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REVIEW OF DIFFUSIONAL CREEP OF Al_2O_3

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ABSTRACT

The diffusional creep mechanisms are reviewed including the extensions of the theories for application to ceramic materials. The creep data for Al_2O_3 are critically analysed to show the relative conditions where normal and dislocation controlled diffusional creep are important. The behavior at intermediate stresses, when both slip and diffusional creep occur is also discussed.

INTRODUCTION

Although the basic diffusional creep theories are nearly twenty five years old, until rather recently their greatest applicability has been to sintering and in allowing measurements of surface tension by zero creep method. The diffusional creep mechanisms have been interesting theoretically because they can be derived with a high degree of rigor since arbitrary assumptions regarding the deformation structure are minimal; as a result explicit expressions for the creep rate exist which have no disposable parameters and so are susceptible to qualitative experimental confirmation. More recently, it has been realized that diffusional creep may be the dominant mechanism for many long time applications, and is not simply limited to very low stresses at temperatures near the melting point. Recent studies, as reviewed by Jones (1969), Bird et al (1969), and Burton and Greenwood (1970), have shown quantitative agreement between theory and experimental creep and diffusion data for metals.

In the case of ceramics, it has become widely accepted that diffusional creep is an important deformation mechanism. This view has resulted from a realization of the relative difficulty

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of slip on secondary systems in many ceramics and from the accumulation of considerable steady state creep data, for many oxides and other ceramics, which at least qualitatively conform to diffusional creep kinetics, e.g. Coble (1965), and Passmore and Vasilos (1968). However, detailed analysis of the data has often indicated considerable disagreement among the results of various investigators and with the predictions from self diffusion data. These discrepancies, result in part from the possibility of multiple diffusion paths along boundaries and dislocations, as well as through the lattice, and, in addition to the extreme sensitivity of the diffusion coefficients to impurities and stoichiometry variations. These conditions often make it difficult to be certain whether the cation or anion will be the slower and so rate controlling. Consequently, plausible explanations are available for many disparities, but the results and inferences from them have been viewed with considerable skepticism.

This paper will review the basic physical processes involved in diffusional creep and the resultant kinetic equations. The creep data for Al_2O_3 will then be analysed in detail to indicate the range of stress; temperature and grain size over which diffusional creep is important and, further, to indicate values of the controlling diffusivities. Consideration will also be given to the causes for failure to satisfy certain of the kinetic predictions, particularly proportionality between stress and strain rate.

THEORY

The initial considerations of diffusional creep were for single component materials and so the theories were most directly applicable to pure metals. However, the extension to ceramics (or alloys) is often straight forward requiring only a determination of the effective diffusivity, except where there is a shift away from diffusion as the rate limiting step.

Basic Mechanism

Upon application of a normal stress on a surface of a body, such as a grain in a polycrystal, for which the surfaces can act as perfect sources or sinks of point defects, the chemical potential of the atoms and of the point defects will be altered by the external work which is done when an atom moves from a normal lattice position to create a vacancy or an interstitial. This will result in an alteration of point defect concentrations which will depend upon the sign and magnitude of the normal stress. For a single component material the vacancy concentration will be raised at a surface with a normal tensile stress by the amount

$$\Delta C = C_o \frac{\sigma_n \Omega}{kT} \quad (1)$$

for the case where

$$\frac{\sigma_n \Omega}{kT} < 1 \quad (2)$$

where C_o is the stress free equilibrium concentration of vacancies, σ_n is the normal stress, Ω the atomic volume and kT is Boltzmann's constant times the temperature. Non-linear terms will become important if the condition on $\sigma_n \Omega / kT$ is not satisfied. The result, as shown in Figure 1, is that under any non-hydrostatic stress the vacancy concentrations on orthogonal faces will be different. This will eventually cause a steady state concentration gradient between the orthogonal surfaces and a steady state mass flux from surfaces under normal compression to those under normal tension. If the dominant defects are interstitials rather than vacancies the result is similar except that the interstitial concentration gradient is opposite in sign to that for vacancies.

There will be an initial transient of decreasing strain rate during which the concentration gradient drops from a very high value near the surfaces to the steady state value. This period will also be accompanied by a redistribution of the stress which will drop to zero in the region of the grain corners and increase to a maximum at the centers of the grain faces so that the concentration gradients are nearly uniform along each surface. The exact stress distribution will be determined by the compatibility requirement that coherency is maintained across the grain boundaries, unless cracking is occurring. This transient has been analyzed, considering only lattice diffusion, by Lifshitz and Shikin (1965) and shown to be dominated by the diffusional transients if the body is effectively elastically rigid. For this case the longest relaxation time, τ , will be

$$\tau = \frac{d^2}{KD_d} \quad (3)$$

where d is the grain size, and D_d the defect diffusivity, and K is a geometric constant. If elastic strains are important, as indicated by the condition

$$\lambda = \frac{\Omega C_o E}{kT} \ll 1 \quad (4)$$

where E is the elastic modulus, then the stress redistribution will

Figure 1 Defect concentration gradients expected at short times (left) and at steady state (right) in a body with an applied shear stress as shown.

Figure 2 Idealization of diffusional creep as a grain boundary sliding problem showing the mutual requirements for sliding along boundaries and diffusional transport of mass between orthogonal boundaries. The dotted lines denote the direction of mass transport.

be much slower with the longest relaxation time given by

$$\tau_E = \frac{\tau}{\lambda} \quad (5)$$

Analysis of the creep transient in MgO by Gordon and Terwilliger (1972) indicates that the elastic strains are important in the relaxation. Even for this slower case the transient strain is only a few times the elastic strain and so is very much smaller than typically found in dislocation creep. Upon removal of the stress much of this transient strain will be recovered with a similar relaxation time, as observed by Beauchamp, et al (1962) and Chang (1966) for Al_2O_3 and BeO. For a constant strain rate application, the transient will be manifested by a gradual increase in stress to the steady state value.

In principal, the mass transport can occur by diffusion through the lattice, controlled by D_l , and also by diffusion along the grain boundary, in a region of width δ where the diffusivity is enhanced to a value of D_b . The diffusion through the grains and along the boundaries can occur independently of each other within the restriction that the local stress and total flux will be such as to preserve coherency at the boundaries. Raj and Ashby (1971) have shown that even in cases where lattice diffusion dominates the steady state creep, boundary diffusion will be important during the transient in relaxing the initially high stresses or fluxes at grain corners or ledges.

The steady state problem of grain elongation by diffusion has been analyzed by Nabarro (1948), Herring (1950), and Lifshitz (1963), and others for the case of lattice diffusion control and by Coble (1963) and others for the case of dominance by grain boundary diffusion. For polycrystalline bodies the results are all found to be of the form

$$\dot{\epsilon} = \frac{14\sigma\Omega D_l}{kTd^2} + \frac{14\pi\sigma\Omega\delta D_b}{kTd^3} \quad (6)$$

except for thin foils, Gibbs (1966), or wires, Herring (1950), where the grain size is larger than the thickness. The numerical constants vary slightly depending upon the assumed grain shape, but for approximately equiaxed grains the results are rather insensitive to the details of the assumption; the values given are for σ and $\dot{\epsilon}$ as tensile stress and strain rate, respectively.

Herring (1950) recognized that the stress redistribution would be affected if grain boundary sliding can allow relaxation of all shear stresses in the plane of the boundary and that this would result in an increase in the strain rate by a factor of 5/2. However, it was subsequently shown by Lifshitz (1963) and by Gibbs (1965) that grain boundary sliding is actually required to maintain compatibility at all the grain boundaries. This comes from the need

for grains to shift their relative positions with respect to each other as they elongate; it is accomplished by concurrent sliding along some boundaries while mass is added to or removed from other boundaries by diffusion.

It has more recently been shown, particularly by Raj and Ashby (1971) and Stevens (1972), that this dual process can be alternatively reviewed as grain boundary sliding with diffusional accommodation. For boundary sliding to occur it must be accommodated by deformation of the grains, particularly at triple points, ledges, or other points of constraint. This accommodation can occur by diffusion instead of by slip as suggested by Gifkins et al (1966, 1968). This can be visualized in Figure 2a where the problem is idealized to show sliding along the horizontal grain faces which is accommodated by removal or addition of mass to the vertical boundaries by diffusion. Ashby et al (1970) further refined the analysis and showed, as suggested in Figure 2b, that the rate of sliding will be limited by diffusion between the highest steps, which generally are further apart. For an equiaxed polycrystal the limiting obstacles are the neighboring grains. A calculation, Raj and Ashby (1971), of the creep rate, based on diffusion limited boundary sliding for equiaxed grains, gives the same results as calculated from grain elongation, Eqn. (6). In fact, these are simply alternative descriptions of the same process. Both considerations, however require that the atomic resistance to sliding is relatively easy so that the diffusive transport is the rate limiting step.

An analysis by Green (1970) shows quantitatively that a gradual effective hardening may occur as deformation proceeds, resulting in elongated grains and an increase in the diffusion distances. This elongation may, of course, not be obtained in practice since grain boundary migration will tend to maintain an equiaxed grain shape. It has also been shown by Ashby and Verrall (1973) and W. R. Cannon and Nix (1973) that if significant rearrangement of the grains occurs as a result of grain boundary sliding the total strain will be appreciably higher than that calculated in Eq. (6). This would result from grains changing their neighbors causing an increase in the number of grains along the tensile direction in the body. A calculation by Ashby and Verrall (1973), based upon a particular model of grain rearrangement by sliding, and with the necessary accommodation by diffusion, gave a strain rate expression similar to Eqn. (6) but with the coefficient higher by a factor of about 7. However, if significant grain rearrangement does not occur, W. R. Cannon (1972) has shown that Eqn. (6) is correct and does not need to be modified to account for the strain resulting from the required sliding accommodation. At the low strains typically achieved in the testing of ceramics Eqn. (6) probably provides the best estimate of the creep rate. At high strains modifications from the opposing effects of grain elongation and grain rearrangement may be important.

Concurrent grain growth under load will give rise to an

effective hardening as the diffusion distances increase. Terwilliger, Bowen, and Gordon (1970) and Tigai and Zisner (1968) have shown that this effect can be very important in pure MgO, and that it can be quantitatively assessed in some cases. Contrary to the results of Terwilliger et al (1971), Cannon and Rhodes (1971) found that the grain growth in Al_2O_3 can be strain enhanced so that the application of the results of stress free grain growth studies may not provide a satisfactory prediction of the effective hardening.

To summarize, diffusional creep will occur by a flux of point defects and the creep rate will be as given by Eqn. (6) provided that:

- a) the grain boundaries are the principle sources and sinks for defects, and
- b) they are sufficiently good sources that the defect concentrations at the boundaries are at the equilibrium value for the local stress and temperature, and
- c) the boundary sliding necessary to satisfy compatibility occurs easily.

If either of the latter two conditions are not satisfied then the creep rate will be slower than predicted by Eqn. (6), a condition often referred to as interface control. Ashby (1969), Burton (1972), and Ashby and Verrall (1973) have derived simple models to account for a significant chemical potential drop at the boundaries to create point defects. These models generally predict non-linear stress-strain rate behavior which in some cases may involve an effective threshold stress, or Bingham type behavior. Qualitatively similar behavior has been reported in ceramics by Heuer et al (1969) and R. M. Cannon et al (1975) for fine grained Al_2O_3 , by Crouch (1972) for Fe_2O_3 , by Burton and Reynolds (1973) for UO_2 , by Seltzer and Talty (1974) for ZrO_2 , and by Passmore et al (1966) for fine grained MgO. There is also considerable similar behavior in the superplastic metals and for fine grained metals with fine, refractory particles at the grain boundaries. Particularly for the ceramics the data indicate that at moderate stresses the behavior approaches a linear stress-strain rate relation, if slip does not intervene; but at low stresses the strain rate is lower than predicted causing a range of non-linear stress dependence. There are still sufficient unexplained features that the problem cannot yet be regarded as well understood.

Edge dislocations can also act as sources and sinks for point defects, and so diffusion between orthogonal sets of edge dislocations can lead to climb of the dislocations giving a macroscopic strain. However, for steady state diffusional creep to occur the dislocations can not simply climb out of the crystal, but must be regenerated. Nabarro (1967) analyzed this problem assuming that the dislocations were arrayed in a stable Frank network, with the free segments climbing as Bardeen-Herring (1951) sources to give continuous dislocation multiplication. The resultant strain rate is non-linear in stress since the network size becomes finer with

increasing stress. Nabarro's result for tensile stress and strain rate is:

$$\dot{\epsilon} = \frac{\Omega}{2\pi b^2 \ln \frac{4G}{\pi\sigma}} \frac{\sigma^3 D_l}{G^2 kT} \left[1 + \frac{4}{3} \frac{D_c}{D_l} \left(\frac{\sigma}{G} \right)^2 \right] \quad (7)$$

where G is shear modulus, b the Burgers vector and D_c is the core diffusion coefficient which is assumed to be effective in a radius b around the dislocation; the term $\ln \frac{4G}{\pi\sigma}$ is about 10 for most cases. The contribution from enhanced pipe diffusion along dislocations normally would be more important at lower temperatures. Groves and Kelly (1969) have shown that deformation of a polycrystal by this mechanism will require 6 independent slip systems so that climb will be required by dislocations on secondary as well as primary systems.

An alternative expression for the climb rate has been derived by Weertman (1968) and by Nix et al (1971). Using this, Weertman then obtained the following expression:

$$\dot{\epsilon} = \frac{\pi \beta^2 \Omega}{20b^2} \frac{\sigma^3 D_l}{G^2 kT} \quad (8)$$

for control by lattice diffusion, where β is the coefficient in the Taylor relation

$$\rho = \left(\frac{\beta \sigma}{bG} \right)^2 \quad (9)$$

which was assumed to describe the stress dependence of the dislocation density, ρ . Weertman assumed the β values typically found from creep tests of metals deforming by climb and glide were applicable since in both cases the internal stress fields of the dislocations are an appreciable fraction of the applied stress. Bird et al (1969) show that β is about unity. For many studies Weertman's equation gives a strain rate an order of magnitude faster than Nabarro's. If the dislocation density is independent of stress, then a linear stress dependence might result, but deviations would be expected at low stresses which are insufficient to activate the Bardeen-Herring sources.

Because of the high strain rate sensitivity, diffusional creep will generally only be important at low stresses where slip becomes relatively slower. However, since it can provide isotropic deformation it can be particularly important in strongly anisotropic materials such as non-cubic ceramics and metals. In these materials, at stresses between the primary and secondary flow stresses, diffusion can provide strain components not achievable by slip on primary slip systems, and so can provide essential satisfaction

of the von Mises condition. For these intermediate stresses, slip will occur in favorably orientated grains in which the critical shear stress is reached on the easy slip planes. The creep rate will still be controlled by the diffusional creep since it will be the slower process compared to primary slip. Although the strain rate will be slightly faster than predicted by the diffusional creep equations, (6) or (7), the functional dependencies will be approximately as predicted. At coarser grain sizes where the Nabarro climb mechanism will be the more important of the diffusional modes, climb will be required on these secondary dislocations under conditions for which they do not glide.

Diffusional mass transport can also contribute to crack growth (or shrinkage, i.e. sintering) under stress. The slow growth of small pores on grain boundaries under a normal tensile stress has been well documented for metals as well as ceramics. Small cracks or pores at grain boundaries which develop from grain boundary sliding or from failure to satisfy the von Mises criterion, can grow by diffusion at boundaries where there is a higher vacancy concentration, Eqn. (1), due to the normal tensile stress.

When the void fraction becomes sufficiently high, the diffusion required to accommodate grain boundary sliding is considerably reduced and much higher strain rates result. Therefore, highly porous bodies or bodies undergoing significant cracking, generally show only approximate agreement with the theoretical constitutive relations and may exhibit much higher creep rates. Since the early analyses of pore growth by diffusion of Balluffi and Seigle (1957) and Hull and Rimmer (1959) there have been many extensions and refinements as discussed recently by Weertman (1974).

Modifications for Ceramics

For ceramics both the cations and anions must diffuse and at steady state the total fluxes of the two components must be in the stoichiometric ratio. Since the diffusivities of the two components will generally be significantly different, initially there will be a greater flux of the faster species. This will cause a slight charge separation which produces an internal electric field which will enhance the slower species and retard the faster one. At steady state the flux of defects on each sublattice will be given by expressions of the form

$$j_i = - \frac{D_d^i}{\Omega_i kT} (\Delta C_i + q_i C_i \nabla \phi) \quad (10)$$

where q_i is the effective charge on the i^{th} defect, $-\nabla \phi$ is the

Nernst field and D_d^i is the defect diffusivity. For transport in the compound $A_\alpha O_\beta$ the steady state requirement is that at the defect sources both species must be accumulated at the stoichiometric ratio. This requires that at boundaries:

$$\frac{(j_l^a)_b - \delta \nabla \cdot j_b^a}{(j_l^o)_b - \delta \nabla \cdot j_b^o} = \frac{\alpha}{\beta} \quad (11-a)$$

where $(j_l^i)_b$ is the normal lattice flux at the boundary, and j_b^i is the flux in the boundary; alternatively at dislocations:

$$\frac{\int j_l^a \cdot \bar{r}_c d\theta - \pi r_c^2 \nabla \cdot j_c^a}{\int j_l^o \cdot \bar{r}_c d\theta - \pi r_c^2 \nabla \cdot j_c^o} = \frac{\alpha}{\beta} \quad (11-b)$$

where j_c^i is the flux along the dislocation with core radius r_c . These requirements specify $\nabla \phi$. Solutions for several different creep, sintering, or surface diffusion problems have been given by Ruoff (1965), Readey (1966), Lifshitz et al (1965, 1967), Blakely and Li (1966), Reijnen (1970), Gordon (1973) and Fryer (1972). The exact solutions have been for cases assuming the same diffusion path for both species. They indicate that the previously presented expressions for diffusional creep are correct with the following substitutions:

$$D_{eff} = \frac{(\alpha + \beta) D_e^a D_e^o}{\beta D_e^a + \alpha D_e^o} = \frac{D_e^a D_e^o}{x_O D_e^a + x_A D_e^o} \quad (12)$$

and

$$\Omega = \frac{\Omega_c}{\alpha + \beta} \quad (13)$$

where Ω_c is the volume of the molecule $A_\alpha O_\beta$. For boundary defect sources;

$$D_e^i = D_l^i + \frac{\pi \delta D_b^i}{d} \quad (14)$$

and for climb controlled diffusional creep:

$$D_e^i = D_l^i + \frac{4}{3} \left(\frac{\sigma}{G} \right)^2 D_c^i \quad (15)$$

When the two ions diffuse by different paths, the solutions have only been approximate, Gordon (1973), but they appear to be reasonable. Blakely and Li (1966) have shown, however, that where volume diffusion is only important near the surfaces or boundaries, the lattice diffusivities will be significantly changed by the space charge cloud.

It can be seen that the creep rate will be controlled by the slower diffusing species along its fastest path.¹ These relations hold whether the diffusivities are extrinsic or intrinsic as long as the slow species is properly identified.² Consequently, aleovalent impurities which alter the diffusivity of the slow species will similarly affect the diffusional creep rate.

Very significant effects on the creep rates can be achieved by atmosphere changes which alter the stoichiometry of the base material or alter important impurities. This has been demonstrated for MgO and Al₂O₃ by Terwilliger et al (1970), and Hollenberg and Gordon (1973), for transition metal oxides and UO₂ as reviewed by Clauer et al (1971) and Seltzer et al (1971), and shown by Crouch (1972) for Fe₂O₃. Processes such as precipitation or defect association which alter the self diffusion coefficient will also influence the creep rate. However, uncharged defects or complexes which contribute to self diffusion, but not to electrical conduction will likely not contribute to creep.

At steady state there is constant charge separation to provide the required Nernst field. When diffusion occurs on alternative paths for the two ions, further charge separation does not develop since the flux accumulation everywhere on the boundaries will be such as to satisfy the neutrality (stoichiometry) condition given by Eqn. (11) as well as the strain compatibility requirements. Lifshitz et al (1965, 1967) have shown that the required charge separation results from modifications of the space charge cloud and surface charge normally at each source; for most low stress cases this will require only very small changes of the zero stress values of the surface charge and space charge. In solving a similar problem Charles (1969) has shown that the steady values of the charge separation and of the field develop rapidly from

1

It is seen that for A as the slow species the usual practice of using $D \rightarrow D_e^a$ and $\Omega \rightarrow \Omega_a = \Omega_c/\alpha$ properly accounts for the ambipolar coupling.

2 Pasco and Hay (1973) have erroneously concluded that the extrinsic diffusivity may not be the proper value; this resulted from neglecting the ambipolar coupling field which acts on all of the extrinsic defects even though the concentration gradient given by equation (1) is correct only for C_o taken as the thermal defects in excess of those required to compensate impurities.

movement of the fast species with a relaxation time given by:

$$\tau_a = \frac{L^2}{D_d^f} \quad (16)$$

where L is the Debye distance, typically of the order of 10^{-6} - 10^{-5} cm for ceramics and D_d^f is the defect diffusivity of the fast species; a similar result can be inferred for the present problem. Comparison with Eqn. (3) and (5) shows that the ambipolar coupling will develop rapidly compared to the other transients. Redistribution of impurities in the electric and stress fields will be much slower, however.

Although these derivations have been for ionic conductors, they are also applicable to ceramics which are electronic conductors, since the same coupling field must be developed to obtain the required flux equality. Any mobile electronic defects present will move in response to the field. However, counter gradients in the concentrations of holes or electrons will develop so that the net flux in both electronic defects, which are also given by relations similar to Eqn. (10), will go to zero. This will require larger values of the local nonstoichiometry (charge separation) necessary to obtain the coupling field. For semiconductors (or alloys) in which the conductivity is so high that electric fields are non-existent, the same steady state solutions still apply, as shown by Herring (1950), but the coupling force becomes the counter gradient in chemical potential which develops from concentration gradients. The more nearly the compound or alloy approaches an ideal solution, the greater will be the local compositional deviations and the greater will be the transients, but the steady state solutions remain the same.

For Al_2O_3 it has been found, Paladino and Coble (1963), that:

$$D_l^o \ll D_l^a \quad \text{and} \quad (17)$$

$$\delta D_b^o \gg \delta D_b^a \quad (18)$$

and so for the normal boundary mode:

$$D_{eff} = \frac{5(D_l^a + \frac{\pi \delta D_b^a}{d}) \frac{\pi \delta D_b^o}{d}}{3(D_l^a + \frac{\pi \delta D_b^a}{d}) + 2 \frac{\pi \delta D_b^o}{d}} \quad (19)$$

The net result is shown by a schematic plot of steady state strain rate versus grain size in Figure 3; here several values of the ratio of the anion and cation boundary diffusivities have been assumed to illustrate the effect on the creep rate kinetics which will be observed. At fine grain sizes creep is controlled by cation boundary diffusion; for coarse grain sizes it is controlled by oxygen boundary diffusion, and at intermediate grain sizes by cation lattice diffusion. The oxygen lattice diffusion is sufficiently slow that it likely will never be limiting except for extremely large grain sizes where dislocation mechanisms would become dominant. It can be seen that a region of clear dominance by cation lattice diffusion will only be found if the oxygen boundary diffusion is sufficiently larger than the cation boundary diffusion. In this case the total range of strain rate necessary to experimentally observe all three ranges would not be achievable at a single temperature.

There is currently little theory or comprehensive data to indicate the effects of impurities on boundary diffusion in Al_2O_3 except when high diffusivity impurity phases are present in the boundaries. Although there is not yet complete agreement regarding the lattice defect chemistry of Al_2O_3 , Brook et al (1971) and Hollenberg and Gordon (1973) have shown that the assumption of Frenkel defects on the cation sub-lattice as the predominant defect provides the simplest explanation for impurity effects on ionic conduction and diffusional creep. The effect of impurities on the cation lattice diffusivity can be analyzed from the defect chemistry using this assumption. Neglecting defect complexes, divalent and trivalent cation impurities then lead to the following reactions:

and

and for extrinsic conditions charge neutrality requires for the two cases

$$[Al_i^{\bullet\bullet\bullet}] = \frac{1}{3}[M'_{Al}] \quad (22)$$

and

$$[V_{Al}^{\bullet\bullet\bullet}] = \frac{1}{3}[N^{\bullet}_{Al}] \quad (23)$$

that is, in both cases the defect concentration is increased proportionally to the impurity additions. Diffusion results from either cation interstitials or vacancies, depending upon which is

Figure 3 Schematic plot of strain rate versus grain size for Al_2O_3 , showing the effective grain size dependence to be expected for various values of P , the ratio of the boundary diffusivities $\delta D_b^0 / \delta D_b^a$. The dotted lines show the slopes of -2 and -3 expected for purely lattice or purely boundary control, respectively.

in excess and faster. For additions of fixed valence, such as MgO, at values below the solubility limit the defect content will be fixed and the activation energy for creep or diffusion will be that for defect mobility.

For additions above the solubility limit the equilibrium relations must also be satisfied which are:

$$\frac{[Al_i^{\bullet\bullet\bullet}] [M'_{Al}]^3}{[MO]^3} = \frac{\frac{1}{3} [M'_{Al}]^4}{[MO]^3} = e^{-\Delta G_1/kT} \quad (24)$$

giving

$$3[Al_i^{\bullet\bullet\bullet}] = [M'_{Al}] = (3)^{1/4} [MO]^{3/4} e^{-\Delta G_1/kT} \quad (25)$$

and for NO₂ additions

$$\frac{[V_{Al}^{\bullet\bullet\bullet}] [N_{Al}^{\bullet}]^3}{[NO_2]^3} = \frac{\frac{1}{3} [N_{Al}^{\bullet}]^4}{[NO_2]^3} = e^{-\Delta G_2/kT} \quad (26)$$

giving

$$3[V_{Al}^{\bullet\bullet\bullet}] = [N_{Al}^{\bullet}] = (3)^{1/4} [NO_2]^{3/4} e^{-\Delta G_2/kT} \quad (27)$$

where ΔG_1 and ΔG_2 are free energies of solution. For this case the activation energy for creep or diffusion will include both the energy of solution, ΔH_i , and of defect mobility, ΔH_m , i.e.

$$\Delta H = \Delta H_m + \Delta H_i \quad (28)$$

Similar reasoning indicates that oxygen lattice diffusion by a vacancy mechanism, will be increased by divalent impurities and reduced by tetravalent impurities.

CREEP OF Al₂O₃

Relation of Polycrystalline and Single Crystal Deformation

Aluminum oxide is extremely anisotropic and it has been amply demonstrated that slip on the basal system is much easier than on

the non-basal system. Figure 4 presents the flow stress versus temperature for the various slip systems from tests on single crystals. The stresses plotted are tensile yield tests on single crystals. The stresses plotted are tensile yield stresses for 60° crystals for basal slip $1/3 \langle 11\bar{2}0 \rangle (0001)$, for 90° crystals for prismatic slip, $1/3 \langle 1100 \rangle \{11\bar{2}0\}$, and for 0° crystals for pyramidal slip, $1/3 \langle 0111 \rangle$ on one or both of $\{1102\}$ or $\{1011\}$; these represent Schmid factors of 0.4 to 0.5. In all cases lower yield stresses are plotted except for the higher pyramidal values of Gooch and Groves (1973) which are flow stresses. Activation analyses of the single crystal yield behavior have not conclusively identified the barriers which control slip. However, it has been inferred that the lower yield stresses may be representative of the Peierls stress for the non-basal systems, Tresseler and Michael (1974) and Govorkov et al (1972), and for basal slip at lower temperatures, Conrad (1965). For temperatures above about 1600°C climb around obstacles may be limiting for basal slip, Conrad (1965) and Govorkov et al (1972). Then it is still uncertain whether there is an appreciable contribution to the apparent basal yield stress from forest interactions which would not be present in fine grained materials where annihilation at the boundaries prevents a significant increase in dislocation density. All of the data plotted are for nominally pure samples, the significant hardening from small alloying additions reported by Radford and Pratt (1970) is very likely from precipitates and so would not affect polycrystalline grains where the precipitates are typically at triple points. The basal and pyramidal flow stresses have strain rate sensitivities in the range $n = 4-7$ and so all the data in Figure 4 were taken for $\dot{\epsilon} = 4 \times 10^{-5} \text{sec}^{-1}$. The strain rate dependence for the prismatic yield stresses is quite small, Gooch and Groves (1973).

Steady state flow stresses for 1 and 13 μ polycrystalline material at the same strain rate are also plotted. For the 13 μ material and for 7 to 34 μ material, Folweiler (1961) demonstrated that the kinetics indicated diffusional creep for the entire range of stress investigated from considerably below to well above the basal yield stress. The stress exponents were typically $n = 1.1-1.2$ which is consistent with an increasing contribution of basal slip at higher stresses. The stress and grain size dependence reported by others, particularly W. R. Cannon (1971), confirm this same behavior for grain sizes up to at least 50 μ . The 1 μ material from Heuer et al (1969) and R. M. Cannon et al (1975) exhibited conformance to diffusional creep kinetics at the high stresses, with n decreasing to less than 1.1 as the stress increased up to the highest achievable values of nearly 50 ksi ($\sigma/G \approx 2 \times 10^{-3}$). At the lower stresses the strain rate became slower than for a linear dependence and stress exponents increased to $n \approx 2$ at the lowest strain rates achieved, indicating a shift to control by one of the interfacial processes. The few data points at stresses above 100,000 psi for polycrystalline materials were reported by

Figure 4 Flow stress versus temperature curves for the various slip systems in sapphire and for fine grained polycrystalline Al_2O_3 . The value of G was taken at 1500°C . The polycrystalline samples, ∇ , $\triangledown$, tested under hydrostatic constraint were at $\dot{\epsilon} = 10^{-6} \text{ s}^{-1}$.

Heuer et al (1970, 1971) and Snow (1972) from tests performed under very high hydrostatic constraints to eliminate cracking. The initial yield stresses are plotted and are seen to be in agreement with the extrapolated curves of pyramidal slip as would be required for slip on five independent systems.

Examination by transmission microscopy of polycrystalline Al_2O_3 after creep has been reported by Heuer et al (1969, 1970, 1971), Snow (1972), Becker (1971), and R. M. Cannon et al (1975). In all cases few dislocations were found within grains for samples where the flow stress conformed approximately to that predicted by Eqn. (6), even when the flow stress was above that for basal yield. There is however, evidence to indicate that slip, particularly on the basal system, does occur at stresses above the basal yield, but that the boundaries serve as the primary sources and sinks for dislocations and that there is little increase in the dislocation density during creep. Appreciable increases in dislocation density are apparent after several percent creep, in coarser grained materials, ($\sim 100\mu$), W. R. Cannon (1971), or in fine grained materials at stresses approaching the prismatic flow stress, Becker (1971). The hydrostatically constrained polycrystalline samples showed high dislocation densities with typical cold worked structures of dislocations in tangled arrays; both basal and pyramidal dislocations were present.

Fine Grained, MgO Doped Al_2O_3

Since the original work by Folweiler (1961), which demonstrated that deformation of fine grain Al_2O_3 was controlled by diffusional creep over a wide range of temperature and stress, there have been more than a dozen additional creep studies on Al_2O_3 most of which tended to confirm the original finding but raised questions as to the controlling diffusivity and path and the effects of impurities. All the results must be considered together to obtain a consistent view of the controlling species.

The spurious effects of unknown impurities can be suppressed by initially considering only those materials doped with MgO which will dominate the defect structure. The controlling diffusivity can be inferred by assuming one species and diffusion path to be dominant and calculating the apparent diffusivity from the stress-strain rate data using Eqn. (6). This has been done alternately assuming cation lattice control and then cation boundary control. The results are plotted in Figures 5 and 6 respectively for all of the available creep data on MgO doped Al_2O_3 with grain sizes below 70μ and densities over about 97% of theoretical. For these conditions the kinetics have been shown to have the nearly linear stress dependence and the strong grain size dependence required by the diffusion creep theories; the studies where this was not directly demonstrated have been under conditions where it would be expected.

Figure 5 Comparison of self-diffusion measurements and apparent lattice diffusivities calculated from creep tests of Al_2O_3 doped with MgO from the results of Folweiler (1961), Warshaw and Norton (1962), Coble and Guerard (1963), Stuart (1964), Dawihl and Klingler (1965), Hewson and Kingery (1967), Mocellin and Kingery (1971), W. R. Cannon (1971) and R. M. Cannon et al (1975), represent 1.2μ - $\circ$, Δ , 2.7μ - $\bullet$, and 15μ - $\square$ grain sized samples.

Figure 6 Comparison of apparent cation boundary diffusivities calculated from creep tests of Al_2O_3 doped with MgO and compared with boundary diffusivities inferred from sintering by Johnson and Berrin (1967) and from self-diffusion measurements by Mistler (1967). The + points represent the contribution of cation boundary diffusion to the creep rate of the 15μ samples obtained by subtracting the contribution from lattice diffusion calculated from the curve marked D_b^A in Figure 5.

The diffusivities for the 1μ material of R. M. Cannon et al (1975) were calculated from the high stress data where the behavior was indicated to be in the Newtonian, diffusion limited regime.

R. M. Cannon et al (1975) analysed their data, which covered 1-15 μ grain sizes, assuming both cation boundary and lattice diffusion to be important. The results indicated cation boundary control for the 1μ material and cation lattice control for the larger grained materials, but with a contribution from boundary diffusion especially at the lower temperatures. The lines marked D_{ℓ}^a and δD_b^a on these and the following figures are the resultant values of aluminum diffusivity indicated by this analysis. But for a few important exceptions, it can be seen that all of the available data for coarser grained material agree with this inferred value of D_{ℓ}^a to within a factor of two.³

One major exception is the data of Mocellin and Kingery (1971). The 32 μ samples had an MgO concentration of 0.043% by weight which is below the solubility limit determined by Roy and Coble (1968). At the high part of the temperature range investigated the 64 μ sample with 0.083% MgO were also below the solubility limit. The remainder of the data for MgO doped Al_2O_3 in Figures 5 and 6 was above the solubility limit. Although the other data represent a considerable range of MgO content, there is no apparent effect when it exceeds the solubility limit. Except when variable valence impurities were present there is no effect of test atmosphere apparent. Two of the three data points of Hewson and Kingery (1967) do not exhibit a good fit; these had been reported to demonstrate that increasing the MgO content reduced the creep rate. This hypothesis must be rejected on the basis of the considerable other evidence to the contrary, and further since the MgO concentrations for these samples were above the solubility limit and so should have had the same MgO content in the lattice.

The second exception is the 7 μ material which at low temperatures shows an increasing deviation due to the contribution of boundary diffusion which has a lower activation energy. This contribution can be seen in Figure 6 where the data indicate that below 1300°C the 7 μ material, is dominated by boundary diffusion; the data agree well with the 1μ results. One of the sets of data for the 1μ material, represented by Δ , are for a high purity, undoped material. Surprisingly, there seems to be no difference in the cation boundary diffusivity compared to that for the MgO doped materials. The δD_b^a values calculated for the coarser grained data scatter above the δD_b^a line indicating the decreasing contribution

3

The scatter of nearly two orders of magnitude previously seen in such complications for Al_2O_3 was reduced by using a consistent value of $3/2 L$ for the grain size, and further rechecking the calculations to ensure that the same values of the coefficients and of Ω were used; see the appendix for further details.

of cation boundary diffusion. The data for the coarsest grained samples do not appear to be converging in a manner which would conclusively indicate they are significantly limited by boundary oxygen diffusion and so they only provide an indication of a lower bound to the boundary oxygen diffusivity.

Thus, for grain sizes below that where oxygen diffusion becomes limiting, the diffusional creep of Al_2O_3 doped with MgO (or presumably other divalent impurities) in excess of the solubility limit is described by a combination of cation lattice and cation boundary diffusivities with activation energies of 138 and 100 kcal/mole, respectively. As expected, this value of lattice diffusivity is higher than the measured self diffusion coefficient for oxygen, Oishi and Kingery (1960). The lattice diffusivity and its activation energy are also higher than the measured aluminum self diffusion coefficients for undoped Al_2O_3 (114 kcal/mole), Paladino and Kingery (1962), indicating that the cation lattice diffusivity is increased by the MgO dopant.

Fine Grained Al_2O_3 , Other Dopants

There are several studies of creep in Al_2O_3 with other dopants which are compared in a similar manner in Figures 7 and 8. Hollenberg and Gordon used both Fe and Ti dopants and systematically varied the P_{O_2} to change the $\text{Fe}^{+2}/\text{Fe}^{+3}$ or the $\text{Ti}^{+4}/\text{Ti}^{+3}$ ratios. Limited data on different grain sizes indicated that both these materials were in a range of lattice diffusion control. It can be seen from Figure 7 that the creep rates increase as the amount of either divalent or tetravalent impurity is increased. Analysis by these authors showed that the atmosphere dependence was inconsistent with lattice oxygen control or with a Schottky defect model for cation diffusion. The results are satisfactorily explained by a Frenkel defect on the cation sublattice which results in an increased defect concentration from either aliovalent impurity. Some of the Fe doped samples tested at low stresses exhibited n values very close to one as predicted by theory; however, many of the Fe doped and Ti doped samples had $n = 1.1-1.3$; it is not clear whether this represents a contribution from slip or a shift to interface controlled processes because of the high diffusivities obtained by doping.

Also shown are data for Ni doped Al_2O_3 . The tests of Crosby and Evans (1973) were in a strongly reducing atmosphere and the high lattice diffusivities indicate the presence of considerable Ni^{+2} in solution. The inferred value of D_{Ni} is qualitatively consistent with the results for Fe doped Al_2O_3 . Sugita and Pask (1970) tested in air and so most of the Ni in solution may have been trivalent. These data for 3μ samples indicate strain rates higher than predicted by lattice diffusion, but which agree closely with

Figure 7 Comparison of apparent diffusivities from creep tests of Al_2O_3 with various additives from the results of Passmore and Vasilos (1966), Sugita and Pask (1970), Hollenberg and Gordon (1973) and Crosby and Evans (1973).

Figure 8 Comparison of apparent boundary diffusivities from creep tests of Al_2O_3 with various additives.

the previous boundary diffusion values. These investigators observed no grain size dependence as a result of grain growth during testing. This comparison, however, indicates the magnitude of the creep rates can be satisfactorily explained by diffusional creep; it is likely that the considerable cavitation which occurred during testing obscured the effects of grain growth on the creep rate.

It may be expected that undoped material or material doped with trivalent impurities such as Cr_2O_3 should exhibit lower strain rates. This has been reported by Hollenberg and Gordon (1973) as seen in Figure 7. These data indicated a squared grain size dependence, consistent with lattice diffusion, and a lower activation energy. The calculated diffusivity agrees quite well with the extrapolated values of Al self diffusion. It is, however, highly unlikely that these values represent intrinsic diffusion, but is more likely that the diffusivity is extrinsic and controlled by the other impurities which are present. Perhaps some caution should be taken in this interpretation, however, since the strain rates are slower than would be predicted for boundary diffusion as shown in Figure 8. This may indicate that the cation boundary diffusivity is reduced by the Cr_2O_3 ; alternatively the fact that these data exhibited a strain rate sensitivity of $n = 1.3$ may suggest that the creep rate has been retarded because of an interface control problem.

In general, interpretation of creep data for undoped materials is difficult because of the uncertainty about their impurity content and its effect on the diffusivity. The data of Crosby and Evans (1973) for undoped material (not shown) gave lattice diffusivities higher than expected for MgO doping suggesting the presence of considerable low valence impurity as a result of the reducing atmosphere. The undoped Al_2O_3 tested by Engelhardt and Thümmel (1970) which had 5% porosity and showed a linear stress dependence at low stresses give a lattice diffusivity (not shown) which is very close to that for MgO doped Al_2O_3 , suggesting, again, the presence of appreciable divalent impurity. The test results of Passmore and Vasilos (1966) for undoped 3 μ material exhibit good agreement with the cation boundary diffusivity found in Figure 6 for both MgO doped and undoped Al_2O_3 .

Coarse Grained Al_2O_3

In an attempt to find evidence for control by oxygen boundary diffusivity, the inferred diffusion coefficients were calculated for all the available test data for material of 75 μ or larger. These data are shown in Figure 9. It can be seen that none of the values fall below the cation lattice diffusivity as would be expected if they were in a diffusional creep regime with limitation by oxygen diffusion. Instead the results indicate creep rates equal to or faster than those predicted by diffusional creep. W. R. Cannon

Figure 9 Apparent lattice diffusivities inferred from tests of course grained Al_2O_3 ; alternatively assuming the normal diffusional creep model and the dislocation climb models.

(1971), and Warshaw and Norton (1962) observed strain rate sensitivities of 2.6 and 3-4 indicating a different mechanism than simple diffusional creep. Significant cavitation was observed in the coarse grained specimens of Warshaw and Norton (1962) and Coble and Guerard (1963) which contributed at least in part to the high strain rates. However, the results of W. R. Cannon (1971) cannot be similarly discounted since they were done in compression and indicated very little density change. Further, these specimens provided etch pit evidence of slip and slip bands and microscopic evidence for grain boundary sliding.

W. R. Cannon and Sherby (1973) suggested that the strain rate dependence of $n \approx 3$ may indicate a contribution of diffusional creep by the Nabarro climb mechanism. This seems plausible since the stresses used were below those necessary for non-basal slip although they were above the basal flow stresses. The required diffusivity for deformation by the climb mechanism has been calculated using equation (8) with $\beta = 1$ for all of these data. Some of the results are shown in Figure 9. The results for the data of W. R. Cannon (1971) fall considerably below the D_l^a line as anticipated since oxygen lattice diffusion should be rate controlling based on the measured stress exponent. These values are, however, considerably above the self diffusion values for oxygen. The calculated values for the other creep data were even higher presumably due to cavitation with many of them above the D_l^a line; only those for the coarser grain samples of Warshaw and Norton are plotted. The calculated diffusivities must also be high because of contributions from grain boundary sliding, from slip, and perhaps from normal diffusional creep. In addition, the MgO addition would be expected to increase the oxygen diffusivity compared to that for the undoped Al_2O_3 used for the self diffusion measurements.

Heuer et al (1971) reported test results for 0° sapphire at stresses below most of the measured values for pyramidal slip. The measured stress exponents were in the range of 3 to 5 which are also below those found by Gooch and Groves (1974), Tressler et al (1973, 1974) and Palmour et al (1968). Heuer et al (1971) suggested that the observed creep rates may involve a significant contribution from the Nabarro climb mechanism. The required diffusivities, calculated using Eqn. (8), and are shown in Figure 9. The agreement with measured oxygen diffusivities of Oishi and Kingery (1960) is remarkable.⁴ The low activation energy and the tendency toward high values of the stress exponent at lower temperatures suggest a

⁴ The fact that the calculated values of D_l are lower than D_l^a from measurements of self diffusion or diffusional creep of medium grained materials provides a further confirmation of the hypothesis that for normal diffusional creep the oxygen diffusivity at the boundaries is faster than the cation diffusion.

contribution of pipe diffusion, particularly at the lower temperatures; self diffusion measurements of Anderson (1967) also indicated pipe diffusion to be important for oxygen. A further uncertainty in the quantitative confirmation of this mechanism, arises from the microscopic examination of the sapphire samples which showed evidence of slip on non-basal systems and also indicated that the density of non-basal dislocations was $\sim 6 \times 10^7 \text{ cm}^{-2}$ which was more than an order of magnitude below that predicted by Eqn. (9) for the stresses used.

DIFFUSIVITIES

Cation Lattice Diffusivity

The creep results indicate that the cation diffusivity is extrinsic for all the materials tested, and that it is increased by both divalent and tetravalent impurity additions which is at least qualitatively consistent with a cation Frenkel defect model in which cation diffusion occurs by both vacancies or interstitials. Since the MgO solubility in Al_2O_3 has been measured, Roy and Coble (1968), and shown to have an apparent activation energy of 61 kcal/mole, the activation energy for cation defect diffusion can be determined from the creep data for MgO doped Al_2O_3 .

It can be determined separately from the data of Mocellin and Kingery (1971) for unsaturated MgO additions, and, using Eqn. (28), from the diffusivity determined for the MgO saturated material which was

$$D_L^a = 1.36 \times 10^5 \exp \left(\frac{-138,000 \text{ cal/mole}}{RT} \right) \text{ cm}^2/\text{s} \quad (29)$$

These values are compared in Table I with other available determinations of the cation mobility from the literature.

Table I

Cation Mobility Activation Energy

<u>Method</u>	<u>ΔH kcal/mole</u>
Creep - MgO Saturated	77
Creep - MgO Unsaturated	63
Ionic Conductivity, (Kitazawa & Coble (1974)	57
Ionic Conductivity, (Brook et al (1971)	67
Color Boundary Migration, (Jones et al (1969)	80

These values which are all between 57 and 80 kcal/mole, probably represent both interstitial and vacancy activation energies. These may be similar in Al_2O_3 , although somewhat higher values would be expected for vacancy mobility. The color boundary mobility was determined from an oxidation experiment in which cation vacancies would seem more likely to be the dominant defect. The 14 kcal/mole difference between the unsaturated and saturated creep results may be a real effect due to dissociation of defect complexes which would be more important in the saturated samples with higher concentrations of MgO. The ionic conductivity measurements were both for oxidizing conditions which would be metal deficient for pure Al_2O_3 ; however, the value reported by Brook et al (1971) includes results from divalent impurity doped crystals in which interstitials were expected to be dominant.

Reference to Figure 7 shows that for the Fe, Ni and Ti dopants the activation energies for lattice diffusivity were also in the range of 140-160 kcal. These cases do not represent precipitation, but rather a temperature dependence of the impurity valence state, which in a similar manner results in a significant contribution to the activation energy as has been shown in greater detail by Hollenberg and Gordon (1973). For the Ti doped material tested in high P_{O_2} precipitation was also occurring resulting in an apparent activation energy of about 205 kcal/mole. Ti, Bagley et al (1970), and Fe, Rao and Cutler (1973), have been reported to increase the rate of initial sintering of Al_2O_3 , whereas MgO, Jorgenson (1965), has been observed to slow the initial rate. The cause of these differences in behavior compared to creep are uncertain as are some differences in the magnitudes of boundary and lattice diffusivities deduced from sintering. The different defect concentrations in the space charge region near the boundaries, may account for some of the differences.

Boundary Diffusivities

For the MgO doped materials and some undoped Al_2O_3 the cation boundary diffusivity was found to be:

$$\delta D_b = 8.60 \times 10^{-4} \exp \left(\frac{-100,000 \text{ cal/mole}}{RT} \right) \text{ cm}^3/\text{s} \quad (30)$$

It may be surprising that such close agreement for the boundary diffusivity should be found for Al_2O_3 with and without the MgO doping and for both sintered and hot pressed materials. The spinel phase which forms is non-wetting and is found as small grains at the triple points and so does not form a grain boundary film. The undoped, 1 μ material used by R. M. Cannon et al (1975) had only 100-300 ppm total cation and anion impurities; if this is assumed to be uniformly distributed around the grain boundaries it re-

presents less than $1/2$ of a monolayer for a 1μ grain size and so cannot account for a second phase film at the boundaries. For the other $1-3\mu$ materials the background impurity content is only 2 to 3 times the above value and so a boundary film would also not be expected. For the sintered materials of 7μ or greater similar grain boundary diffusivities suggest that high diffusivity boundary films are also not important. It may be that most of the SiO_2 impurity is taken into solution due to compensated solubility with the excess MgO ; this would reduce the amount of low melting grain boundary phase to a sufficiently low level that it is not important. For undoped materials with higher impurity levels, boundary films could be expected to contribute to high values of cation boundary diffusivity.

Examination of all of the available data for MgO doped Al_2O_3 fails to provide a conclusive indication of a shift to control by oxygen diffusion. The doped materials of Hollenberg and Gordon (1973) similarly did not indicate a shift to control by oxygen diffusion. Crosby and Evans (1973) reported a grain size dependence of 2.7 for the undoped materials which were from $15-45\mu$, which may indicate a contribution of boundary diffusion, however there were insufficient data to indicate whether it is from enhanced cation boundary diffusion or from oxygen boundary diffusion control. The highest calculated values of δD_b^o for the coarsest materials shown in Figure 8 gave an indication of the magnitude of δD_b^o which must exist. The line shown as a lower bound to δD_b^o was calculated assuming that at the highest apparent values of δD_b^a the oxygen and aluminum diffusivities were just equal for the data of Mocellin and Kingery (1971) and the Ti doped Al_2O_3 of Hollenberg and Gordon (1973).

It is not obvious, of course, that δD_b^o will be the same for the various dopants and so the indicated value is only an approximate bound. For the material with divalent dopants the amount of silicate phase at the boundaries would likely be reduced due to compensating solubility effects. For the Ti doped material this would not be the case. Recently Gordon (1974) reported $\delta D_b^o = 3.4 \times 10^{-14}$ at 1450°C from coarse grained Fe doped Al_2O_3 . This value would suggest higher values of δD_b^o for Ti doped Al_2O_3 than for divalent doped Al_2O_3 . These results do indicate that δD_b^o is at least 10^2 times δD_b^a .

There is very little other data on δD_b^o for Al_2O_3 with which to compare these results. On Figure 6 and 8 are shown a value of δD_b^o with $\Delta H = 109$ kcal/mole which was calculated by Mistler (1967) from the self diffusion data of Oishi and Kingery (1960) using a Harrison volume fraction model. It is apparent that this value is too low indicating the simple model was not applicable and that the effective diffusivities measured were in a range where the boundaries were saturated and lattice diffusion was limiting. Johnson and Berrin (1965) deduced values of δD_b^o from sintering data and obtained values, Figure 6, which were lower in magnitude and higher in activation energy than the values of δD_b^a found here.

These values may be indicative of cation boundary diffusion, but are likely in error due to neglect of surface transport in the analysis. Kitazawa and Coble (1974) measured values of the defect diffusivity of oxygen in the grain boundaries by a permeability technique; they found values much higher than those indicated here for δD_b^O and with activation energies of 20-50 kcal/mole. Further, they found a marked dependence of MgO doping on the apparent oxygen defect diffusivity.

There are four different determinations of the surface diffusivity for Al_2O_3 . Robertson and Chang (1966), Robertson and Eckstrom (1969) and Shackelford and Scott (1968) determined wD_s from grain boundary grooving measurements. Yen and Coble (1972) determined wD_s from pore spheroidization measurements. These results gave activation energies from 75 to 130 kcal/mole, but were within an order of magnitude of each other in absolute magnitude over most of the temperature range. Most of these results lie in a band which ranges from 2 to 10 times higher than the δD_b^O values shown in Figure 8, and are below the δD_b^O value. It is likely that all of those represent the surface diffusion of Al as the slower species. Chang (1967) and Robertson (1969) have pointed out that other oxides, especially UO_2 for which there is good data, also exhibit a similarity between the values of surface and grain boundary cation diffusivity.

The absolute value indicated for δD_b^O is quite high, i.e. in the range of $10^{-12} \text{ cm}^3/\text{s}$. A value of δ of 10^{-5} cm which may be possible for the space charge cloud would infer a value of D_b^O of $10^{-7} \text{ cm}^2/\text{s}$ which seems very high for transport in unfaulted lattice. Alternatively, assuming δ of 10^{-7} cm , representative of the structurally disordered region, would infer a value of D_b^O of $10^{-5} \text{ cm}^2/\text{s}$. This value is typical of that expected for a liquid, and so may be plausible for the distorted, core region of the boundary. It seems likely that there must be a significant contribution to the boundary diffusivity from the core. A similar analysis for the cation boundary diffusivity gives D_b values which are several orders of magnitude lower. These may still suggest a considerable contribution of the distorted region to the boundary diffusivity, because for samples below the isoelectric temperature the cation interstitial concentration is depressed in the space charge cloud around the boundary, Kingery (1974). The activation energy of 100 kcal/mole is appreciably higher than that for cation mobility in the lattice and so implies a significant temperature dependence of the boundary defect concentration or structure.

SUMMARY

Diffusional creep with the grain boundaries as defect sources has been analysed to a high degree of rigor compared to other creep theories; the modifications necessary for application to steady

state creep of ceramics are direct and easy to apply. The major uncertainty in the theory remains the exact value of the numerical coefficient due to uncertainty about the extent of grain rearrangement which may occur. For the Nabarro climb model for diffusion with dislocation sources there is greater uncertainty as to the detailed accuracy of the theoretical creep rate equations.

Analysis of the creep rate for Al_2O_3 indicates that for low stresses the creep is dominated by diffusional creep. At intermediate stresses, which are above the basal yield, but below the much higher non-basal yield stresses, slip will occur on favorably orientated basal slip systems. However, as earlier suggested by Groves and Kelly (1969) and Gooch and Groves (1974 b), it appears likely that much of the strain required to satisfy the von Mises condition results from diffusional creep. For medium and fine grained materials this is still the normal grain boundary controlled diffusional creep. In this case the kinetics appear to be reasonably well described by the theoretical constitutive equations, although the contribution of basal slip results in a small increase in the creep rate which causes stress exponents slightly greater than unity. The regime of interface control, where diffusion is not the rate limiting step, is only partially understood, but it can be a problem at very fine grain sizes, or when diffusion is very rapid, giving rise to stress exponents appreciably greater than one. For coarser grained materials diffusional creep by the Nabarro climb mechanism becomes faster. A constitutive relation which properly accounts for the contributions of glide, climb, and grain boundary sliding does not appear to be available, although Eqns. (7) or (8) provide approximations. Only at stresses approaching the non-basal yield stresses which are between σ/G of 10^{-3} - 10^{-2} does it appear that polycrystalline deformation without cracking can occur without an important contribution from diffusional creep, even at temperatures approaching the melting point.

When analyzed together, the creep results of fine and medium grained Al_2O_3 are in satisfactory agreement with each other and with the predictions of the diffusional creep relations. For MgO doped Al_2O_3 control is by cation diffusion at least up to a 60μ grain size. The lattice diffusivity appears to be enhanced by MgO additions, and when the MgO is above the solubility limit the creep data indicated:

$$D_l^a = 1.36 \times 10^5 \exp \left(\frac{-138,000 \text{ cal/mole}}{RT} \right) \text{ cm}^2/\text{s}$$

The boundary diffusivity is insensitive to MgO doping and is:

$$\delta D_b^a = 8.60 \times 10^{-4} \exp \left(\frac{-100,000 \text{ cal/mole}}{RT} \right) \text{ cm}^3/\text{s}$$

The hypothesis, initially advanced by Paladino and Coble (1963), that boundary oxygen diffusion is rapid relative to aluminum diffusion is confirmed by the present analysis.

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APPENDIX

There has been a significant scatter in the values of D_l and δD_b reported by various investigators which has been due in large part to differences in the values of the coefficients and of Ω used for the strain rate equation. For all the curves of D_l and δD_b in Figures (5-9) the coefficients in Eqn. (6) were used with $\Omega_a = 2.12 \times 10^{-23} \text{ cm}^3$. For the values of D_l calculated for the climb mechanism Eqn. (8) was used with $\Omega = 1.52 \times 10^{-23} \text{ cm}^3$ and $b = 4.93 \times 10^{-8} \text{ cm}$ which is the average of $1/3 \langle 11\bar{2}0 \rangle$ and $1/3 \langle 0111 \rangle$. All grain sizes used in calculations or in the text were converted to $G = 1.5L$, if L , the mean linear intercept, had been used by the original author.

Much of the confusion has persisted because the values used were often not reported or were misrepresented and often no strain rate data were reported which would allow a check. In most cases the diffusivities were recalculated from strain rate data. However, as this data often was in theses which are not generally available, the following summarize the corrections made to the various sets of results.

Cannon, R. M., et al (1975): Used same values

Cannon, W. R., (1971): Grain size measurements from several micrographs indicated the values reported were $\bar{L}$. Changing coefficients and using G gave $D_l = 1.61D$ (Reported).

Coble and Guerard, (1963): Re-examination of the original data indicated a factor of 12 error in most of the strain calculations. Recalculation brought the data for 14-35 μ samples of MgO doped, MgO - CrO₃ doped, and Lucalox into good agreement with an average value of D_l about 12 times that previously reported.

Crosby and Evans, (1973): Calculations were from reported $\dot{\epsilon}$ and G data.

- Dawihl and Klingler, (1965): Strain rates and D_l were calculated from G and deflection curves.
- Folweiler, (1961): D_l calculated from $\dot{\epsilon}$ and G data are about 1/3 those reported. R. F. personally confirmed $G = 1.5L$ has been reported.
- Hewson and Kingery, (1967): In the M.S. Thesis of C. W. H. it is seen that $(G/2)$ and Ω_a has been used in the calculations. Measurements from micrographs indicated G was reported. Correcting for the proper coefficient gave $D_l = 2.86D$ (Reported).
- Hollenberg and Gordon, (1973): Calculations from the $\dot{\epsilon}$ and G data in the Ph.D. Thesis of G. W. H. generally gave similar results to the reported values of D_l .
- Mocellin and Kingery, (1971): A. M. personally confirmed Ω and G had been used; however, the reported value of δD_b was^a in error by a factor of 10 too low. This is corrected along with small changes for the coefficients used in Eqn. (6).
- Stuart, (1964): Measurements of micrographs (3rd Quarterly Report indicate that L was reported. Calculations then confirmed $D_l = 4.29 D$ (Reported).
- Sugita and Pask, (1970): Measurements of Micrographs indicated G was reported; D_l was calculated from $\dot{\epsilon}$ and G data.
- Warshaw and Norton, (1962): In the Ph.D. Thesis of S. I. W. it is seen that $(L/2)$ was used in the calculations; measured from micrographs confirmed that L was reported. Calculations from $\dot{\epsilon}$ data confirmed $D = 4.24 D$ (Reported).

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