ON THE INTERFACE REACTION IN DIFFUSIONAL CREEP AND DISCONTINUOUS PRECIPITATION

E. Arzt

Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, D-7000 Stuttgart 1, F.R.G.

Résumé - L'émission et l'absorption de lacunes par des interfaces peuvent déterminer la vitesse des processus de diffusion. On décrit l'application d'un modèle de cette "reaction interface" dans le fluage par diffusion et la precipitation continue.

Abstract - Vacancy emission and absorption at interfaces can control the rate of diffusional processes. The application of a model for this interface reaction to diffusional creep and discontinuous precipitation is described.

Many high temperature processes in materials require internal interfaces to act as sinks and sources for vacancies. Among these are diffusional creep, sintering, creep cavity growth, grain boundary sliding, and precipitation phenomena. Classically, the kinetic descriptions of these processes assume long-range diffusion to be rate-controlling rather than vacancy absorption and emission at the interfaces (the "interface reaction"). When the diffusion distances are small, however (this corresponds to small grain size, small powder particles, high cavity densities, fine grain boundary serrations, fine microstructure, respectively), then this assumption is no longer justified and the details of the interface reaction have to be considered.

Our recently developed model for the interface reaction \(j_1\), which invokes discrete sinks and sources at the interface, explains some of the effects of solute atoms and hard particles on diffusional creep. The results of these model calculations are briefly reviewed here and applied to mechanisms which involve vacancy diffusion from and to interfaces. Some of the still unsolved problems, which merit further attention both from a theoretical and experimental point of view, are identified.

Model for the Interface Reaction: Climbing Grain Boundary Dislocations

When a difference \(\Delta \mu\) in chemical potential is maintained between two interfaces which can act as sinks and sources of vacancies, then a flux of vacancies is set up from the interface with the higher to that with the lower chemical potential. The current arriving at the sink by long-range diffusion is given by:

\[
j_1 = \frac{D_{\text{eff}} \Delta \mu}{kT \Omega \Delta x}
\]

(1)

where \(D_{\text{eff}}\) denotes the "effective" long-range diffusivity (volume diffusion plus all contributing short-circuits), \(\Omega\) the atomic volume, \(kT\) the thermal energy, and \(\Delta x\) the distance between sink and source interfaces. The difference in
chemical potential $\Delta \mu$ may be brought about by applying an external stress (as in diffusional creep, grain boundary sliding, or creep cavity growth), by capillary stresses (as in pressureless sintering) or by thermodynamic driving forces (as in the growth of a precipitation front). Some of these cases will be dealt with later.

In order for diffusion to continue, the arriving vacancies have to be absorbed by the interface acting as a sink and new vacancies have to be released at the source interface. The exact details of how this happens are certainly complicated and not well understood. The key to a better understanding of these processes lies in the recognition, e.g. 2-5/, that the structure of boundaries is well-defined and would be disrupted if atoms were removed from or added to them at random. Therefore the suggestion was put forward /6-8/ that a divergence of the diffusive flux can occur only at discrete "defects" in the boundary, thought of as climbing grain boundary dislocations or, more generally, interface dislocations. Their Burgers vectors are not lattice vectors and usually smaller in magnitude, and therefore these dislocations are constrained to remain in the boundary when they move.

![Diagram](image)

**Fig. 1** - model for the vacancy absorption and emission at interfaces: discrete, dislocation-like sinks and sources whose mobility controls the process /1, 6, 7/

The general treatment of the interface reaction, which now follows, is necessarily brief; it is based on a model first suggested by Ashby /6,7/ and on a recent analysis /1/, where further details can be found. As a model for describing the sink/source behaviour of an interface, consider an array of straight, parallel dislocations with Burgers vectors perpendicular to the interface (Fig. 1). These dislocations are evenly spaced, so that they all climb at the same speed $v$ when vacancies are added to or removed from their cores. The flux of vacancies that can be absorbed or emitted by such an array is:

$$j_2 = \frac{\rho b v}{\Omega} \quad (2)$$

where $\rho$ is the surface density of the dislocations (in m$^2$/m$^2$) and $b$ their Burgers vector. Eq.2 describes the kinetics of the interface reaction.

The climb velocity $v$ is determined by the dislocation mobility $M$:

$$v = \frac{M}{b^2} (\Delta \mu - \Delta \mu_0) \quad (3)$$
In pure materials $M$ depends mainly on the boundary diffusivity $D_B$:

$$M = \frac{D_B b}{kT} \quad (4)$$

Solute atoms which segregate to the dislocation cores can reduce $M$ to $1/1$:

$$M = \frac{D_s \Omega}{\beta C_0 kT b^2} \quad (5)$$

where $D_s$ is the solute diffusivity, $C_0$ its overall concentration, and $\beta$ a "segregation factor" (usually $\beta$ varies between 3 and 20 $/1/$).

A threshold $\Delta \mu_0 \neq 0$ appears in eq.3 when particles are present at the interface: they pin the dislocations and thereby suppress the interface reaction unless the driving force exceeds this threshold. It is proportional to the Orowan stress $/1/$:

$$\Delta \mu_0 = C_1 \Omega \frac{G b}{1} \quad (6)$$

where $G$ is the shear modulus, 1 the planar spacing of the particles in the interface, and the numerical value of $C_1$ depends on the mechanism by which the particles are overcome by the dislocations.

After having introduced the basic features of this model for the interface reaction, we can now proceed to point out the consequences of eqs. 1-6. Long-range diffusion (as described by eq.1) and the interface reaction (eqs. 2-6) are coupled, sequential processes so that the slower one determines the overall rate. When the mobility of the dislocations is high, then according to eqs. 2 and 3 more vacancies could be handled by the interfaces than are required by the long-range diffusion process and, therefore, eq.1 describes the total rate: this is the "classical" case of diffusion control. When on the other hand the dislocation mobility is restricted and the diffusion distances are short, the interface reaction may not be able to cope with the vacancy demand generated by the long-range diffusion field and eq.2 then describes the overall rate: in this limit the process is said to be "interface-controlled".

When the interface reaction determines the rate, the equations for the kinetics are quite distinct from the classical equations. Generally, the diffusion distance becomes less important or even disappears from the equations, while the stress exponent in the rate equation may become greater than 1 (if the dislocation density is stress-dependent). Two such examples are treated in the following.

**Case Study 1: Diffusional Creep**

When a polycrystalline solid is subjected, at high temperature, to low stresses which are insufficient for movement and generation of lattice dislocations it deforms by stress-directed diffusion of vacancies from the grain boundaries under tension to those under compression (Fig. 2). The "classical" result for the creep rate due to Nabarro $/9/$, Herring $/10/$ and Coble $/11/$ is obtained from eq.1 with $S = j_1 \Omega / d$, $\Delta x = C_2 d$ ($d$ is the grain size, $C_2$ a grain shape constant) and $\Delta \mu = \sigma \Omega$ ($\sigma$ is the applied stress):
$\dot{\varepsilon}_1 = \frac{D_{\text{eff}} \Omega \sigma}{C_2 kT d^2}$

with $D_{\text{eff}} = D_V + (\pi \delta / d) D_B$, where $D_V$ and $D_B$ are the volume and boundary diffusivities and $\delta$ the boundary thickness.

Although this equation is remarkably successful for pure materials, it fails to explain the behaviour of technical alloys containing solutes and particles: creep is often slower than predicted by the model, the stress dependence is non-linear, the grain size dependence is at variance with the model, and threshold stresses below which no detectable creep occurs remain unexplained.

![Diagram](image)

**Fig. 2** - The interface reaction in diffusional creep, where an applied stress causes a diffusive flux of vacancies from grain boundaries under tension to those under compression /1/.

Some of these inconsistencies can be resolved on the basis of "Interface Controlled Diffusional Creep" /1/. If it is assumed that the density of interface dislocations increases linearly with the applied stress (this assumption is analogous to the often observed increase of lattice dislocation density with the square of the stress), then the creep rate in solid solutions becomes (with $C_3$ a constant):

$$\dot{\varepsilon}_2 = \frac{J_2 \Omega / d}{C_3 \beta C_0 \Omega \sigma^2}$$

This prediction is in marked contrast with the Nabarro-Herring result, i.e. $\varepsilon \propto \sigma / d^2$ (for lattice diffusion) and with Coble's $\varepsilon \propto \sigma / d^2$ (for grain boundary diffusion). A relationship as in eq.8 has in fact been found for many fine-grained, and superplastic, alloys. For a more detailed comparison with experimental results we refer to /1/.

Threshold stresses for diffusional creep due to a dispersion of hard particles can now be explained, too. The creep rate predicted by eqs. 2,3, and 6 scales as

$$\dot{\varepsilon}_2 \propto (\sigma - C_1 G b / 1)$$

Comparison with experimental measurements is more difficult here because the effect can be very small. Nevertheless, thresholds of up to 30 MPa have been measured under conditions appropriate for interface-controlled diffusional creep /1/, though with a higher temperature dependence than suggested by eq.9.
Case Study 2: Discontinuous Precipitation

Discontinuous precipitation is a solid-state reaction in which a two-phase (usually lamellar) structure grows into a supersaturated solid solution (Fig. 3). The reaction front is an incoherent phase boundary, which acts both as a fast diffusion path and as a sink and source for matter. Most "classical" models predict a growth velocity $V_1$ of the following form /12-14/:

$$ V_1 = \frac{D_{\text{eff}} \Delta C}{s C_o} $$

(10)

with $D_{\text{eff}} = 2D_V + D_B \delta /s$; again $D_V$ and $D_B$ are the volume and boundary diffusivities, $\delta$ the thickness of the boundary, $s$ is the interlamellar spacing, $C_o$ the solute concentration in the supersaturated matrix and $\Delta C$ the difference in concentration between matrix and lamellae. The same result is obtained from eq. 1 with $V_1 = j_1 \Omega$, $\Delta x = s$, and $\Delta \mu/kT = \Delta C/C_o$.

![Phase boundary diagram](image)

In the limit of interface-controlled discontinuous precipitation, eqs. 2, 3 and 5 lead to the following expression:

$$ V_2 = j_2 \Omega = \frac{\rho \Omega D_s \Delta C}{\beta C_o^2 b^3} $$

(11)

It should be noted that now the interlamellar spacing has no influence on the growth velocity. Comparison with eq. 10 shows that eq. 11 will be valid when the following condition is met:

$$ s << \frac{D_{\text{eff}} \beta C_o b^3}{D_s \rho \Omega} $$

(12)

Thus, at high supersaturation and extremely fine interlamellar spacing, an interface-controlled velocity which is independent of $s$ would be expected. But it is difficult at present to delineate this regime of interface control quantitatively, as no information is available about the sink and source density $\rho$.
\[ \dot{\epsilon}_1 = \frac{D_{\text{eff}} \Omega \sigma}{C_2 kT d^2} \] (7)

with \( D_{\text{eff}} = D_V + (\pi \delta / d) D_B \), where \( D_V \) and \( D_B \) are the volume and boundary diffusivities and \( \delta \) the boundary thickness.

Although this equation is remarkably successful for pure materials, it fails to explain the behaviour of technical alloys containing solutes and particles: creep is often slower than predicted by the model, the stress dependence is non-linear, the grain size dependence is at variance with the model, and threshold stresses below which no detectable creep occurs remain unexplained.

![Figure 2](image)

Some of these inconsistencies can be resolved on the basis of "Interface Controlled Diffusional Creep" /1/. If it is assumed that the density of interface dislocations increases linearly with the applied stress (this assumption is analogous to the often observed increase of lattice dislocation density with the square of the stress), then the creep rate in solid solutions becomes (with \( C_3 \) a constant):

\[ \dot{\epsilon}_2 = J_2 \Omega / d = \frac{C_3 \Omega D_s \sigma^2}{\beta C_0 kT \sigma d} \] (8)

This prediction is in marked contrast with the Nabarro-Herring result, i.e. \( \dot{\epsilon} \propto \sigma / d^2 \) (for lattice diffusion) and with Coble's \( \dot{\epsilon} \propto \sigma / d^2 \) (for grain boundary diffusion). A relationship as in eq.8 has in fact been found for many fine-grained, and superplastic, alloys. For a more detailed comparison with experimental results we refer to /1/.

Threshold stresses for diffusional creep due to a dispersion of hard particles can now be explained, too. The creep rate predicted by eqs. 2, 3, and 6 scales as

\[ \dot{\epsilon}_2 \propto (\sigma - C_1 G b / l) \] (9)

Comparison with experimental measurements is more difficult here because the effect can be very small. Nevertheless thresholds of up to 30 MPa have been measured under conditions appropriate for interface-controlled diffusional creep /1/, though with a higher temperature dependence than suggested by eq.9.
Case Study 2: Discontinuous Precipitation

Discontinuous precipitation is a solid-state reaction in which a two-phase (usually lamellar) structure grows into a supersaturated solid solution (Fig. 3). The reaction front is an incoherent phase boundary, which acts both as a fast diffusion path and as a sink and source for matter. Most "classical" models predict a growth velocity $V_1$ of the following form /12-14/:

$$ V_1 = \frac{D_{\text{eff}} \Delta C}{s C_o} $$

(10)

with $D_{\text{eff}} = 2D_{V} + D_{B} \delta /s$; again $D_{V}$ and $D_{B}$ are the volume and boundary diffusivities, $\delta$ the thickness of the boundary, $s$ is the interlamellar spacing, $C_o$ the solute concentration in the supersaturated matrix and $\Delta C$ the difference in concentration between matrix and lamellae. The same result is obtained from eq. 1 with $V_1 = j_1 \Omega$, $\Delta x = s$, and $\Delta \mu/kT = \Delta C/C_o$.

![Phase boundary diagram](image)

Fig. 3: The interface reaction in discontinuous precipitation: under the action of thermodynamic driving forces, atoms are added to a phase boundary.

In the limit of interface-controlled discontinuous precipitation, eqs. 2, 3 and 5 lead to the following expression:

$$ V_2 = j_2 \Omega = \frac{\rho \Omega D_s \Delta C}{\beta C_o \delta} $$

(11)

It should be noted that now the interlamellar spacing has no influence on the growth velocity. Comparison with eq. 10 shows that eq. 11 will be valid when the following condition is met:

$$ s \ll \frac{D_{\text{eff}} \beta C_o \delta}{D_s \rho \Omega} $$

(12)

Thus, at high supersaturation and extremely fine interlamellar spacing, an interface-controlled velocity which is independent of $s$ would be expected. But it is difficult at present to delineate this regime of interface control quantitatively, as no information is available about the sink and source density $\rho$.
Open Questions, Areas for Further Research

The assumption of discrete, dislocation-like sinks and sources at interfaces has lead to a formalism which seems to have some merit as a first-order description of diffusion problems in the limit of short diffusion distances. The theory as it stands explains some phenomena unforeseen by the classical models based on diffusion control. Yet some observations still remain unexplained, e.g. the high temperature dependence of threshold stresses for diffusional creep.

The two applications described in this paper make it clear that further experimental studies will be necessary in order to lend more mechanistic support to these hypotheses. It seems that the gap between the structure and the high-temperature mechanical properties of interfaces could be narrowed by TEM investigations with the specific aim of proving or rejecting the basic mechanisms proposed here. The following points would appear, from a theoretical point of view, worth pursuing further experimentally:

- Identification of the interface dislocations which act as vacancy sinks and sources (in-situ observation?): What is a typical average Burgers vector for such dislocations? Which parameters determine the density of these dislocations? When is the assumption of a stress-dependent density of interface dislocations justified? Some information about these points is available for "special" grain boundaries; but it would be desirable to extend these studies to non-special grain boundaries and phase boundaries.

- Interaction of interface dislocations with particles: Are particles by-passed by bowing or by climb/glide of dislocations? Or do we have to consider core spreading at the interface? If by-pass occurs by glide/climb in or near the particle/matrix interface, then atom rearrangements in this phase boundary can become the rate-limiting step and therefore information on the structure of such a boundary would be valuable.

Conclusive answers to these questions would greatly improve our understanding of interface-controlled diffusional processes.

References

6. M.F. Ashby, Scripta Met. 3 (1969) 837
7. M.F. Ashby, Surf. Sci. 31 (1972) 498
10. C. Herring, J. Appl. Phys. 21 (1950) 437
12. C. Zener, Trans. AIME 167 (1946) 550