that for a sphere deforming in a viscous manner by a vacancy diffusion mechanism the viscosity depends on the sphere size. The expression of Mackenzie and Shuttleworth does not consider grain size, and the viscosity concept has lost favour to more detailed calculations of vacancy-diffusion rates.

The hot-pressing rate due to a vacancy-diffusion mechanism has been calculated by several authors [2-5]. It is assumed that vacancies created on the powder surface migrate to the grain boundaries where a diminished vacancy concentration is maintained by the compressive stresses. The hot-pressing rate is thus proportional to applied stress, the stress multiplication factor at the powder contacts and the vacancy diffusion path. The stress multiplication factor increases with increasing porosity and values have been calculated [6, 7] by assuming the powder geometry. More recently a value has been calculated [8] where the porosity is assumed to attain an equilibrium shape.

Ramakrishnan [9] hot-pressed magnesium oxide powder at temperatures between 1200 and 1600°C. Comparison of tests at different temperatures but identical pressures gave an activation energy for sintering of 2.0×10^5 J mol^{-1}. Vasilos and Spriggs [10] obtained values between $3{\cdot}3 \times 10^5$ and 4×10^5 J mol^{-1} also by comparison of separate sintering tests at differing temperatures. Razinger and Fryer [11] have measured the activation energy for sintering by changing the temperature during hot-pressing. They obtained a value of 5.1×10^5 J mol^{-1} in the region 84% to 96% dense. The present paper obtains activation energies by instantaneously changing the temperature and comparing the change in rate. The hot-pressing stress is also instantaneously changed to obtain the stress dependence. A wide range of conditions is studied in the region 40% to 95% dense, 1180 to 1380°C and stresses from 1.5 to 22 MN m^{-2}. It is shown that the results differ from those obtained by comparing the rates of separate tests. During pressing, the rate decreases rapidly, presumably due to the increasing grain size increasing the diffusion path and densification decreasing the effective stress.

The observed rates are compensated for the change in grain size and then compared with the stress multiplication factors proposed by various authors.

2. Experimental

Analar magnesium oxide powder was pressed in a graphite die consisting of a cylinder 19 mm diameter and 24 mm long with a 6 mm diameter hole passing along the central axis. The powder was packed in the 6 mm hole and die wall friction was minimized by allowing the die to "float" whilst two graphite pistons acted on the powder. Also the length of the powder column was kept short relative to the diameter. In the region of interest, 60% to 100% dense, the column length was 4 to 2.4 mm long. Movement of the graphite piston was followed by a linear variable differential transformer which sensed the position of the pistons with alumina rods 1.2 mm diameter. The dilatometry was insensitive to strains in the apparatus caused by temperature changes and stress changes, since the transducer acted directly onto the specimen without reference to the push rods or furnace walls. At maximum sensitivity a change of 0.02 µm in the piston displacement could be measured. The temperature of the powder was measured by a thermocouple inserted in the graphite die. Tests were carried out in argon to prevent oxidation of the graphite. The same graphite die was used throughout. The powder density during pressing was calculated by relating the piston travel to the final density on removal from the die. The load was applied to the die when the powder had attained the desired temperature.

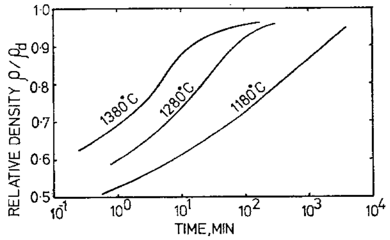

Figure 1 The increase in density with time during hot-pressing at a stress of 22.3 MN m^{-2}.

3. Results

Fig. 1 shows the variation of density with time for three separate tests performed at 1180, 1280 and 1380°C and an apparent stress of 22.3 MN m^{-2}. When the density is plotted linearly and time logarithmically, the data lie on a slightly S-shaped line. The flattening off above 90% dense is expected because the open porosity changes to a closed porosity containing gas, which reduces the closed pore sintering rate. All three specimens pressed to over 95% dense. A linear plot of the data against time might lead to the conclusion that a lower end-point density is reached if tests are not continued for sufficiently long times.

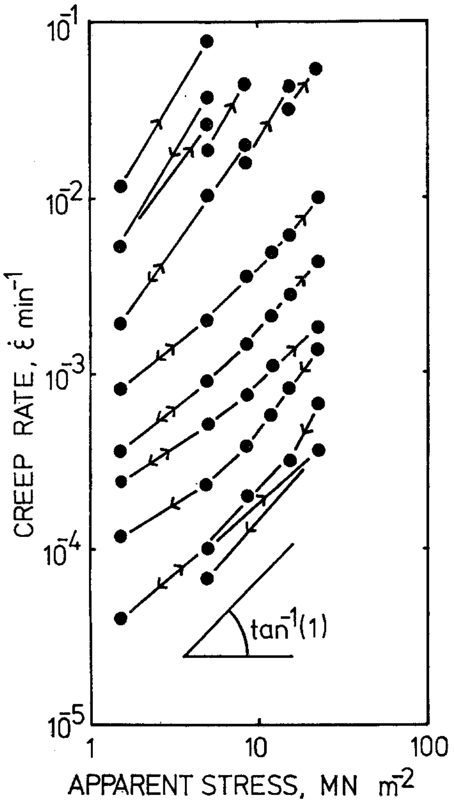

Figure 2 The dependence of creep rate on applied stress at 1280°C. The fastest rates are at 41% dense whilst the slowest are at 86% dense.

Fig. 2 shows the effect of instantaneously changing the applied load at 1280°C. At a given stress, the pressing rates continuously decreased with increase in density. The fastest rate in Fig. 2 was at 41% dense whilst the slowest rate was at 86% dense. The arrows refer to the direction of the stress change. The stress was decreased in stages from 22.3 to 1.5 MN m^{-2} and then increased again in stages until 22.3 MN m^{-2} was reached. The specimen was allowed to compress for a while at the higher stress so that a new set of creep rates could be obtained during the subsequent stress decrements. At the lower stresses the creep rates obtained when increasing the stress were identical to those obtained when decreasing the stress. However, when the higher stresses had again been reached, the accumulated strain was sufficient to result in a slightly lower creep rate than the value previously obtained when decreasing the stress. The effect was small and only observed at high stresses or high creep rates. The creep rate when the compact was over 60% dense was clearly linearly dependent on stress. At 40% dense the creep rate varied as the square of the stress.

The activation energy for hot-pressing was measured by comparing the rate of pressing before and after a rapid change in temperature. Activation energies were measured for four specimens at temperatures between 800 and 1400° C. The values obtained are listed in Table I.

TABLE I

Temperature (°C)	Density (%)	Stress (MN m^{-2})	Activation Energy (10^5 J mol^{-1})
800–900	23	2.0	2.8
900–1000	24	2.0	2.5
1000–1100	76	48.2	5.4
1100–1200	78	48.2	4.4
1200–1300	87	48.2	4.3
1300–1400	88	22.3	5.2
1300–1400	93	22.3	5.1

The activation energy obtained at low temperatures on low-density material was significantly less than that at higher temperatures and high densities. The average value for temperatures between 1000 and 1400° C was 4.9×10^5 J mol^{-1}. For a given density and temperature, the stress was chosen to give a slow creep rate. When the temperature was altered, 5 min elapsed before the new temperature was achieved and readings commenced. A slow creep rate was chosen to reduce the amount of strain occurring during this 5 min period and so to reduce the change in creep rate caused by the increase in density. The error introduced into the activation energy is later shown to be of no consequence. The grain size of three separate specimens was measured after hot-pressing for 20, 80 and 320 min at 1300° C and 22.4 MN m^{-2}. Measurements were taken from scanning electron micrographs of fracture surfaces. The small grain size and high porosity made conventional polishing and optical microscopy difficult. The grain diameter after 20, 80 and 320 min was 0.7, 1.4 and 2 μm respectively. The increase in grain diameter fitted a cubic growth law.

The fraction of closed porosity was measured in high density pellets. The pellets were weighed in air and methanol. The methanol was introduced by vacuum impregnation. It was found that pellets pressed to 93% and 89% density contained 4.0% and 2.4% closed porosity respectively. The creep rate of compacts over 90% dense is dependent to a large extent on the reduction in volume of closed porosity. The present paper considers mainly the open porosity which exists at lower densities.

4. Theory

The contribution of diffusional flow and dislocation creep to hot-pressing depends on grain size and stress. If the magnesium oxide deforms in a manner similar to Herring-Nabarro creep [12] then the observed creep rate ϵ_{NH} varies linearly with stress and is given by:

$$\left(\frac{T\epsilon_{\mathrm{NH}}}{D_{\mathrm{L}}}\right) = 10\,\frac{\mu\Omega}{kd^2}\left(\frac{\sigma}{\mu}\right) \tag{1}$$

where σ is the effective stress at contacts, D_{L} is the lattice diffusion coefficient, Ω is the atomic volume, μ is the shear modulus, T is the absolute temperature and k is Boltzmann's constant. If the oxide deforms by a dislocation creep process, the creep rate varied as the cube of stress and is given by [13]:

$$\left(\frac{\dot{\epsilon}_{\mathrm{dis}}T}{D_{\mathrm{L}}}\right) = 2.6 \times 10^4 \left(\frac{\sigma}{\mu}\right)^3 \cdot \tag{2}$$

The creep rates obtained from Equations 1 and 2 are plotted in Fig. 3. It is seen that for an apparent stress in the range 1.5 to 22 MN m^{-2} and a grain size of less than 2 μm, the deformation mechanism is likely to be diffusional flow, provided that the stress multiplication factors are not too large.

The rate of change of density during sintering has been calculated for relaxed surfaces satisfying the surface tension restraints [8]. The sintering rate for a volume diffusion mechanism is

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\rho}{\rho_{\mathrm{d}}}\right) = 14\,\frac{D_{\mathrm{L}}\Omega}{d^2kT}\left(\frac{K\gamma + L\sin\theta\gamma + \sigma\phi}{A}\right) \tag{3}$$

where ρ is the density ρ_{d} the value when fully dense, t is time, D_{L} the volume diffusion coefficient, γ the surface tension, Ω the atomic volume, d the grain diameter, K the porosity curvature, L/A the ratio of periphery to area of grain boundary contacts, θ the dihedral angle, k Boltzmann's constant and T is the absolute temperature. The effect of hydrostatic stress on

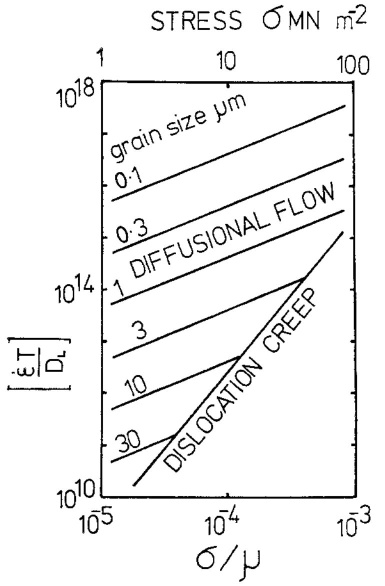

Figure 3 The expected deformation rates and mechanisms for magnesium oxide.

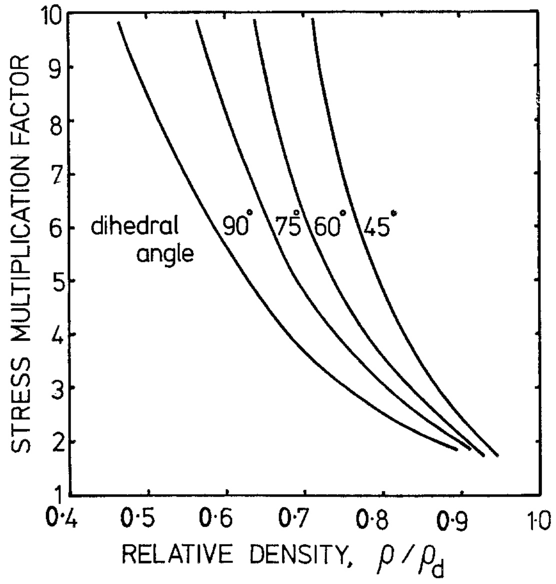

Figure 4 The stress multiplication factor, ϕ, versus density for dihedral angles ranging from 45° to 90°.

the sintering rate can be incorporated by including a term for the compressive stress on the boundaries. If σ is the applied stress on the specimen, then $\sigma\phi$ is the stress on the boundary where ϕ is the stress multiplication factor at the grain contacts. Values of the stress multiplication factor are given for relaxed surfaces in Fig. 4 [8]. The values are equal to the ratio of the grain-boundary area, including that area removed by porosity, to the actual boundary area.

Equation 3 is identical to the Herring-Nabarro creep rate with the exception of the constant and the surface tension forces. Exact equivalence is not expected since during NH creep,vacancy flow is between grain boundaries with no change in volume. During hot-pressing, the diffusion path is shorter for a given grain size.

The observed values of the constant in the Herring-Nabarro creep rate may be up to one order of magnitude higher than the theoretical value. Ashby [14] has proposed that the enhanced creep rates can result from grain-boundary sliding. Grains do not elongate during deformation, but slip past each other and maintain an equi-axed structure. The equi-axed structure has been observed after large strains in MgO [15]. The diffusion path for a sliding mechanism is reduced and rates may be an order of magnitude faster. During the diffusion creep of fully dense materials, the requirement of maintaining contact at triple points severely restricts the ease with which grains can slide past each other. In porous materials this restriction is relaxed. The stress system during hot-pressing is not truly hydrostatic and it is to be expected that significant sliding occurs. Indeed without sliding some evidence of slight grain elongation would be expected in the present experiments, since the powder was only 15% dense when the load was first applied.

5. Comparison of theoretical and experimental results

5.1. The effect of stress

The creep rate, $\dot{\epsilon}$, is related to the hot-pressing rate $\dot{\rho}/\rho d$ by the relationship $\dot{\epsilon} = (\dot{\rho}/\rho d)/(\rho/\rho d)$. The stress drop tests (Fig. 2) showed that the observed creep rate was linearly proportional to stress. As the stress was reduced at a constant density, the rate tended to approach zero as the stress tended to zero. Hence it is concluded that in the present tests, the terms $K\gamma + L\gamma \sin\theta/A$, in Equation 3, do not contribute significantly to the rates. This is to be expected, since the surface tension forces are much smaller than the applied forces during hot-pressing. Sintering results from the sole action of the surface tension forces and to observe rates during the intermediate stage of sintering, experiments are performed at higher temperatures than hot-pressing. The terms are included in the present analysis for completeness.

5.2. The reduction of pressing rate with densification

During hot-pressing, the observed rate decreased rapidly with densification. This behaviour is analysed according to Equation 3. Fig. 5 shows the grain-size compensated hot-pressing rate versus stress multiplication for MgO hot-pressed at 22.4 MN m^{-2} and 1280° C. The grain size was calculated by interpolating between the measured values.

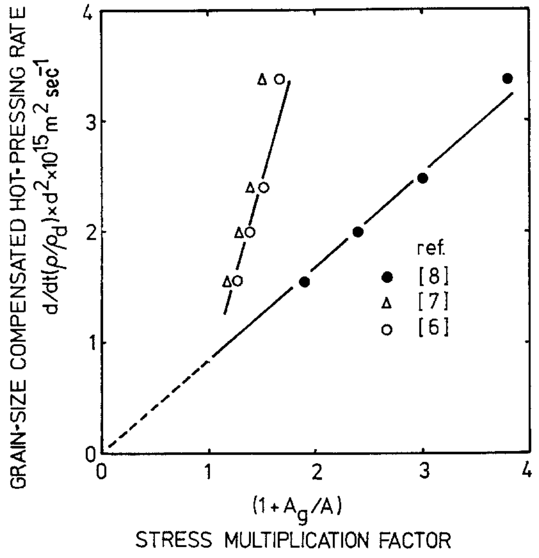

Figure 5 The grain-size compensated hot-pressing rate versus stress multiplication factor for magnesium oxide at 2180°C, 22.3 MN m^{-2}.

When the hot-pressing rate is linearly proportional to stress, doubling the stress multiplication factor from say 2 to 4 should also double the hot-pressing rate. Although the stress multiplication factor is always greater than unity, it follows that the data should extrapolate through the origin, i.e. stress multiplication factor zero, hot-pressing rate zero.

The hot-pressing rate is not expected to be zero when the stress multiplication factor tends to unity, i.e. zero pore size. This is because the equation is relevant for open porosity (density less than 90%) and the area of flux is dependent more on the grain-boundary area than the pore area. At high densities when closed porosity forms the converse is true, and neglecting surface tension forces, the closure rate tends to zero. All the present comparisons are in the region of open porosity.

The slope of the data in Fig. 5 is equal to $14\Omega D_L\sigma/KT$ and the lattice diffusion coefficient is 9×10^{-17} m^2 sec^{-1}. If the best line is drawn through the points and Fig. 5 plotted according to McClelland [6] and Spriggs [7], the diffusion coefficient is $\sim 3 \times 10^{-16}$ m^2 sec^{-1}. During densification the increasing grain size and decreasing stress multiplication factor combined to decrease the hot-pressing rate.

5.3. The activation energy

The activation energy obtained by rapidly changing the temperature at constant load and nearly constant density was $\sim 4.9 \times 10^5$ J mol^{-1} for densities in excess of 75%. This activation energy should correspond to the activation energy for lattice diffusion, since from Equation 3 for an instantaneous change in temperature, the hot-pressing rate varies as D_L/T. The activation energies for anion and cation diffusion in MgO [16, 17] are 2.6×10^5 J mol^{-1} and 3.3×10^5 J mol^{-1} respectively. Hensler and Cullen [15] have pointed out, however, that these values probably refer to extrinsic diffusion. In purer materials the activation energy will be higher and nearer the intrinsic value. Cummerow [18] measured an activation energy of 6.7×10^5 J mol^{-1} for the creep of pure MgO single crystals.

The variation of hot-pressing rate with temperature is also illustrated in Fig. 6. The graph is constructed by comparing the rate at six densities for three separate tests at 1180, 1280 and 1380° C and all at an apparent stress of 22.4 MN m^{-2}. The apparent activation energy for sintering varies between 2.4×10^5 J mol^{-1} and 6.6×10^5 J mol^{-1}. This activation energy does not correspond to the lattice diffusion coefficient if the temperature dependence for grain growth is different from that for lattice diffusion. Since this is quite likely, when compacts pressed at different temperatures attain a given density, the stress multiplication factors may be identical but the grain sizes differ. Consequently, the difference in rates is not solely due to the temperature difference.

The lattice diffusion coefficient calculated in this work is compared in Fig. 7 with values obtained by other authors. The data from hot-pressing and diffusion creep agree fairly well and are near the values obtained for Mg ion diffusion. The error bars arise mainly from uncertainty

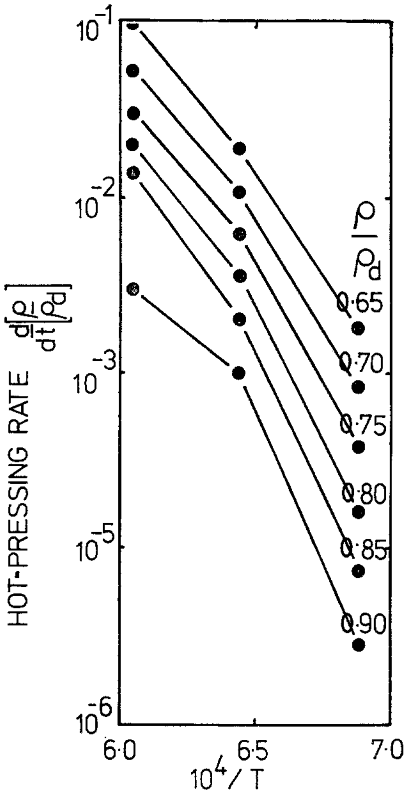

Figure 6 The variation of hot-pressing rate with temperature.

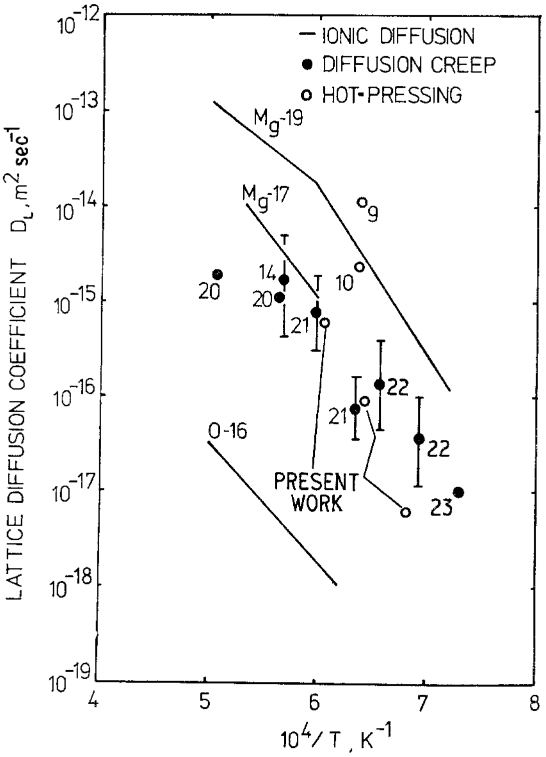

Figure 7 Diffusion coefficients for magnesium oxide measured by radio tracer, diffusion-creep and hot-pressing techniques.

in the grain sizes. The diffusion coefficients due to Vasilos and Spriggs [10] and Ramakrishnan [9] for hot-pressing, were calculated by re-interpreting their data according to the present theory. The difference in diffusion coefficients arises solely from the difference in hot-pressing rates, the temperature and stresses being almost identical. Vasilos and Spriggs [10] used reagent grade magnesium oxide whereas this study used Analar powder. The difference in impurity content may account for the difference in diffusion coefficients.

The activation energy for volume diffusion was measured by changing the temperature during hot-pressing. The temperature took about 5 min to increase by 100°C and stabilize sufficiently to continue dilatometry. During the period of temperature change the specimen densified, thus reducing the hot-pressing rate below that of a truly instantaneous temperature change. The magnitude of this effect can be calculated by considering the empirical form of the density/time data. From Fig. 1 the density increases with time according to the relationship

$$\frac{\rho}{\rho_d} = \alpha_0 + \alpha_1 \ln \alpha_2 t \qquad (9)$$

where α_0, α_1 and α_2 are constants. Differentiating Equation 9 the rate of hot-pressing is

$$\frac{\dot{\rho}}{\rho_d} = \frac{\alpha_1}{t} \qquad (10)$$

putting $\dot{\rho}/\rho_d = \dot{\epsilon}$ and differentiating Equation 10 with respect to the strain

$$\frac{d\dot{\epsilon}}{d\epsilon} = \frac{-\alpha_1}{t^2}\frac{dt}{d\epsilon}\,. \qquad (11)$$

Putting $d\epsilon/dt = \dot{\epsilon}$ and substituting for t from Equation 10

$$\frac{d\dot{\epsilon}}{\dot{\epsilon}} = -\frac{d\epsilon}{\alpha_1}\,. \qquad (12)$$

If $d\epsilon$ is the strain during the temperature change, then $d\dot{\epsilon}/\dot{\epsilon}$ is the fractional change in the hot-pressing rate. During temperature changes, stresses were chosen to give relatively small creep rates, say about 10^{-4} min^{-1}.

If readings are recommenced after 5 min the strain is 5×10^{-4}. For a process having an activation energy 5×10^5 J mol^{-1}, increasing the temperature from 1300 to 1400° C increases the rate by a factor of ten. The maximum possible strain ($d\epsilon$) during heating is then 5×10^{-3}. From Fig. 1 the gradient α, on a semi-log plot is $-0.1/2.3$. Substituting for α_1, and $d\epsilon$ in Equation 12 the fraction change in the strain rate $\Delta\dot{\epsilon}/\dot{\epsilon}$ is equal to 0.1. Since the change in strain rate due to the temperature rise is about 10 this effect is two orders of magnitude smaller.

6. Conclusions

Magnesium oxide powder hot-pressed in an argon atmosphere was densified by a vacancy diffusion mechanism. The rate of hot-pressing was linearly proportional to the stress and the rate at which the hot-pressing rate decreased as densification proceeded could be accounted for by the increase in the diffusional path resulting from grain growth. The area of contacts between grains also increased, decreasing the effective stress on the boundary. Grain size was considered to increase as a function of time and the stress multiplication factor at grain contacts was considered to be a function of density. The data fitted a volume diffusion mechanism and gave a diffusion coefficient of $D_L = 0.3 \exp(-4.9 \times 10^5/RT)$ m^2 sec^{-1} where R is in J mol^{-1} K^{-1}.

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References

1. J. K. MACKENZIE and R. SHUTTLEWORTH, *Proc. Phys. Soc.* **62** (B) (1949) 833.
2. R. L. COBLE, *J. Appl. Phys.* **41** (1970) 4798.
3. G. C. KUCZYNSKI, *Trans. Met. Soc. AIME* **185** (1969) 169.
4. W. D. KINGERY and M. BERG, *J. Appl. Phys.* **26** (1955) 1205.
5. D. L. JOHNSON, *J. Amer. Ceram. Soc.* **53** (1970) 574.
6. J. D. MCCLELLAND, *ibid* **44** (1964) 47.
7. R. M. SPRIGGS and T. VASILOS, *ibid* **47** (1964) 47.
8. W. BEERE, *Acta Met.* **23** (1975) 131, 139.
9. P. RAMAKRISHNAN, private communication.
10. T. VASILOS and R. M. SPRIGGS, *J. Amer. Ceram. Soc.* **46** (1963) 493.
11. J. RAZINGER and G. M. FRYER, *J. Brit. Ceram. Soc.* **71** (1972) 223.
12. D. L. JOHNSON, *Scripta Met.* **3** (1969) 567.
13. W. R. CANNON and O. D. SHERBY, *J. Amer. Ceram. Soc.* **56** (1973) 157.
14. M. F. ASHBY and R. A. VERRALL, *Acta Met.* **21** (1973) 149.
15. J. H. HENSLER and G. V. CULLEN, *J. Amer. Ceram. Soc.* **50** (1967) 584.
16. E. Y. OISHI and W. D. KINGERY, *J. Chem. Phys.* **33** (1960) 905.
17. R. LINDNER and G. D. PARFITT, *ibid* **26** (1957) 182.
18. R. L. CUMMEROW, *J. Appl. Phys.* **34** (1963) 1724.
19. B. C. HARDING, D. M. PRICE and A. J. MORTLOCK, *Phil. Mag.* **23** (1971) 399.
20. E. PASSMORE, R. H. DUFF and T. VASILOS, *J. Amer. Ceram. Soc.* **49** (1966) 594.
21. G. W. TERWILLIGER, H. K. BOWEN and R. S. GORDON, *ibid* **53** (1970) 241.
22. T. VASILOS, J. B. MICHEL and R. M. SPRIGGS, *ibid* **47** (1964) 203.
23. J. F. WYANT, *ibid* **34** (1951) 374.

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