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## Diffusion and plasticity at high temperature

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**Résumé.** — La déformation plastique à haute température met en jeu des migrations atomiques, quel que soit le mécanisme de déformation. Les lois de comportement contiennent donc un coefficient de diffusion et la vitesse de déformation obéit à une loi d'Arrhenius. Dans cet article, qui ne concerne qu'un seul type de déformation, le fluage visqueux, on s'efforce de préciser la nature des processus de diffusion — et du coefficient de diffusion — mis en jeu dans le cas des alliages et des composés.

**Abstract.** — High temperature plastic deformation requires atomic migration whatever the mechanism of deformation. The constitutive equations contain a diffusion coefficient and the deformation rate follows an Arrhenius law. This paper will only discuss the case of viscous creep in order to elucidate the nature of the diffusion processes and the expression of the diffusion coefficient involved in alloys or compounds.

### 1. Introduction.

The driving force for atomic migration is necessarily a gradient of a thermodynamic potential, which can be either the usual chemical potential — whence a flux proportional to the gradient of concentration, i.e. the *Fickian term* — or any other potential, such as an electric, thermal, or mechanical potential, giving rise to a *drift* (or « transport ») *term* in flux equations. In the simplest way :

$$\mathbf{J} = -D \nabla C - (DC/kT) \nabla \Phi .$$

This last term, rather than Fickian diffusion, is involved in high temperature deformation and this transport process can make up a controlling step of the whole plasticity process (power law or recovery creep), or the main step when the deformation derives from the flow of matter (viscous or diffusional creep ; cavitation).

While the case of elemental materials (i.e. pure metals) is rather simple and well understood, the alloys and compounds raise several problems, because several chemical species are involved in the diffusional process. The fluxes of these species cannot be independent but their differences require some coupling — from which an « effective » diffusion coefficient is derived — and lead so some chemical segregation. Because of this segregation, the Fickian term is no more negligible, and after a transient stage, a steady state (S.S.) is reached where both terms in flux equations are involved to determine  $J_{ss}$ , the steady state current (Fig. 1).

In polycrystalline materials, grain boundaries (G.B.'s) make these segregation and coupling problems still more complicated, mainly in alloys and compounds. G.B.'s can act either as short-circuits (G.B. diffusion), or as traps (G.B. segregation), or as source and sinks of point defects (vacancies or interstitials), or still as a component of plastic deformation (grain boundary sliding).

Because of the limitation of space, I chose to limit this paper to the so-called viscous or diffusional creep. Diffusional creep is perhaps the best case to begin with, as the plastic deformation is due to the transport of matter, i.e. to diffusional processes. A *viscous* type constitutional equation is easily derived [1] where the creep rate does not depend on time and is inversely proportional to the square of the grain size (volume diffusion controlled or Nabarro-Herring creep [1-2] or to the cube of the grain size (grain boundary diffusion controlled, or Coble creep [3]).

Nevertheless, this relation is derived from a simple model, which considers an isolated square shaped crystal, submitted to biaxial normal stresses — or to a shear stress.

Constraints on the deformation process imposed by adjacent grains or by surface tension effects cannot be neglected, as they make the local stress state different from the macroscopic one. I shall not discuss this topics here, but I shall focus on transport processes. In this respect other constraints are forgotten in the simple model : the surface of the crystal, or the grain boundaries in a polycrystalline specimen are assumed to be perfect sources and sinks of point defects (\*). The change in the shape of the crystal which requires grain boundary sliding is no more taken into account.

## 2. Nabarro-Herring Creep.

Let us consider a square shaped crystal, submitted to a biaxial stress as shown in figure 2 (deviatoric part). A vacancy flow is generated from the top and bottom faces to the side faces. Let us restrict our discussion to the flux of vacancies through the volume of the crystal. In a substitutional binary AB alloy, the diffusivities of A and B species are different : there will be a *transient stage*, in which the vacancies exchange preferentially with, let us say, species A (if  $D_A > D_B$ ), producing a *segregation* [8]. In a later stage, the chemical gradients due to this segregation will stop this process by tending to eliminate any differences in diffusional fluxes of both species, and a *steady state* will be obtained (Herring [2] ; R. Fuentes-Samaniego *et al.* [9, 10] (Fig. 1).

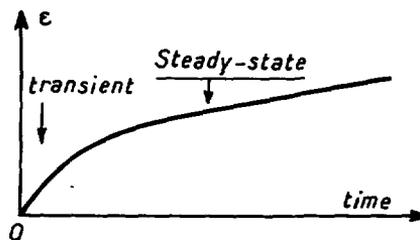


Fig. 1. — Viscous creep deformation *versus* time.

(\*) The observation of a threshold stress on pure metals and ceramics ( $\text{Al}_2\text{O}_3$ ) at intermediate temperatures, which is strongly *temperature dependent*, shows that G.B. per se are not necessarily perfect sinks or sources. A model based on grain boundary dislocation climb by jog nucleation and movement would be able to account for this threshold stress (Misra *et al.* [4]). Another model suggests a  $\sigma^2$  dependence at low stresses (Burton [5], Ashby-Verral [6, 7]).

*Transient stage* : The flux of A, B and vacancies are given by (see e.g. Philibert [11]) :

$$\begin{aligned} J_A &= -\frac{L_{AA}}{T} \nabla(\mu_A - \mu_V) - \frac{L_{AB}}{T} \nabla(\mu_B - \mu_V) \\ J_B &= -\frac{L_{BA}}{T} \nabla(\mu_A - \mu_V) - \frac{L_{BB}}{T} \nabla(\mu_B - \mu_V) \\ J_V &= -J_A - J_B \end{aligned} \quad (1)$$

with  $L_{AB} = L_{BA}$ . The  $L_{ij}$  s are the so-called phenomenological coefficients.

During the first stage, the chemical potential gradient of vacancies is larger than the chemical potential gradient of the A and B species (initially  $\nabla\mu_A = \nabla\mu_B = 0$ ), whilst the stress state creates a vacancy chemical potential gradient  $\nabla\mu_V \propto \Omega(\sigma_z - \sigma_x)$  where  $\Omega$  is the average atomic volume (Fig. 2).

There :

$$J_V = -\frac{L_{AA} + 2L_{AB} + L_{BB}}{T} \cdot \nabla\mu_V. \quad (2)$$

As well known the deformation rate is given by :

$$\dot{\epsilon} \approx J_V \Omega / L$$

where  $L$  is the grain size.

The difficulty which we have to cope with lies with the phenomenological coefficients  $L_{ij}$ .

The simplest assumption gives :

$$\begin{aligned} L_{AA} &= \frac{n_A D_{A^*}}{k}, \\ L_{BB} &= \frac{n_B D_{B^*}}{k}, \\ L_{AB} &= 0, \end{aligned} \quad (3)$$

where  $D_{A^*}$  and  $D_{B^*}$  are the tracer diffusion coefficients in the alloy, supposed to be constant in the involved range of composition and  $n_i$  the concentrations. From equations (1), (2) and (3), the vacancy flux is given by :

$$J_V = -\frac{n}{kT} \bar{D} \nabla\mu_V, \quad (4)$$

with

$$\bar{D} = N_A D_{A^*} + N_B D_{B^*} \quad (5)$$

where  $N_A$  and  $N_B$  are mole fractions and  $n = n_A + n_B$ .

Fuentes-Samaniego *et al.* [9] chose for the  $L_{ij}$  the values Manning derived for his model alloy [12] (a mean field model for a disordered alloy, with two vacancy jump frequencies according to its exchanges with A or B atoms, whatever be its other neighbours). They end up with :

$$\bar{D} = \frac{1}{f_0} (N_A D_{A^*} + N_B D_{B^*}) \quad (5a)$$

where  $f_0$  is the correlation factor for tracer diffusion in the lattice. This transient stage will be

governed by the diffusion of the fastest component and the creep rate will decrease progressively down to the steady state regime, governed by the diffusion of the slowest species as we shall see in the next paragraph. This conclusion holds as far as the G.B.'s do not migrate (see below).

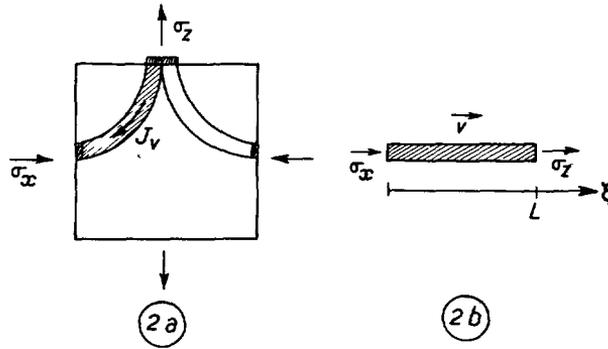


Fig. 2. — Stress state and diffusion path in a grain.

**3. Steady state stage.**

A non divergent velocity field is assumed, so that the problem may be translated in a linear one, i.e. with a series of parallel tubes (Fig. 2). Let us consider one of these small tubes as an element of volume submitted to a vacancy flux  $J_v$ . Due to this flux, one end of the tube is progressing at a velocity  $v$  while the other is regressing (Fig. 2b). Diffusion of A and B have to be described in a frame of reference moving at  $v$  so that for the steady state :

$$J_A = J_B = 0 \tag{6}$$

and in the fixed frame of reference :

$$\begin{aligned} J_A^0 &= n_A v = - \frac{N_A}{1 - N_V} J_V^0 \\ J_B^0 &= n_B v = - \frac{N_B}{1 - N_V} J_V^0 \end{aligned} \tag{7}$$

which ensures that everywhere the composition remains constant since (steady state) :

$$J_A^0 / J_B^0 = N_A / N_B . \tag{8}$$

The vacancy flux is given by :

$$\begin{aligned} J_V^0 &= (n - n_V) v , \\ J_V &= J_V^0 - n_V v = - n v . \end{aligned}$$

In the mobile frame of reference flux equations have to include a third term on the right hand side, namely  $n_i v$ .

Neglecting the cross terms :

$$\begin{aligned}
 J_A &= -\frac{L_{AA}}{T} \frac{d}{d\xi} (\mu_A - \mu_V) - n_A v \\
 J_B &= -\frac{L_{BB}}{T} \frac{d}{d\xi} (\mu_B - \mu_V) - n_B v .
 \end{aligned}
 \tag{9}$$

The Gibbs-Duhem relationship can be written :

$$N_A \frac{d}{d\xi} (\mu_A - \mu_V) + N_B \frac{d}{d\xi} (\mu_B - \mu_V) = -\frac{d}{d\xi} \mu_V .$$

It follows from this equation and condition  $J_i = 0$  (Eq. (6)) :

$$\frac{d\mu_A}{d\xi} = -N_B \frac{D_{B^*} - D_{A^*}}{D_{A^*} D_{B^*}} kTv \tag{10a}$$

$$\frac{d\mu_B}{d\xi} = -N_A \frac{D_{A^*} - D_{B^*}}{D_{A^*} D_{B^*}} kTv \tag{10b}$$

$$\frac{d\mu_V}{d\xi} = \left( \frac{N_A}{D_{A^*}} + \frac{N_B}{D_{B^*}} \right) kTv . \tag{10c}$$

We have to integrate these equations from one end to the other of our tube, with the mass conservation condition :

$$\int_0^L N_i d\xi = N_i^0 L .$$

With  $N_i^0$ , initial composition of the alloy, and

$$\mu_V(L) - \mu_V(0) = (\sigma_z - \sigma_x) \Omega . \tag{11}$$

Let us assume the  $D$ 's don't vary significantly in the involved range of composition :

$$v = D_{SS} \frac{\sigma_z - \sigma_x}{kT \cdot L} \Omega \tag{12}$$

with

$$\boxed{\frac{1}{D_{SS}} = \frac{N_A^0}{D_{A^*}} + \frac{N_B^0}{D_{B^*}}} \tag{13}$$

an expression known as the Herring' formula [2].

This is just the same relation as the one derived by assuming a constant composition thanks to a coupling of fluxes  $J_A^0$  and  $J_B^0$  (Li *et al.* [13]) with some phenomenological forces. The above derivation gives a simple physical meaning to this coupling, as the velocity terms in equation (9).

Integrating the chemical potentials for A and B leads to

$$\begin{aligned}
 \text{Log} \frac{(\gamma_A N_A)_L}{(\gamma_A N_A)_0} &= -N_B^0 R , \\
 \text{Log} \frac{(\gamma_B N_B)_L}{(\gamma_B N_B)_0} &= -N_A^0 R ,
 \end{aligned}
 \tag{14}$$

with the segregation parameter  $R$  :

$$R = D_{SS} \frac{D_{B^*} - D_{A^*}}{D_{A^*} D_{B^*}} \frac{(\sigma_z - \sigma_x)}{kT} \Omega , \tag{15}$$

whence, for an ideal solution, with small gradients :

$$\nabla N_A = N_A^0 (1 - N_A^0) \frac{D_{A^*} - D_{B^*}}{N_A^0 D_{B^*} + N_B^0 D_{A^*}} \frac{\Omega \nabla \sigma}{kT} \tag{16}$$

Moreover, for an ideal solution

$$N_B(0) = \frac{1 - \exp(N_B^0 R)}{1 - \exp R} \tag{17}$$

$$N_B(L) = \frac{1 - \exp(-N_B^0 R)}{1 - \exp(-R)}$$

As for as  $R$  is small enough, the segregation between two faces is approximately given by [8, 9] :

$$\Delta N_B = N_B(L) - N_B(0) \approx RN_B^0 (1 - N_B^0) \tag{18}$$

whose maximum is  $R/4$ . Predicted concentration profiles were calculated for ideal and regular solution, on the basis of Manning's model (Fig. 3).

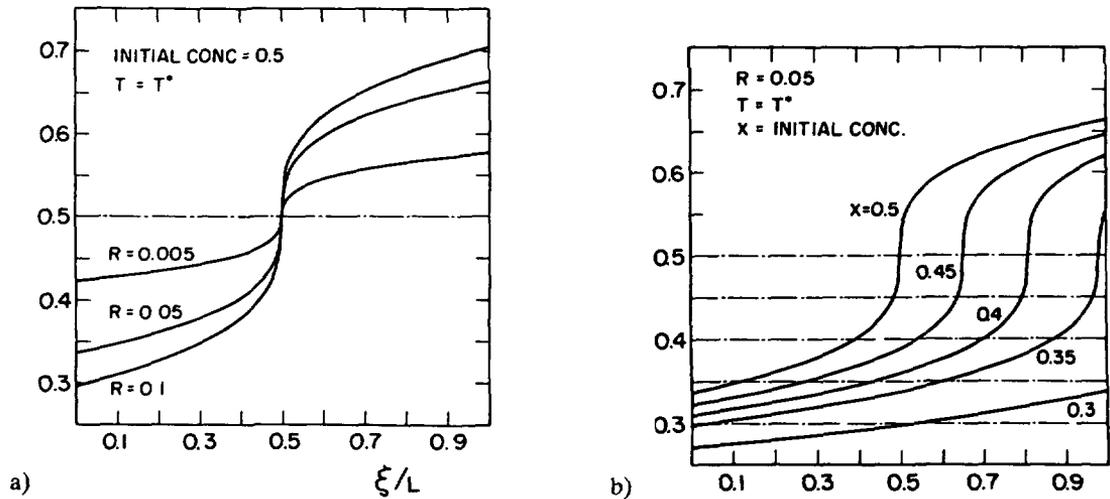


Fig. 3. — a) Concentration profiles for different values of the segregation parameter  $R$  in a regular solution. Initial concentration 50-50. After [9]. b) Concentration profiles for different values of the initial concentration in a regular solution. After [9].

The above calculation predicts a higher segregation at lower temperature, where the controlling mechanism would probably be grain boundary diffusion. Moreover, in a regular solution at temperatures lower than the critical temperature, *demixing* is expected. Interestingly the first experimental evidence in favour of the Nabarro-Herring mechanism

came from an observation of some « dehomogenisation » in a Mg – 0.5 % Zr alloy : ZrH<sub>2</sub> precipitates were created by annealing the material, so that during creep only magnesium atoms were migrating toward GB's perpendicular to the tensile axis, creating precipitate free — or denuded — zones near these GB's [14, 15].

#### 4. Coble creep.

The driving force for mass flow is the same as above, but the whole mass flow now takes place by diffusion along the grain boundaries. let the prime denote G.B. quantities and let us use the classical model of a G.B. stripe characterized by a diffusivity  $D'$  and a thickness  $\delta$ . The flux of matter is then written :

$$J' \delta = - \frac{D' \delta}{\Omega kT} \nabla(\mu - \mu_V). \quad (19)$$

Since the deformation is uniform on a face, the quantity of material deposited per unit area and unit time should be constant

$$\frac{\partial n}{\partial t} = - \delta \operatorname{div} J' = \text{constant} > 0. \quad (20)$$

But for a binary alloy in the steady state, the composition remains constant a condition which now reads :

$$\frac{\operatorname{div} J'_A}{N_A} = \frac{\operatorname{div} J'_B}{N_B}. \quad (21)$$

A transient stage is expected, where mutatis mutandis, the same equations (2, 5) as above will apply, and its followed by this stationary stage.

Following Li *et al.* [13], this problem can be solved by introducing a coupling force between atom fluxes :

$$\begin{aligned} J'_A \delta &= - \frac{n_A D'_A \delta}{kT} (\nabla(\mu_A - \mu_V) + F_A) \\ J'_B \delta &= - \frac{n_B D'_B \delta}{kT} (\nabla(\mu_B - \mu_V) + F_B) \end{aligned}$$

with  $n_A F_A + n_B F_B = 0$  (see e.g. Philibert [11] p. 211). Assuming  $n_A$  and  $n_B$  independent of the position on an interface, the condition on  $J'_i$ , equation (21) gives :

$$\operatorname{div} F_A = \frac{1}{kT} \frac{D'_B \delta \nabla^2(\mu_B - \mu_V) - D'_A \delta \nabla^2(\mu_A - \mu_V)}{D'_A \delta + \frac{n_A}{n_B} D'_B \delta}$$

and therefore :

$$\operatorname{div} J'_A \delta = - \frac{1}{kT} \frac{n_A n_B D'_A \delta D'_B \delta}{n_B D'_A \delta + n_A D'_B \delta} \nabla^2 \left[ \frac{n_A}{n_B} (\mu_A - \mu_V) + (\mu_B - \mu_V) \right].$$

With  $\mu_m = N_A \mu_A + N_B \mu_B$  for a « molecule » of AB, and  $\Omega = 1/(n_A^0 + n_B^0)$  the « molecular » volume, one ends up with :

$$\operatorname{div} J'_A \delta = - \frac{n_A D' \delta}{kT} \nabla^2(\mu_m - \mu_V).$$

Integrating with assumption of quasi constant  $n_i$ ,  $D'_i$  :

$$J'_A \delta = - \frac{n_A D' \delta}{kT} \nabla(\mu_m - \mu_v) \quad (22a)$$

and

$$J'_V \delta = - J_A - J_B = \frac{D' \delta}{kT\Omega} \nabla(\mu_m - \mu_v) \quad (22b)$$

i.e. the same relation as for a pure metal, equation (19), with the effective grain boundary diffusivity :

$$\bar{D}' \delta_{SS} = \frac{D'_A \delta D'_B \delta}{N_B^0 D'_A \delta + N_A^0 D'_B \delta} \quad (23)$$

which is formally identical to the steady state volume diffusivity (Eq. (13) above).

The same conclusions as above for volume diffusion can be derived about the possibility of segregation or demixing, although this quantities should have to be calculated in the case of G.B. diffusion. They are probably not very different in both cases.

### 5. General case.

In the general case of viscous flow, both volume and G.B. diffusion contribute to mass transport. The strain rate retains the same form as for Nabarro-Herring creep, but with the introduction of a *composite diffusion coefficient*, that is a combination of the volume and G.B. self-diffusion coefficients :

$$D_{\text{comp}} = D \left[ 1 + \frac{\beta \delta}{L} \frac{D'}{D} \right] = D + \frac{\beta \delta}{L} D' \quad (24)$$

with  $\beta \approx 3$ , a geometrical factor depending on the shape of the grains.

Let us recall that an identical formula was derived by Raj and Ashby [16] to describe grain boundary sliding. The origin of this identity lies in the fact there cannot be any viscous creep without G.B. sliding — nor G.B. sliding without accommodation by mass transport by volume and G.B. diffusion (or by plastic flow by dislocations if the stresses are high enough). Both processes are necessarily coupled.

In a binary alloy, we have now to face with this composite diffusivity and with the effective  $D$ 's we derived above.

As the boundary conditions are not the same for volume and G.B. mass transport, it seems physically more reasonable to consider the specimen as a « composite » material : we shall couple A and B fluxes first separately in the volume « phase » and in the G.B. « phase », and finally according to equation (24) for the composite

$$D_{\text{comp}} = \frac{D_A D_B}{N_A D_B + N_B D_A} + \frac{\beta \delta}{L} \frac{D'_A D'_B}{N_A D'_B + N_B D'_A} \quad (25)$$

with the simplest formula describing the steady state (Eqs. (13) and (23)).

According to equation (25) the process will be governed by the *slowest species diffusing along its easiest path*. This conclusion does not hold any more when G.B.'s are allowed to migrate. As noticed by Chen [17] a migrating G.B. leaving its excess concentration behind to an alloyed or dealloyed zone in its wake will facilitate the G.B. diffusion of the *fastest species* (see Eq. (5) applied to G.B. diffusion), by reducing the concentration gradient (or

segregation) on the G.B. which raises during the transient stage in the case of a stationary G.B. In such a case, equation (23) does not apply any more, and because the fluxes are no more to be coupled, a relation similar to equation (5) will result, so that [17]:

$$\dot{\epsilon} = \text{constant} \frac{\overline{D'}\delta}{L^3} \sigma \frac{\Omega}{kT}$$

with

$$\overline{D'}\delta = N_A^0 D'_A \delta + N_B^0 D'_B \delta .$$

The creep rate will be governed by the *fastest* species diffusing along G.B.'s. This process could be akin to « DIGM » (Diffusion Induced Grain Boundary Migration) and still be enhanced when one of the component species — let us say B — has a tendency to G.B. equilibrium segregation — in which case the flux would be proportional to  $N_B D'_B \delta$  with  $N_B \gg N_B^0$ .

The creep rate will be quite larger than predicted by the usual rule. This is the reason why according to Chen [17] this induced G.B. migration and alloy decomposition or unmixing could be observed during superplastic deformation.

Such effects do not seem to have been experimentally observed as yet — although some changes in the morphology of  $\gamma'$  precipitates in superalloys could be relevant to this mechanism [8].

## 6. Stoichiometric compounds.

In the case of ionic crystals,  $A_\alpha B_\beta$ , the condition of electroneutrality imposes that the two fluxes obey the relation :

$$\frac{|J_A|}{\alpha} = \frac{|J_B|}{\beta} \quad (26)$$

The coupling of fluxes is realized *via* the internal electric field, the so called Nernst field,  $E_d$  :

$$\begin{aligned} J_A &= -D_{A^*} \frac{\partial n_A}{\partial x} + q_A E_d \frac{D_{A^*}}{kT} n_A , \\ J_B &= -D_{B^*} \frac{\partial n_B}{\partial x} + q_B E_d \frac{D_{B^*}}{kT} n_B . \end{aligned} \quad (27)$$

The condition for constant composition in an intermetallic compound imposes the same condition as (26) which is made possible by introducing a coupling force  $F_A, F_B$  in the flux equations, formally similar to the electric field. In both cases, one ends up [13] with an effective or molecular diffusion coefficient :

$$D_{\text{mol.}} = \frac{D_{A^*} D_{B^*}}{\alpha D_{B^*} + \beta D_{A^*}} , \quad (28)$$

corresponding to the transport of a « molecule »  $A_\alpha B_\beta$ . Expression (28), is identical to equation (13) derived above for steady state in alloys. The simplest form of the equation works as far as the two sublattices are really independent, i.e. there are no cross terms in flux equations ( $L_{AB} = 0$ ).

But if some departure from stoichiometry is allowed, a transient stage introducing some

segregation is expected. Such a segregation does not seem to have been observed as yet.

When  $D_{A^*} \gg D_{B^*}$ , the molecular diffusion coefficient reduces to :

$$D_{\text{mol.}} \approx D_{B^*}/\alpha . \quad (29)$$

Many oxides, where the diffusivity of oxygen is very much lower than that of the metal, have their creep rate controlled by the volume diffusivity of the slowest species, i.e. the oxygen.

This result can be confirmed, in non stoichiometric oxides by the  $p(\text{O}_2)$  dependence of the creep rate, as  $D_M^*$  and  $D_{\text{ox}}^*$  do not vary with the same power of  $p(\text{O}_2)$ . Several results are in agreement with this prediction : see the critical reviews by Cannon and Langdon [18], and Castaing and Monty [19] (Fig. 4).

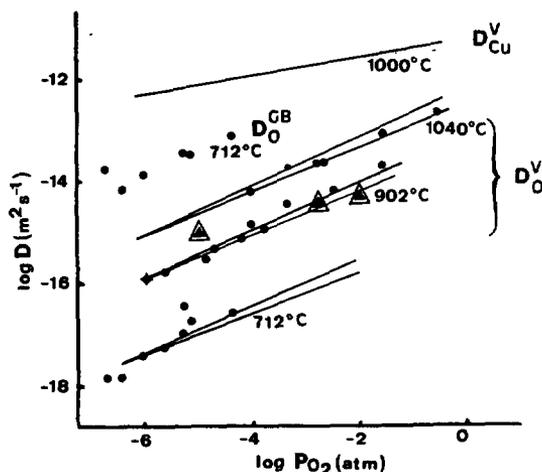


Fig. 4. — Variation with  $p\text{O}_2$  of the self-diffusion coefficients of copper  $D_{\text{Cu}}^{\text{V}}$  and oxygen  $D_{\text{O}}^{\text{V}}$  in  $\text{Cu}_2\text{O}$ . Triangles correspond to  $D_{\text{O}}^{\text{V}}$  calculated from pure diffusional creep at 902 °C. After [19].

But in other cases ( $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{BeO}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{UO}_2$  [18]) a better agreement between creep and diffusion data is found with the (volume) fastest species. This observation contradicts the usual opinion, based on the « composite » model, that the creep process would be controlled by the *slowest species* moving along its *fastest path*. A very fast diffusion of oxygen along G.B.'s has been assumed, so that the creep rate would be controlled by the lattice cation diffusion, in spite that  $D_{\text{cation}}^* \gg D_{\text{ox}}^*$  (see for the case of  $\alpha - \text{Al}_2\text{O}_3$ , Cannon *et al.* [20]).

As a matter of fact, the uncertainties in the diffusion coefficient values make such a conclusion rather frail, as one generally observes that when  $D_{\text{cat}}^* > D_{\text{ox}}^*$ , then also  $D'_{\text{cat}} > D'_{\text{ox}}$  holds (see e.g. [21]), rather than the assumed inequality  $D'_{\text{cat}} < D'_{\text{ox}}$ , unless preferential doping, i.e. grain boundary segregation, would drastically modify the nature of point defects in G.B. — an assumption suggested by recent results of Prot *et al.* [22] for a very fast diffusion of oxygen along subboundaries in  $\text{Al}_2\text{O}_3$  single crystals and G.B.'s in polycrystalline specimens (with an activation energy very much larger than the volume one!).

A good theoretical derivation of the  $D_{\text{comp}}$  coefficient is still lacking for such a model. The way the fluxes have to be coupled is not clear, and when cations and anions diffuse mainly by different paths, a general expression for the electric field seems difficult to obtain. The situation is more straightforward for morphology changes due to capillarity (Blakely and Li

[23], when the kinetics of G.B. grooving or ripple smoothing is governed by the (faster) cation species : if oxygen lattice diffusivity is slow, the anions are easily transported through the vapour phase. Such a behaviour was observed in the case of G.B. grooving of NiO bicrystals by Dhalenne *et al.* [24]. But the oxygen surface transport — or its G.B. transport for creep — nevertheless raises some (as yet) unanswered questions for the flux coupling.

Another case is worth to be discussed : solid solutions confined to one of the two sublattices : such as  $(A, A')_{\alpha} B_{\beta}$ , or, to take an usual example, an oxide such as  $(A, B)O$  or  $AB_2O_4$ .

It is well known that any *thermodynamic potential gradient* provides a driving force for mass transport and can cause kinetic *demixing* or *decomposition* when the diffusivities of the constituents are different. Such phenomena have been observed due to gradients of temperature, of electrical potential, or of oxygen activity in the case of oxides. Let us quote the very elegant experiments by Schmalzried *et al.* [25].

In the same way one expects segregation (or demixing) in an  $(A, B)O$  oxide solid solution submitted to a stress gradient, when the mobilities of AO and BO are different — a condition realized with a very high oxygen diffusivity and  $D_A \neq D_B$ . If  $D_A > D_B$ , a higher concentration in species A is expected near those grain boundaries submitted to the higher tensile stress. This concentration gradient will build up during a transient stage, until it opposes to further segregation when the steady state is reached. In the same way a stoichiometric compound such as  $A_2BO_4$  can be broken down into its constituent binary oxides AO and  $BO_2$ .

A theoretical treatment of both processes has been given by Dimos *et al.* [26]. In the limit of fast oxygen diffusion, Dimos *et al.* essentially follow the same lines of derivation as above for alloys, and they arrive at the same formula for the segregation, equations (16) and (18), with  $\Omega$  as the molar volume assumed identical for AO and BO.

They also show that such a demixing is impossible in the limit of fast cation diffusion ( $D_A, D_B \gg D_{ox}$ ). Moreover they derived a value of the relaxation time characteristic of the transient regime :

$$\tau = L^2 / \pi^2 \tilde{D} \quad (30)$$

where  $\tilde{D}$  has the form of a Darken-type interdiffusion coefficient :

$$\tilde{D} = N_B^0 D_A + N_A^0 D_B \quad (31)$$

Demixing can be viewed as an *interdiffusion* process in a moving frame of reference, with velocity  $v$  (cf. Fig. 2b). The kinetics of demixing obey the law :

$$\Delta N(t) = \Delta N^{SS} [1 - \exp(-t/\tau)] \quad (32)$$

where the SS superscript holds for the steady state.

Dimos and Kohlstedt [27] tried to observe such a demixing during creep of yttria-stabilized zirconia. They did observe a Nabarro-Herring creep between 1 400 °C and 1 600 °C, with a grain size between 2.5 and 14.5  $\mu\text{m}$ . From creep data, they calculated an effective diffusion coefficient :

$$D_{\text{creep}} = 3 \times 10^3 \exp(-5.84 \text{ eV}/kT) \text{ cm}^2 \text{ s}^{-1}$$

in agreement to within a factor of 5 with the values of the tracer diffusion coefficients determined for Ca and Zr in calcia stabilized zirconia. The difference between formula (5) for  $D_{\text{transient}}$  and (13) for  $D_{SS}$  is immaterial. But kinetic demixing was *not* observed, a result

probably due to  $D_{Zr}$  and  $D_Y$  being almost equal. Similar failure occurred in (Co, Mg) O (Dimos *et al.* [28]) due to the fact that diffusion creep was limited by oxygen diffusion, although  $D_{CO} \sim 6$  to  $8 D_{Mg}$ .

More recently a segregation of aluminium and chromium in elongated grains of chromia spinel ( $Cr, Al, Fe^{3+}$ )<sub>2</sub> ( $Mg, Fe^{2+}$ ) O<sub>4</sub> has been measured in ultramafic rock from the upper mantle (Ozawa [29], and comment by Sammis [30]). The observed zonation of Al was measured with the electron microprobe on spinel grains about 100  $\mu m$  in diameter and found rather high : about 10 % across a grain (Fig. 5). This gradient is consistent with the lineation and the shape of spinel grains, i.e. with the stress level the rock was submitted to. Probably, geological times and very low creep rates offer better conditions than laboratory experiment conditions. Unfortunately the diffusion coefficients of Cr and Al in spinel are not known. Qualitative arguments favour larger diffusivity of Al, consistent with the enrichment of this element at the elongated (i.e. more tensile) grain boundaries, whilst again oxygen diffusivity is assumed to be very fast along grain boundaries.

Assuming  $D_{Al} \gg D_{Cr}$ , (16) reduces to :

$$\nabla N_A = N_A \frac{\Omega \nabla \sigma}{kT} \quad (33)$$

Using (Sammis, [30])  $N_A = 0,5$ ,  $\Omega = 10^{-4} m^3 mol^{-1}$ ,  $T = 1200 K$  as a typical upper mantle temperature, Ozawa's observed composition difference  $\Delta N_A \sim 0.1$  corresponds to a deviatoric stress of 10 MPa. According to Ashby's map [40] for this material this would correspond to a regime where oxygen diffusion occurs along G.B.'s and a strain rate of  $10^{-8}$ - $10^{-9} s^{-1}$ .

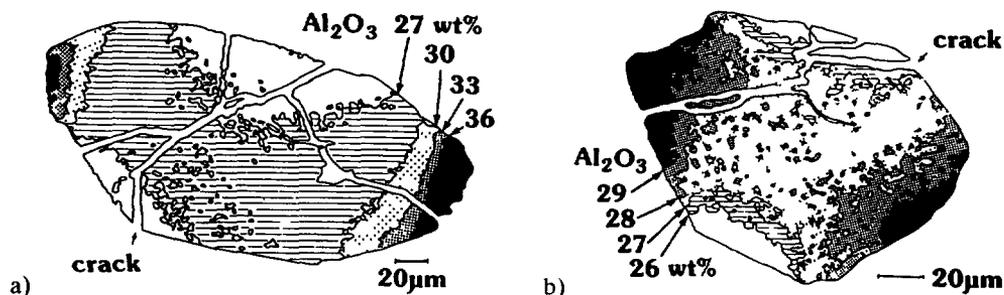


Fig. 5. — Compositional zonings of chromium spinel measured with the Electron Microprobe on thin sections parallel to (a) and perpendicular to (b) the mineral lineation. After [29].

### 7. Liquid phase enhancement.

Grain boundary liquid diffusion is a special type of G.B. diffusion which can generate creep deformation, (Rutter [31]), and probably operates in some ceramic materials (intergranular amorphous or glassy films due to the sintering process) and in many geomaterials where it is known as « pressure solution » (\*). As noticed by Pharr and Ashby [32], liquid-enhanced creep is familiar to skiers, due to the peculiar plasticity of wet snow and to dentists using the temporary plasticity of dental amalgams.

(\*) Although the driving force is not a pressure *stricto sensu*, but the equivalent (Von Mises) stress. Creep has not to be confused with pressure induced densification.

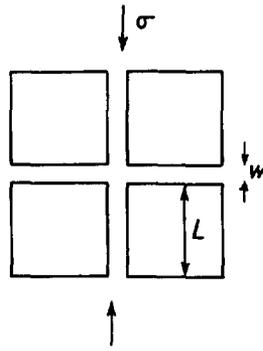


Fig. 6. — Liquid enhanced creep (Schematic).

A liquid film may enhance creep in two ways, either as a *lubricant* which facilitates the sliding of grains over each other or as a *high diffusivity* path — i.e. a series of three processes : dissolution, diffusion and redeposition.

In the first case, a strain proportional to the stress and inversely proportional to the liquid viscosity is expected (Fig. 6) :

$$\dot{\epsilon} = \text{constant} \left( \frac{w}{w + L} \right) \frac{\sigma}{\eta} \tag{34}$$

where  $w$  and  $L$  are defined in figure 6.

In the second model, i.e. diffusional flow, the process may be limited either by the dissolution rate or by the diffusion flow in the liquid film. Let us describe the dissolution kinetics by some kinetic constant  $k_1$ , which measures, in units of  $kT$ , the rate at which the atoms are exchanged between the crystal and the liquid. One ends up with [33] :

$$\dot{\epsilon}_k = \text{constant} \cdot \frac{\sigma \Omega k_1}{kT L} \tag{35}$$

On the other hand, if the kinetics is limited by the diffusion in the liquid, the situation becomes similar to Coble's model [3], with  $\delta = w$  and  $D = C_L D_L$ , where  $C_L$  and  $D_L$  are the solubility and diffusivity of the solid in the liquid phase :

$$\dot{\epsilon}_d = \text{constant} \cdot C_L D_L \frac{w \sigma \Omega}{L^3 kT} \tag{36}$$

Eventually if the solid and glassy phases will form a low melting point eutectic, the above diffusivity can be related to the viscosity  $\eta$  of this liquid through the Stokes-Einstein equation [33] :

$$\dot{\epsilon}_d = \text{constant} \cdot \frac{\sigma \Omega}{\eta L^3} \tag{37}$$

As both processes occur in series, the net creep rate will be given by :

$$\frac{1}{\dot{\epsilon}} = \frac{1}{\dot{\epsilon}_k} + \frac{1}{\dot{\epsilon}_d} \tag{38}$$

According to the slower process, the creep rate will vary as  $L^{-1}$  or  $L^{-3}$

The model of figure 6 is not very realistic ; if the liquid forms a continuous film in the G.B.'s, gradients of normal tractions could not be sustained as the fluid will flow to equalize pressure differences and will be squeezed out. Some solid contact between grains is necessary, whereby normal tractions and their gradients can be sustained. To solve this problem, Raj and Chyung [33] assumed an island structure of the G.B.'s, with channels filled by the liquid phase : their constants in equations (36) and (37) must contain a factor  $1/(1-x)$  where  $x$  is the fraction area of liquid film (this only represents a small part of the glassy phase, as most of it is concentrated in triple junctions (Fig. 7).

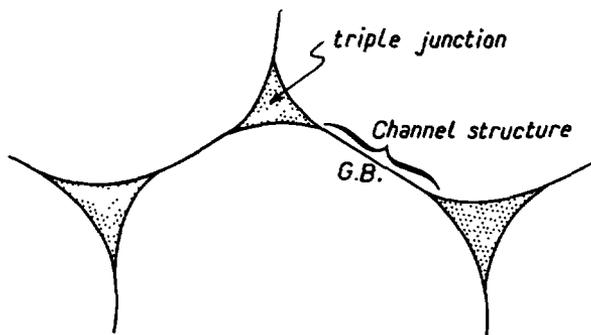


Fig. 7. — Microstructure with a residual glassy phase.

Facing the same problem, Pharr and Ashby [32] put forward a different model, based on a coupling of plasticity and dissolution processes. Their model is akin to pressure induced sintering. Necks between two grains are growing by (creep) plasticity. Due to capillarity forces, the liquid which is wetting the grains penetrates the boundary between two grains, thus eroding the neck between them. As the neck is eroded the local stress rises, so plastic flow occurs there causing further plastic deformation, i.e. neck growth. Pharr and Ashby derived the rate equation :

$$\dot{\epsilon} = \text{constant} \cdot \frac{C_L D_L \gamma \Omega}{L^3 kT} f(\sigma) \quad (39)$$

where  $\gamma$  is the solid/liquid interfacial energy,  $f(\sigma)$  is proportional to  $(\sigma_1 - \sigma_2)$ , so that the strain rate in uniaxial compression is still linearly dependent on stress. The model and equation (39) are valid only for *compressive* states of stress.

Experimental results verify the main predictions of these models : the creep rate is proportional to the stress (more exactly, the deviatoric part of the stress). The steady state creep rate vary with the temperature according to an Arrhenius law. But the grain size dependence is generally unknown.

## 8. Conclusion.

Viscous creep in alloys and compounds still deserves a lot of research. In spite of a very simple and direct relation between diffusion and plastic deformation, all the details of the process are not fully understood. The difficulty is to find experimentally a « pure » case, in the accessible range of temperature and other parameters (composition, grain size,  $p(O_2)$ ...). In many cases this range covers two different regimes, so that the experimentally determined parameters (stress exponent, etc...) are not relevant. The possibility of chemical segregation will deserve more investigations.

The situation is still worse with power law creep — where matter transport is only one of

several important steps — as the deformation is essentially due to dislocation glide. the diffusion limited step could be the climb of these dislocations, or the solute dragging of gliding dislocations [34, 35, 36]. Dislocations can also play a role of short-circuits (« pipe » diffusion). Up to now the attempts to predicting the effective diffusivity and the activation energy for creep of alloys and compounds have not been very successful [37, 38, 39].

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