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Creep in Polycrystalline Aggregates by Matter Transport Through a Liquid Phase

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Polycrystalline aggregates which contain some liquid in grain interfaces can deform by matter transport, through the liquid phase. If the applied stress is multiaxial, then the deviatoric component of the stress will produce creep, that is, a change in shape of the aggregate without any change in volume, while the mean stress will cause the aggregate to densify. Constitutive equations for creep rate and densification rate are derived. It is shown that the rate may be controlled either by the interface kinetics of dissolution/precipitation of the crystal from the liquid or by the diffusion rate of matter through the liquid. The first process can be related to the kinetics of crystal growth from solution, and the second, to the viscosity of the liquid. The results of the analysis are used to interpret experiments on densification rate of a rock salt polycrystalline aggregate immersed in saturated brine.

INTRODUCTION

The idea of pressure solution originally proposed by *Sorby* [1863] to explain metamorphic segregation in rocks has recently been extended to explain time dependent deformation in geological systems [*Durney*, 1972; *Elliot*, 1973; *Rutter*, 1976; *Stocker and Ashby*, 1973]. The concept is analogous to the classical mechanism of diffusional creep [*Coble*, 1964] which occurs in polycrystals at elevated temperatures. In diffusional creep, matter is transported across distances which are of the order of the grain diameter; this produces a change in grain shape which manifests itself as strain that can be measured. The kinetics of diffusional creep is generally controlled by diffusion of matter, atom by atom, through the grain interfaces [*Coble*, 1964] and through the crystal lattice itself [*Herring*, 1950]. Such creep is produced only if the applied state of stress has a nonzero deviatoric component and occurs at high temperatures where solid state diffusion occurs at an appreciable rate.

In solution-precipitation creep, matter is believed to be transported by diffusion through the thin liquid film at grain interfaces. (The expression 'solution-precipitation' creep rather than 'pressure solution' is used to identify creep in the partially liquid systems because, in the steady state, when the crystals change their shape, they must dissolve and then precipitate out of the fluid at the same rate.) As such it is similar to the case of boundary diffusion controlled diffusional creep [*Elliot*, 1973]. The significant point is that solution-precipitation creep is possible at relatively much lower temperatures than diffusional creep. For example, in aggregates of rock salt immersed in brine, creep is possible even at room temperature [*Thompson*, 1862], whereas pure rock salt aggregates would show significant diffusional creep only at temperatures above 800 K [*Heard*, 1972]. Other examples are found in ceramic-liquid systems which contain a eutectic liquid phase in grain boundaries [*Clarke*, 1979] such as those found in the upper mantle of the earth [*Yoder*, 1976]; here the creep rate scales with the homologous temperature with respect to the eutectic temperature, rather than the melt temperature of the ceramic phase which can be relatively much higher [*Lange et al.*, 1980].

In some respects, however, diffusional creep and solution-precipitation creep are different. The purpose of this paper is to emphasize these differences and to develop constitutive equations which are particularly adapted for flow in partially fluid aggregates. In particular, three specific problems are posed and possible solutions to them are presented:

1. In diffusional creep it is necessary to sustain a gradient in the normal traction (or pressure) along the interfaces, in that this provides the fundamental driving force for net flux of molecules. In partially fluid systems, in steady state deformation, one cannot reconcile the existence of a pressure gradient with the existence of a continuous film of liquid along the grain interfaces. (In the case of a solid surface in contact with a fluid the normal traction on the surface will be equal to the fluid pressure.) If a pressure gradient exists, then the fluid will flow and redistribute itself in a manner such that the pressure in all regions becomes equal.
2. In addition to considering diffusion of molecules through the liquid, one must also consider the mechanism by which the crystal dissolves and grows from the liquid solution. This process is related to the kinetics of crystal growth from a liquid phase, a situation which is peculiar to creep in the partially liquid systems.
3. Whereas diffusional creep is possible only if the deviatoric component of the stress state is nonzero, solution-precipitation is possible under hydrostatic state of stress as well. Under hydrostatic pressure the fluid can be squeezed out, producing a volumetric contraction in the aggregate. The paths for matter transport for creep and densification are shown by the schematic in Figure 1. In creep the grain changes shape, while in densification the grains pack closer together as matter is removed from grain interfaces and deposited in the interstitial space. In geologic materials the term filter pressing is used to describe the process of squeezing the melt out of a partially molten rock. If the partial melt contains so much fluid that the grains are floating and not in contact, then the melt can be removed simply by a filtering process which separates the liquid component from the solid component. If, on the other hand, the liquid volume fraction is so small that the solid particles are in contact, then further removal of liquid must be accommodated by change in shape of the grains, by a mechanism of the type shown in Figure 1*b*. This latter process is being called densification.

A possible solution to the first problem is presented by postulating an atomic structure for the interfaces which contain a fluid phase. For the second problem, rate equations for creep

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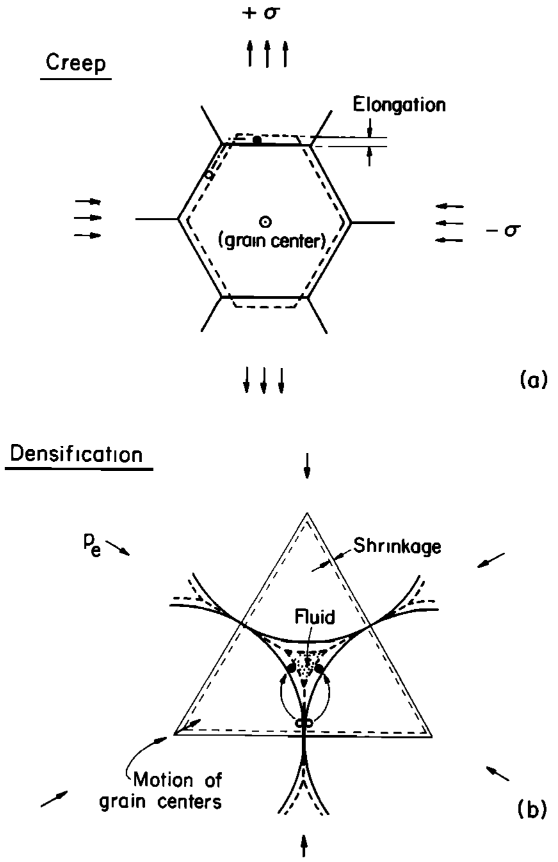

Fig. 1. (*a*) A deviatoric applied stress can lead to mass transport which produces change in shape without a change in volume. (*b*) A mean applied stress produces densification by mass transport. As the liquid pocket is filled by the crystal, the liquid is squeezed out through interconnected channels.

are related to the kinetics of crystal growth and dissolution. Finally, constitutive equations for creep and densification are obtained.

Some of the work presented here derives from two recent papers; those results are presented without detailed derivation with reference to these publications [*Raj and Chyung*, 1981; *Raj*, 1981]. The first reference is particularly relevant. Finally, the results of creep experiments on a rock salt aggregate immersed in a saturated solution of brine are described.

MICROSTRUCTURE

Three Grain Junctions

In a polycrystalline aggregate which contains a small amount of a liquid phase in the interfacial regions, the fluid will form an interconnected network if the dihedral angle (or the wetting angle) formed by the liquid with crystalline grain boundary is less than $\pi/3$ [*Raj*, 1981]. The network will consist of pipes along the three grain junctions which will be connected to each other at the four grain junctions. The cross section of these pipes, in an ideal situation in which the interface energies are isotropic and the liquid is uniformly distributed, is shown in Figure 2*a*. The half dihedral angle θ is defined by the equation

$$\cos\theta = \frac{\gamma_b}{2\gamma} \tag{1}$$

where γ_b is the energy of the crystal-crystal interface and γ is the energy of the crystal-fluid interface; R, the radius of curvature of the interfaces, can be related to v_g, the volume fraction of the liquid phase in the aggregate, through the following equation [*Raj*, 1981]:

$$v_g = \frac{8}{\pi}\left\{2\cos^2\theta\,\sin\frac{\pi}{3} - \frac{\pi}{2} + 3\left(\theta - \tfrac{1}{2}\sin 2\theta\right)\right\}\frac{r^2}{d^2} \tag{2}$$

where d is the 'equiaxed' grain size as shown in Figure 2*b*. This result is based on the assumption that the fluid which segregates at triple junction is of much greater volume than the fluid which is segregated at the two grain junctions; this appears to be borne out by transmission electron microscopy of polycrystals which contain a small amount of a fluid phase [*Clarke*, 1979].

The point about interconnectivity of the fluid in the aggregate is important when considering densification. As can be seen in Figure 1*b*, densification is possible only if the fluid can flow out of the three grain junctions. Thus densification is possible only if the dihedral angle is $<\pi/3$. Indeed, the liquid has a characteristic pore pressure only when it is interconnected within the aggregate.

Two Grain Junctions

In order to explain solution-precipitation creep, as envisioned by the present mechanism, it is essential that it should be possible to sustain a gradient in the normal traction at two grain junctions and yet provide access for the fluid phase. The access of the fluid is necessary in order to provide paths for rapid transport of matter. A plausible structure of two grain junctions which admits both of these features is explained in the work of *Raj and Chyung* [1981]. The model consists of an island structure where regions of good fit (where regions from adjacent crystals meet rigidly with each other) are separated by regions that contain the fluid. All normal stress is supported at the islands, while the interpenetrating fluid regions provide a path for rapid diffusion. (Detailed experimental studies of the atomic structure of two grain junctions containing a liquid are not available, although several observations of glass in two and three grain junctions have been reported in the literature [*Clarke*, 1979].) We assume that the islands occupy an area fraction x and that the height of the ledges is h. If b is the lattice spacing, then the important structure parameter relevant to the flow equations is $\alpha = xh/b$, which as a first approximation should be of order unity.

Another consequence of the island structure is that the deviatoric stress, which drives the creep process, will be greater than the applied stress by a factor $1/(1 - x)$ because the applied load is supported only at the islands. This stress enhancement factor is included in the creep equations presented later.

CONSTITUTIVE EQUATIONS FOR FLOW UNDER MULTIAXIAL STRESS STATES

Stress Components and Pore Pressure

The stress state of the aggregate can be defined in terms of the principal stresses, σ_1, σ_2, and σ_3, applied to the solid and by the pore pressure of the interpenetrating liquid phase, p_0. The principal stresses lead to a definition of the von Mises deviatoric stress σ_e, such that

$$\sigma_e = \frac{\{\frac{1}{2}[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2]\}^{1/2}}{(1 - x)} \tag{3}$$

and an effective pressure p_e, such that

$$p_e = -\left(\frac{\sigma_1 + \sigma_2 + \sigma_3}{3(1 - x)}\right) - p_0 \tag{4}$$

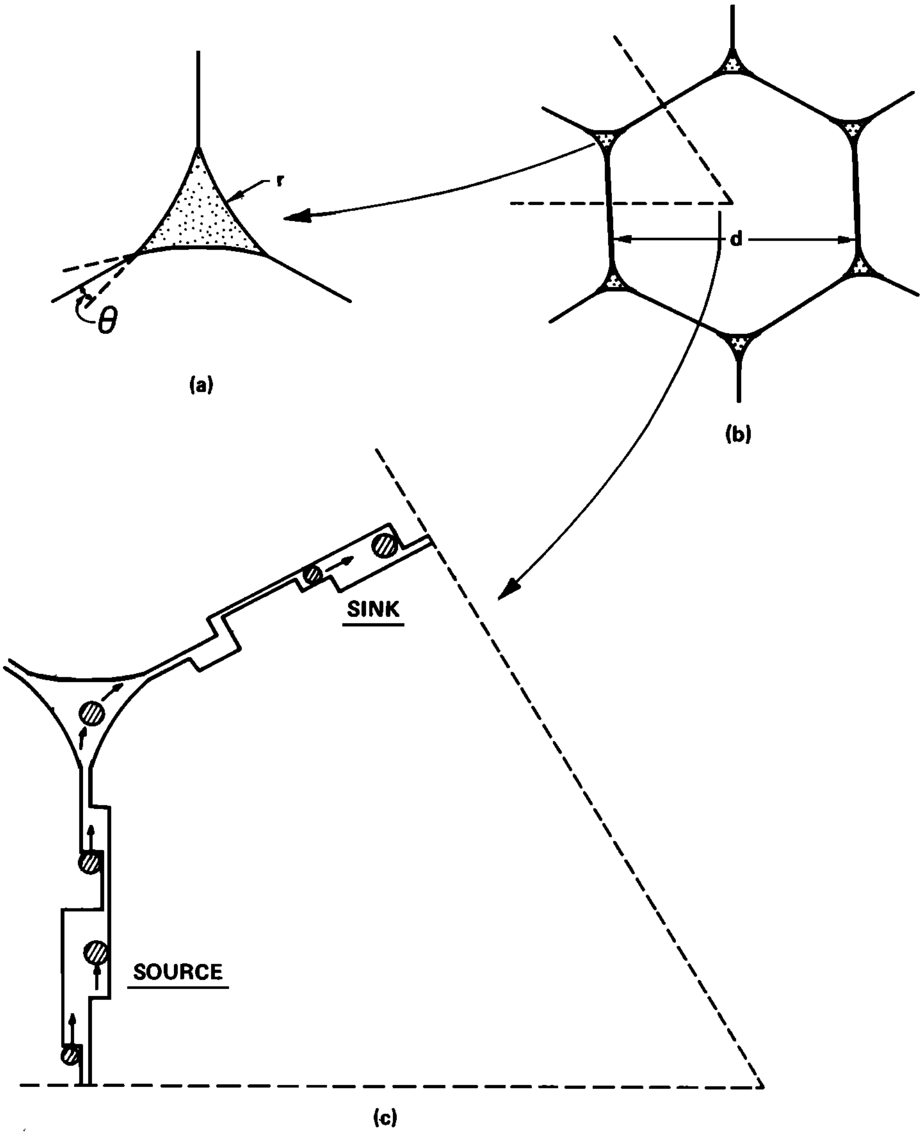

Fig. 2. (*a*, *b*) A cross section of the three grain junctions. The geometry of the glass pocket is completely defined by r, the radius of curvature, and θ, the dihedral angle. The total volume fraction of the fluid phase can be derived in terms of r and θ as was done in (2). (*c*) Atomic process by which matter is transported from one interface to another. Three steps are involved in the transport cycle. Atoms must be detached from the crystal (interface reaction), be transported by diffusion through the fluid phase, and then be reattached to the crystal at a different interface.

Now σ_e will give rise to deviatoric strain rate $\dot{\varepsilon}_e$, while p_e will cause a rate of change in the volume of the aggregate, which we call the densification rate $\dot{\beta}$. The sign of $\dot{\beta}$ is defined such that it is positive when the p_e is positive, i.e., when the volume of the aggregate shrinks. The factor $(1 - x)$ arises from the proposed island structure of the two grain junctions, as described above.

Thermodynamics

In order to obtain deformation by mass transport, it is necessary to have a driving force which provides the basic thermodynamic condition for the molecules to move in a net direction. Of course, this alone does not suffice; the kinetics of transport must also be rapid enough to provide physically meaningful rates of deformation.

It is sometimes said that the driving force for solution-precipitation creep arises from the pressure dependence of the solubility of the crystal in the liquid phase. This is not correct. We believe that the correct thermodynamic analysis has been provided by *Robin* [1978], who has explained that the driving force for diffusional transport comes from the gradient in the normal tractions along an interface. The solubility of the crystal is undoubtedly important from a kinetic standpoint, but as regards the thermodynamic driving force, it is irrelevant.

The driving force for deviatoric creep ($\dot{\varepsilon}_e$) and densification ($\dot{\beta}$) are denoted as g_e and g_p. Their units would be J m^{-1} per atom. Appendix A shows how they can be derived from the first law of thermodynamics. As a result, the following expressions are obtained for both:

$$g_e = \frac{2\sigma_e\Omega}{d} \tag{5}$$

and

$$g_p = \frac{2[p_e - (\gamma/r)]\Omega}{d} \tag{6}$$

where d is the grain size. We have assumed here that the diffusion distances are of the order of one half of the grain size.

This should be true if the polycrystal contains equiaxed grains. However, there may be situations where the grain shape is nonisotropic or the diffusion distances relate to some other microstructural parameter; in these instances, $d/2$ should be replaced by the physically correct diffusion distance. Note that whereas g_e does not change much as creep progresses (other than a small change in d due to grain elongation), g_p decreases with increasing density. The reason is that g_p depends on r (see Figure 2), which is related to the volume fraction of the liquid phase v_g, given by (2). As the material densifies, r gets smaller and so does g_p. Eventually g_p will become zero, with a finite amount of liquid still remaining in the aggregate. The implication is that fluid cannot be completely removed from the polycrystal by applying effective pressure. For a given effective pressure, equilibrium will be reached when

$$r_0 = \frac{\gamma}{p_e} \tag{7}$$

Note that r_0 also defines the equilibrium volume fraction of retained fluid, through use of (2).

The assumption, implicit in (1) and (7), that the energy of the crystal-liquid interface γ is isotropic and that it does not change with the size of the liquid pocket at three grain junctions is significant. The question of the molecular structure of the transition layer from the crystal to the liquid has not yet been satisfactorily resolved. If the interface is diffuse [*Frank*, 1952; *Tiller*, 1969; *Hilliard and Cahn*, 1958], then γ will not vary much with orientation, although it will begin to change with the size of the pocket r (in Figure 2*a*) when r becomes about equal to the width of the transition layer. On the other hand, solid-solid and solid-vapor interfaces of crystals are known to be sharp and hence energetically quite anisotropic [*Herring*, 1951]; in this case the free energy and shape of the interface is likely to be temperature dependent because of the importance of the entropy arising from steps or roughness of the interface [*Spaepen*, 1980]. How do these considerations influence the result in (7)? This is a difficult question to answer at the present time. A similar issue arises in the theory of nucleation of microcrystals from a supersaturated solution where the critical nucleus size may be only a few tens of atmoic diameters and where the size of the critical nucleus depends on γ. A discussion of the problem is given in the work of *Christian* [1965]. The first-order assumption that γ does not change with nucleus size appears to provide a reasonable qualitative explanation of experimental results. Undoubtedly the assumption is quite approximate, but the next level of sophistication may require other assumptions regarding atomic structure which can be resolved only by high-resolution experimental studies of interfaces. This is an area of considerable current interest (for example, see *American Society for Metals* [1979]).

Kinetics

The kinetics of the creep process will depend on the mechanism by which the molecules are detached from the crystal at a 'source' site, are transported through the fluid, and are reattached to the crystal at a 'sink' site. This is shown schematically in Figure 2*c*. In general, two kinetic processes are involved: the interface reaction by which an atom is attached to, or detached from, the crystal and the rate of transport through the fluid. These processes must occur in series for the ransport cycle to be complete; therefore the slower one of them will be rate controlling.

As a first approximation, the dissolution of a crystal in an undersaturated solution and growth from a supersaturated solution may be assumed to be analogous to the situation in Figure 2*c*. The advantage of this assumption is that data from independent experiments on crystal growth from solution can be applied to interpret data on creep and densification. The disadvantage is that rather severe assumptions must be made about the structure of the interface, e.g., the island structure. A short discussion of these points is given here.

A macroscopic theory for the dissolution (or growth) of a crystal into a solution can be found in early literature. For example, *Moelwyn-Hughes* [1947] derives an expression showing that the interface velocity, which is proportional to the dissolution rate of a flat interface, depends on the interface reaction and on the diffusion of solute in the solution. Two limiting cases can be considered. In the diffusion limited case [*Readey and Cooper*, 1966] the dissolution rate, defined as the interface velocity, changes with time, approximately as $t^{-1/2}$. In the interface limited case the dissolution rate remains constant with time and is linearly proportional to the degree of undersaturation. In those instances where the liquid is quite fluid and where the crystal has some solubility in the liquid, the interface reaction is usually found to be rate limiting. For the interface limited case, one must also consider the atomic mechanisms by which solute atoms transfer from the crystal, which is highly ordered, to the liquid in which the solute is randomly distributed. It is now agreed upon that atoms attach to steps in the crystal surface [*Christian*, 1965]. If the surface is atomically flat, then steps must be nucleated before a crystal can grow. The steps can be present as a result of screw dislocations in crystal, whose axis is aligned normal to the interface, or they may be nucleated under the influence of the driving force. As the driving force for dissolution or growth is increased, an atomically flat interface undergoes a roughening transition. Below this transition the interface velocity is limited by the nucleation rate of the steps, and above it the steps nucleate easily and the velocity becomes dependent on the rate at which atoms can attach to the ledge sites created by the steps. Above the transition the interface velocity is linearly proportional to the driving force. By applying the results of such analyses [*Weeks and Gilmer*, 1979; *Uhlmann*, 1972] to experiments, one can usually determine which of the atomic mechanisms are admissible under the experimental conditions.

The island structure of the interface, postulated for the problem at hand, is similar to the structure of the interface which is assumed to exist above the roughening transition when a crystal grows from solution. The question is whether conditions which may prevail on the surface of a crystal immersed in an infinite solution can be applied to the junction of two misoriented crystals which have a thin liquid film between them. One can also ask whether the islands are formed under the influence of applied stress, or whether they are present intrinsically. For our creep mechanism to operate it is necessary that the islands should be thermodynamically stable; otherwise they would grow and disappear, and slowly the aggregate woulds stop creeping. In the author's view the islands are stabilized from entropy considerations. In those instances where the dihedral angle θ is small, the cost in enthalpy of including crystal-liquid-crystal instead of a crystal-crystal interface is likely to be small and may well be offset by the configurational entropy due to the islands. A rigorous analysis of the problem is beyond the scope of this paper. Suffice it to say here that the creep model developed with the concept of the island structure, which allows us to apply crystal growth and dissolution data to estimate

TABLE 1. A Summary of the Creep Equations for Multiaxial Loading

	Interface Controlled Creep	Diffusion Controlled Creep	Net Creep Equation
$\dot{\varepsilon}_e$, deviatoric creep rate	(A): $\frac{\sigma_e\Omega}{kT}\frac{k_1'\bar{c}}{d}$	(B): $2.3\frac{\sigma_e\Omega}{\eta d^3}\bar{c}\alpha$	(C): $\frac{\sigma_e\Omega}{d}\frac{k_1'\bar{c}/kT}{(k_1'\bar{c}\eta d^2/2.3kT\bar{c}\alpha)+1}$
$\dot{\beta}$, densification creep rate	(D): $\frac{3\left(p_e-\frac{\gamma}{r}\Omega\right)}{kT}\frac{k_1'\bar{c}}{d}$	(E): $6.9\frac{\left(p_e-\frac{\gamma}{r}\right)\Omega}{\eta d^3}\bar{c}\alpha$	(F): $\frac{3\left(p_e-\frac{\gamma}{r}\right)\Omega}{d}\frac{k_1'\bar{c}/kT}{(k_1'\bar{c}\eta d^2/2.3kT\bar{c}\alpha)+1}$

$\bar{c}$ is the solubility of the crystal in the fluid. It will be pressure and temperature dependent according to (8). α, to a first approximation, may be assumed to be unity. σ_e and p_e are defined by (2) and (3).

creep rate in partially fluid aggregates of polycrystals, appears to give good comparison between theory and experiment. As we apply the model to different systems [*Raj and Chyung*, 1981; *Tsai and Raj*, 1982*a*, *b*], with reasonable success, our confidence is increased that we are on the right course.

Given the assumption of an island structure and in view of the preceding discussion, we can proceed with the theory that the interface velocity would be linearly proportional to the driving force, when the process is interface reaction controlled. The diffusion controlled case, which is analogous to Coble creep [*Coble*, 1964], is also linear in stress; therefore the solution to the coupled problem can be obtained by simple superimposition. A mechanical analog is a convenient way to represent the coupled problem. It would consist of two dashpots mounted in series so that each one adds to the resistance to flow. The total resistance, then, is the series sum of the contribution from each dashpot.

The analysis for the creep rates when interface reaction is rate controlling and when diffusion is rate controlling is given in Appendix B. The results are presented in Table 1. The equations in the last column in the table are derived by using the dashpot analog [*Raj and Chyung*, 1981]. They reduce easily to the interface controlled case if $k_1'\bar{c} \gg 1/\eta d^2$ and to the diffusion controlled case if $k_1'\bar{c} \ll 1/\eta d^2$: Here d is the grain size, and the parameters η and $k_1'\bar{c}$ are described below.

The equations in Table 1 contain three new parameters, η, k_1', and $\bar{c}$. η is simply the viscosity of the fluid phase. $k_1'\bar{c}$ is the lineal growth velocity of the crystal interface (m s^{-1}) under a driving force of 1 kT per molecule; it may be measured independently through crystal growth type of experiments. The normalized growth velocity of the interface is written as $k_1'\bar{c}$ to emphasize that the creep rate will be proportional to the solubility of the crystal in the liquid in both interface and diffusion limited cases. In fact, k_1' and $\bar{c}$ are inseparable quantities, since only the product can be measured experimentally. More exactly, k_1' represents the jump frequency of the solute atoms from the crystal into the liquid, across the interface. Thus the interface velocity is determined by the jump frequency of atoms multiplied by the number of atoms involved in the jump which is proportional to the concentration of solute atoms in the solution. Since we are concerned here with molecular rather than elemental crystals, the slower among the molecular species will control the rate of mass transport.

The parameter $\bar{c}$ represents the solubility of the crystal molecules in the fluid phase. It is likely to be pressure and temperature dependent as follows:

$$\bar{c} = \bar{c}_0 \exp\left[-(p_0\Delta V + \Delta H)/kT\right] \qquad (8)$$

where p_0 is the pore pressure in the fluid, ΔH is the heat of solution (its sign is positive if the reaction is endothermic) and ΔV is the difference in the partial molar volume of the solute in the fluid and in the crystal phase. (The average solubility of the crystal phase in the fluid will depend on the strain energy in the crystalline grains as well. However, that effect is likely to be small in comparison to the influence of the fluid pressure p_0 on the solubility. If the crystal surface can equilibrate easily with the fluid it contacts, the chemical potential of the molecules near the surface in the crystal and the fluid must be equal. The chemical potential of the molecules will be influenced by the normal traction on the surface from the fluid, p_0, and by the strain energy in the crystal. If the stress in the crystal is of order σ, then the strain energy will be of the order of σ^2/E, where E is the elastic modulus. Thus if p_0 and σ are about the same order of magnitude, the strain energy therm will be smaller than the pressure term by a factor of the order of σ/E. Since, in solution-precipitation creep, we are concerned with stresses which are much smaller than the elastic modulus, the influence of strain energy is likely to be small.) $\bar{c}_0$ is a normalizing value for the solubility. Note that $\bar{c}$ depends on the pore pressure, not the effective pressure. Also ΔV may be positive or negative, depending on an increase or a decrease in volume when the crystal dissolves in the fluid.

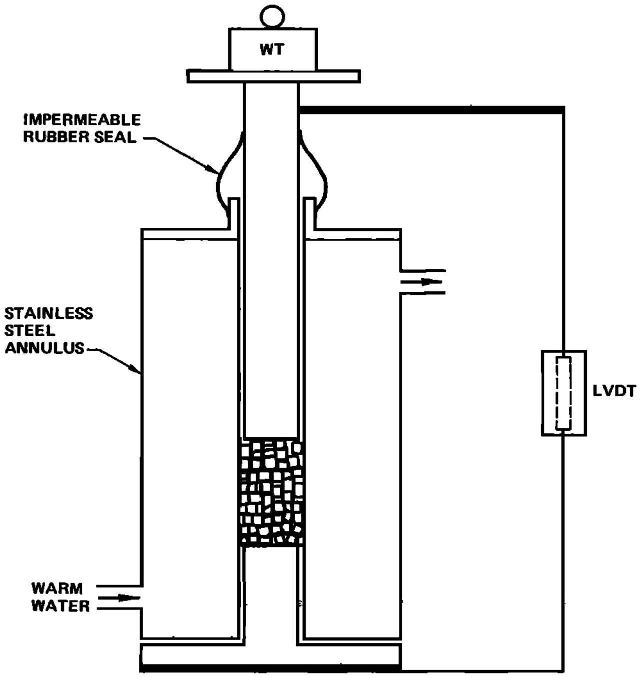

Fig. 3. A schematic of setup which was used to measure densification creep in aggregates of rock salt crystals immersed in saturated brine.

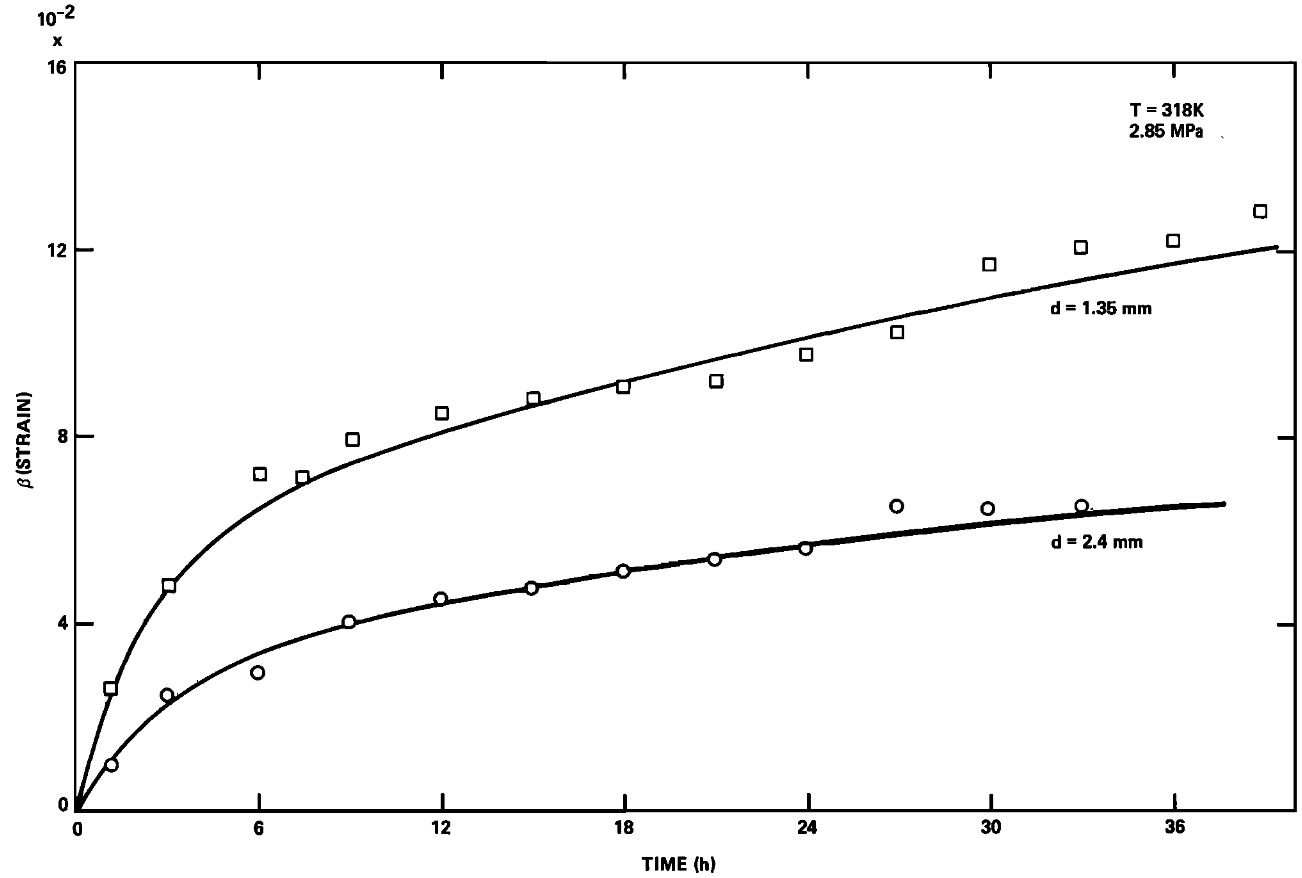

Fig. 4. Typical curves for densification creep.

Discussion of the Flow Equations

The equations for flow are given in the right-hand column in Table 1. They call for a creep rate which is slower than either the interface controlled or the diffusion controlled creep rate. In practice, though, the difference between the two may be so large that only one of them, the slower one, need be considered.

The constitutive equations contain terms which include the loading parameters (σ_e, p_e, p_0, and T), terms which depend on the thermodynamic and kinetic properties of the system (ΔH,

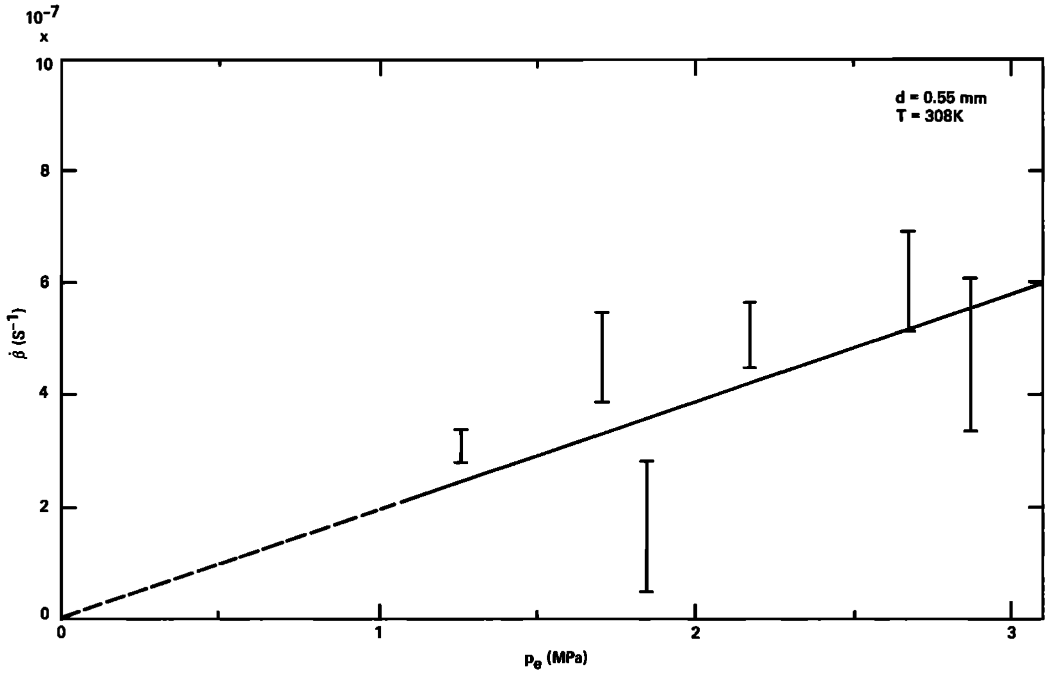

Fig. 5. Stress dependence of the densification creep rate.

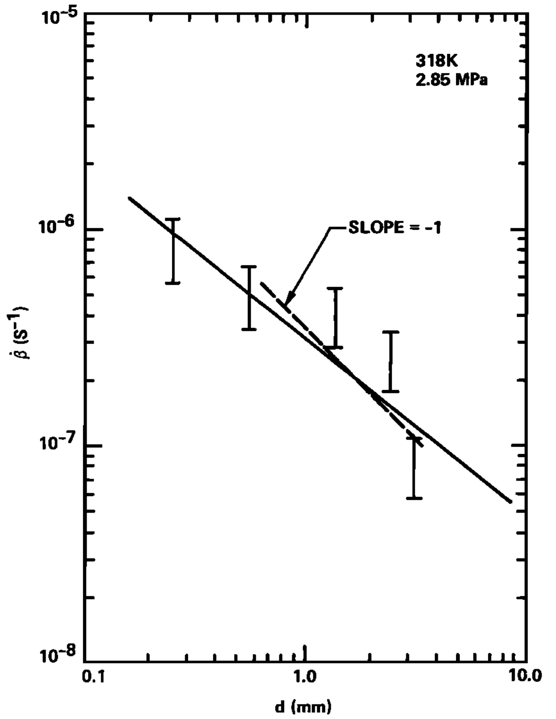

Fig. 6. Grain size dependence of the densification creep rate.

ΔV, k_1', and η), and terms which represent the microstructure (α, x, and d). Although it may be possible to do controlled experiments in simple model systems, it is unlikely that all these parameters would be known in complex multicomponent systems found in the earth. As such, a simple way of distinguishing between interface reaction and diffusion would be to measure the grain size dependence of the creep rate, which is d^{-3} for diffusion control and d^{-1} for interface control. The solubility of the crystal in the fluid phase is important in solution-precipitation creep and is included in the equations through the parameter $\bar{c}$.

The applied pressure and the pore pressure both influence creep flow. The difference between them defines the effective pressure (equation (4)) which leads to densification. On the other hand, the pore pressure, by itself, can influence solubility (equation (8)) and therefore the deviatoric creep rates.

As was discussed earlier the densification creep rate will be nonlinear in time unless $p_e \gg \gamma/r$, for the simple reason that r will decrease with densification. As a result, $\dot{\beta}$ will decrease with time. In fact, when r becomes so small that (7) is satisfied, then densification would stop.

Experiments

The data on the effect of grain size on creep in partially liquid aggregates is meager. Our group has reported measurements of creep in a β spodumene lithia-alumino-silicate glass ceramic system [*Raj and Chyung*, 1981]. The comparison with theory was quite good. The stress dependence of the creep rate was linear, and grain size dependence was d^{-1}, which suggested interface control. Further, the kinetic data for $k_1'\bar{c}$ were obtained independently. They were used in conjunction with equation (A) in Table 1 to compare the magnitudes of the experimental and theoretical creep rates. Good agreement was obtained.

Here another set of data are reported which also support the interface controlled model. Experiments for densification creep were carried out on aggregates of rock salt crystals immersed in a solution of saturated brine (made with distilled water). High-purity salt crystals were obtained from the Harshaw Chemical Company and were cleaved into small crystals in order to prepare aggregates with a varying gain size. The crystallites were packed into a stainless steel chamber shown in Figure 3, and the densification creep was measured by means of an LVDT. The temperature was kept constant to within ±0.1 K with the use of a water bath. The presence of excess saturated water assured that the pore pressure remained constant at 1 atm. The chamber was kept sealed by means of a flexible impermeable rubber. The size of the deformation chamber was 7.6-mm diameter in cross section, while the height varied from 6 mm to 20 mm.

The results from the creep measurements are included in Figures 4 through 6. Typical creep curves are shown in Figure 4. the stress dependence of the creep rate in Figure 5, and the grain size dependence of the creep rate in Figure 6. There is considerable scatter in the data. A possible explanation is that the packing of the crystals was different from test to test which would have resulted in some variability in r and, therefore, in the driving force. At the time that the experiments were done, we had not realized the importance of the initial packing desity. If we were to repeat the experiments, we would first make cold compacts from the crystallites before subjecting them to creep. Nevertheless, the suggestion from the present results is that the densification creep rate, $\dot{\beta}$, is about linearly proportional to p_e, and inversely proportional to d. In accordance with equation (D) in Table 1, the implication then is that the creep rate in our experiments was being controlled by interface reaction.

Summary

1. In deformation induced by diffusional transport, molecules must be removed from one two grain junction and deposited at the neighboring two grain junction. For rapid diffusion through the two grain junction, it is necessary that the fluid have access to all parts of the interface and also support a gradient in normal traction along the interface. This requires a study of the atomic structure of the two grain junctions that contain a liquid. There are no such studies yet available. A possible structure which would reconcile both of these requirements is an island structure in which the stresses are supported at regions of good fit while the interpenetrating fluid provides a path for rapid mass transport.
2. The kinetics of solution-precipitation creep may depend not only on the rate of diffusion through the liquid phase, but also on the interface reaction by which the molecules are attached or removed from the crystal interfaces. The latter process resembles crystal growth (or dissolution) from a liquid solution. In those instances where creep is interface reaction controlled, the kinetics of creep will be related to the kinetics of crystal growth.
3. Expressions for deviatoric creep rate and densification rate have been derived and are summarized in Table 1. Note that the grain size dependence is d^{-3} for diffusion control and d^{-1} for interface control.
4. When an effective pressure (equal to mean stress minus the pore pressure) is applied, the aggregate will densify and liquid will be squeezed out. However, all liquid cannot be squeezed out by this process. The amount of liquid remaining at equilibrium is given by (7).
5. The experimental evidence, which so far is rather limited,

suggests that the interface control may be the more important mechanism in solution precipitation creep.

APPENDIX A

Derivation for g_e

We derive here an approximate form for the average value of g_e. For simplicity we consider the grains to be in the shape of cubes with the faces aligned in the direction of the principal stresses. If we assume, as is the common assumption in theory of plastic flow [*Hill*, 1950], that the direction of the principal strain rates coincides with the direction of the principal stresses, that the constant volume condition is maintained (i.e., the Poisson's ratio equals 1/2), and that the equivalent strain rate is defined by the following equation:

$$\dot{\varepsilon}_e = \frac{\sqrt{2}}{3}\left[(\dot{\varepsilon}_1 - \dot{\varepsilon}_2)^2 + (\dot{\varepsilon}_2 - \dot{\varepsilon}_3)^2 + (\dot{\varepsilon}_3 - \dot{\varepsilon}_1)^2\right]^{1/2} \qquad \text{(A1)}$$

then the rate of doing work in the solid will be $\sigma_e\dot{\varepsilon}_e$. When the grains elongate as a result of creep, a small part of this work is converted into internal energy in the form of increased grain boundary area. The remainder is spent in the dissipative processes of transporting atoms by diffusion. From the first law of thermodynamics,

$$\dot{Q} = \dot{W} - \dot{U} \qquad \text{(A2)}$$

where $\dot{W}$ is the rate of doing work on the system, $\dot{U}$ is the rate of increase in the internal energy of the system, and $\dot{Q}$ is the heat flow rate out of the system. For our problem it easily can be demonstrated that $\dot{U} \ll \dot{W}$, so we shall seek an expression for g_e by equating $\dot{W} \simeq \dot{Q}$. By the arguments given above,

$$\dot{W} = \sigma_e\dot{\varepsilon}_e \qquad \text{(A3)}$$

per unit volume. The dissipated work will be equal to (the driving force per atom $= g_e$) × (number of atoms transported to achieve the strain rate $= \dot{\varepsilon}_s \times d^3/\Omega$) × (average distance travelled by the atom $= d/2$) ÷ (volume of the grain $= d^3$). Hence

$$\dot{Q} = g_e \frac{\dot{\varepsilon}_{ed}}{2\Omega} \qquad \text{(A4)}$$

where Ω is the molecular volume and d is the grain size. Equations (A2) and (A3) lead to the result quoted in (5) in the text.

Derivation for g_p

Again we use the first law of thermodynamics (equation (A2)), except this time $\dot{U}$ is substantial and we include it in the analysis. We consider the densification creep of a saturated aggregate under the influence of an applied pressure p, while the pore pressure of the fluid is p_0. The effective pressure then is

$$p_e = p - p_0 \qquad \text{(A5)}$$

If V is the total volume and V_g is the fluid volume then we have that

$$\dot{V} = \dot{V}_g \qquad \text{(A6)}$$

since the crystalline volume remains constant. $\dot{W}$ is then given by

$$\dot{W} = p_e\dot{V} \qquad \text{(A7)}$$

and the dissipative work by

$$\dot{Q} = g_p \times \frac{d}{2} \times \frac{\dot{V}_g}{\Omega} \qquad \text{(A8)}$$

where g_p is the average driving force per atom, and $d/2$ is average distance of travel (d being the grain size).

When the volume decreases, liquid is squeezed out of the pores at the triple junctions. There is a change in the surface energy configuration of the triple junction since more of the crystal-liquid interface is replaced by the crystal-crystal interface. For the geometry shown in Figure 2, the changes in the surface area are related uniquely to the amount of liquid squeezed out of the triple junction, and it can be shown with the use of the geometrical relations given in the work of *Raj* [1981] that

$$\dot{U} = \frac{\gamma}{r}\dot{V}_g \qquad \text{(A9)}$$

when $\theta < \pi/6$. Applying (A5)–(A8) to (A2), we obtain an expression for g_p quoted as (6) in the text.

Stress Concentrations

An assumption implicit in the thermodynamic analysis used here is that the process is driven by the average stresses rather than by stress concentrations within the aggregate. Although stress concentrations will arise immediately upon the application of stress, they will be smoothed out by diffusion until steady state stresses compatible with long-range creep are established. This problem has been thoroughly examined in the literature where it has been shown that the relaxation time for stress relief is much smaller than the time scale over which significant diffusional creep is observed [*Raj and Ashby*, 1971; *Raj*, 1975].

APPENDIX B

We illustrate here the procedure for obtaining the rate equations quoted in Table 1.

In the general case, the driving force is expended partly in driving the interface reactions and partly in driving diffusion through the fluid. An approximate distribution of the potential distribution when both have about equal weight is shown by the schematic in Figure B1. A simple way to solve the coupled problem is to solve for the two limiting cases independently and then superimpose them using a dashpot analog as described in the text.

Interface Reaction Limited Case

Let us consider the creep problem. Again we assume the grains to be in the shape of cubes (this is an approximation but would yield results which are dimensionally correct and which are numerically correct to within a factor of about 2). In the interface limited case, all of the driving force will appear as a potential drop at the 'source' and 'sink' interface (see Figure B1). The total potential drop is $g_e d/2$ (this has units of energy per molecule), which will be distributed equally between the source and the sink. The rate of advance in the interface will be $k_1'\bar{c}$ × (potential drop across the interface), in units of meters per second, and the strain rate will be equal to the rate of interface advance divided by one half of the grain size. Substiuting for g_e from (5), these steps lead to the following equation for the strain rate:

$$\dot{\varepsilon}_e = \frac{k_1'\bar{c}}{d}\frac{\sigma_e\Omega}{kT} \qquad \text{(B1)}$$

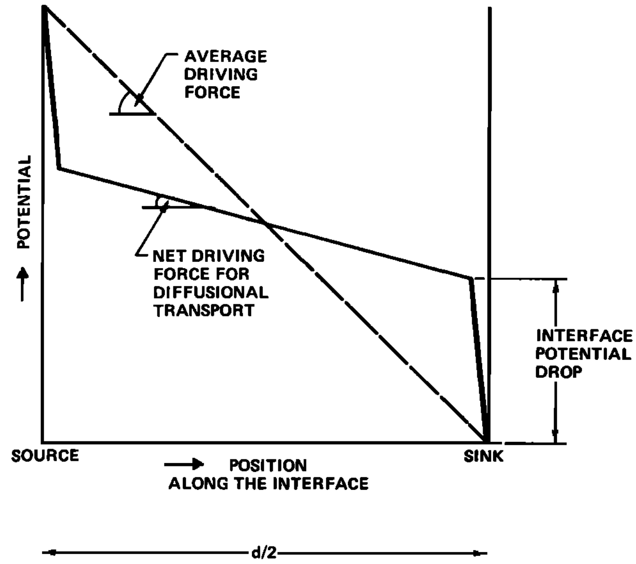

Fig. B1. The total potential drop is used partly to drive the interface reaction and partly to drive diffusional transport. In limiting cases, only one of these will be of overwhelming importance.

Exactly similar reasoning leads to an equivalent result for $\dot{\beta}$; remember that the volumetric creep rate is 3 times the linear creep rate if the total strains are small.

Diffusion Limited Case

We relate this creep rate to the viscosity of the fluid with the use of the Stokes-Einstein equation which correlates viscosity with diffusion:

$$\eta = \frac{kT}{6\pi bD} \tag{B2}$$

where b is the jump distance in diffusion and D is the diffusivity of the solute in the fluid [*Moelwyn-Hughes*, 1947].

For diffusional creep we use the equation for Coble creep in terms of equivalent stress and equivalent strain rate [*Coble*, 1964]. (Coble's equation contains an error of π [*Raj and Ashby*, 1971]. This has been corrected here. Also the result here is expressed in terms of equivalent stress and equivalent strain rate.)

$$\dot{\varepsilon}_e = 44\,\frac{\sigma_e\Omega}{kT}\,\frac{\delta D_b}{d^3} \tag{B3}$$

In (B3), δ represents the cross section for grain boundary diffusion and D_b represents the grain boundary self-diffusion coefficient. In the equivalent case being considered here, $\delta \equiv xh$, where x is the area fraction of the boundary occupied by islands and h is the thickness of the fluid layer. Also D_b is equivalent to $\bar{c}D$ where $\bar{c}$ is the mole fraction of the solute dissolved in the fluid [*Raj and Chyung*, 1981]. Making these substitutions in (B2) and (B3), we obtain

$$\dot{\varepsilon}_e = 2.3\,\frac{\sigma_e\Omega}{\eta d^3}\,\bar{c}\alpha \tag{B4}$$

where $\alpha = xh/b$; as a first approximation we may assume that $\alpha \approx 1$. The equivalent expression for $\dot{\beta}$ is obtained by substituting for σ_e by $(p_e - \gamma/r)$, and by multiplying by 3 to convert linear strain rate into volumetric strain rate.

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