Phase Growth Induced Stresses During Grain Boundary Diffusion

L. Klinger and L. Levin

Department of Materials Engineering, Israel Institute of Technology, Haifa 32000, Israel

ABSTRACT

The kinetics of the formation of a new phase during grain boundary diffusion are considered. Two schemes of diffusion phase growth are analyzed. In the first, the rate of phase growth is controlled by diffusion through the growing phase. In the second, a mass supply from the matrix to the interface controls the diffusional growth of the new phase. The set of equations of the volume and the grain boundary diffusion, in combination with the phase growth equation, was solved. It was shown that, due to the rapid grain boundary diffusion of the active component, the new phase is formed as a narrow wedge growing from the surface into the bulk of the material along the grain boundaries. The wedge length growth with time as $t^{1/4}$, and the width of the wedge base as $t^{1/2}$. The shape of the wedge was found. For both schemes the wedges of the new phase have a parabolic shape but with different orientation: in Scheme 2 wedges have a finite angle at the tip, in Scheme 1 the edges of the wedge converge smoothly. Owing to the different specific volumes of the phases, significant elastic deformations and stresses develop in the regions surrounding the wedges. For the stress calculation, the wedge of the growing phase was presented as an accumulation of edge dislocations on the plane of the grain boundary. The field stress around the wedge of the growing phase was found for both schemes of phase growth. There are significant tensile stresses at the wedge tip and compressive stresses at its base.

It is assumed that the initial system (α-phase), which is composed of components A and B, contains a grain boundary that is perpendicular to the free surface y = 0 (Fig. 1). Let c_0 be the initial concentration of the B component, which is assumed to be chemically active with respect to component C of the environment. Component A is assumed to be inert. The new phase is formed as a result of the reaction: $pB + qC = B_pC_q$. It is assumed that neither the chemical reaction nor the diffusion in the β-phase controls the process, and that it is, on the contrary, entirely controlled by the supply of B component from the α-phase towards the interface.

Let the β-phase wedge width at depth y and time t be designated by w(y,t). Then the growth of w with time is determined by the Stefan condition

$$c_1 \frac{\partial w}{\partial t} = D\left(\frac{\partial c}{\partial x}\right)_{x=w}, \qquad (1)$$

where c_1 is the concentration of B in the β-phase. With the assumption of the infinitely fast "adoption" of B by the β-phase,

$$c_{x=w} = 0 . \qquad (2)$$

Equations (1) and (2) can be considered as the

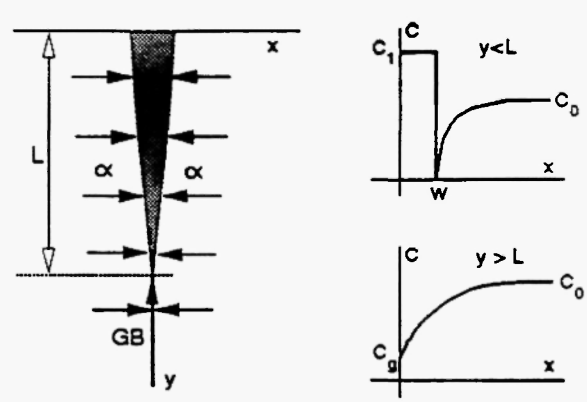

Fig. 1: A wedge of new phase formed during grain boundary diffusion. Concentration profile across the grain boundary.

boundary conditions for the diffusion equation

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right) \tag{3}$$

for $y < L(t)$; is the wedge length at t, and D is the volume diffusion coefficient of B in the α-phase. When $y > L(t)$ the equation for grain boundary diffusion /5/

$$\frac{\partial c_g}{\partial t} = D_g\frac{\partial^2 c_g}{\partial y^2} + \frac{2D}{\delta}\left(\frac{\partial c}{\partial x}\right)_{x=0} \tag{4}$$

applies as the boundary condition for equation (3). D_g is the grain boundary diffusion coefficient, δ is the diffusion width of the boundary, and $c_g = c(x=0)$ is the concentration of the B component on the grain boundary. To continue the analysis it will be assumed that

$$\delta \ll \sqrt{Dt} \ll L(t) . \tag{5}$$

The first inequality allows one to proceed to the quasi-steady-state solution of equation (4), and the second allows one to neglect the dependence c(y) in equation (3).

We shall designate by $\tau(y)$ the time of commencement of the β-phase growth at depth y. The function $\tau(y)$ is the inverse of L(t):

$$\tau(L(t)) = t . \tag{6}$$

With due allowance for the assumptions made, the growth kinetics of the phase at depth y is determined from the following solution of the diffusion problem:

$$c = c_0\left[1 - \frac{1}{\mathrm{erfc}(\gamma)}\mathrm{erfc}\left(\frac{x + 2\gamma\sqrt{D\tau}}{2\sqrt{Dt}}\right)\right] , \tag{7}$$

$$w = 2\gamma\sqrt{Dt}\left(1-\sqrt{\tau/t}\right) . \tag{8}$$

The parameter γ is defined by the following equation:

$$c_0/c_1 = \sqrt{\pi}\,\gamma e^{\gamma^2}\mathrm{erfc}(\gamma) . \tag{9}$$

For $c_0/c_1 \ll 1$, γ can be expressed explicitly

$$\gamma \approx \frac{c_0}{\sqrt{\pi}\,c_1} . \tag{10}$$

The dependencies w(y) and c(y) enter into equations (7) and (8) implicitly via the dependence $\tau(y)$. These dependencies provide for the continuity of the flow at the tip of the β-phase wedge. It follows from eqs. (6), (7) and (9) that

$$\left(\frac{\partial c}{\partial y}\right)_{x=0,y=L} = c_1\gamma^2\left(\frac{t\,dL}{dt}\right)^{-1} . \tag{11}$$

In the region $y > L$ diffusion takes place, but without phase formation. The process follows equation (3) with boundary conditions (4) and:

$$c_{g\ y=\infty} = c_0 , \quad c_{g\ y=L} = 0 . \tag{12}$$

The problem set by (3), (4) and (11) is typical for grain boundary diffusion. Its approximate solution was first given by Fisher /5/ and later – more rigorously – by other investigators. In the present work we confine ourselves to the Fisher approximation, which allows an analytical solution to be reached

$$c = c_0\left[1 - \exp\left(\frac{L-y}{L_F}\right)\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)\right] , \tag{13}$$

where

$$L_F = \left(\frac{\delta D_g\sqrt{\pi Dt}}{2D}\right)^{1/2} . \tag{14}$$

Thereby

$$\left(\frac{\partial c}{\partial y}\right)_{x=0,\ y=L} = \frac{c_0}{L_F} . \tag{15}$$

Equating (15) and (11) yields the equation that determines L(t)

$$\frac{dL}{dt} = \frac{c_1\gamma^2 L_F}{c_0 t} , \tag{16}$$

and since for $t = 0$, $L = 0$,

$$L = \frac{2c_1\gamma^2}{c_0}\left(\frac{2\delta D_g\sqrt{\pi Dt}}{D}\right)^{1/2} . \tag{17}$$

Thus the wedge length grows with time as $t^{1/4}$ and correspondingly τ as y^4. Substituting this equation into (8) produces the shape of the wedge

$$w = w_0\left(1 - \frac{y^2}{L^2}\right) , \tag{18}$$

where

$$w_0 = 2\gamma\sqrt{Dt} \tag{19}$$

is the width of the wedge base that growth with time as $t^{1/2}$. The dependence of the size of the wedge on the initial composition is determined by eq. (8). When $c_0/c_1 \ll 1$, w and L are proportional to c_0/c_1, and therefore the ratio

$$\frac{w_0}{L} = \left(\frac{\pi}{4}\right)^{1/4}\left(\frac{\sqrt{Dt}}{\delta}\right)^{1/2}\left(\frac{D}{D_g}\right)^{1/2} \tag{20}$$

does not depend on the initial composition of the α-phase. For $D/D_g \sim 10^{-4} - 10^{-6}$, and $\sqrt{Dt}/\delta \sim 10^2$ we obtain $w_0/L \sim 10^{-1} - 10^{-2}$. This means that the β-phase is indeed growing in the form of a narrow wedge.

The shape of the wedge as found [eq. (18)] differs from the one that was obtained in a previous work /2/

$$w = w_0\left(1-\frac{y}{L}\right)^2 . \tag{21}$$

The main difference is that while the wedge determined by (18) has a finite angle at the tip, the edges of the wedge given by eq. (21) converge smoothly. It will be shown that this difference significantly changes the stress distribution in the vicinity of the growing phase.

For the sake of stress calculation, the wedge of the growing phase will be presented as an accumulation of edge dislocations on the x = 0 plane. Designating by db the total Burgers vector distributed at the interval dh ($0 < h < L$), we obtain

$$db = \frac{2}{3}\varepsilon_0 dw = \frac{4}{3}\varepsilon_0 w_0 \frac{h dh}{L^2} , \tag{22}$$

where $\varepsilon_0 = (V_\beta - V_\alpha)/V_\alpha$ is the relative change in volume during β-phase formation. The stress field* created by an edge dislocation with a Burgers vector db in a semi-infinite ($y > 0$) isotropic crystal is determined by /6/:

$$d\sigma = \frac{E}{2\pi(1-\nu)}\left[\frac{y-h}{x^2+(y-h)^2} + \frac{(y+h)^2(h-y)-(3h+y)x^2}{\left[x^2+(y+h)^2\right]^2}\right]db , \tag{23}$$

* Calculation is performed only for the spherical component of the stress tensor $\sigma = \sigma_{xx} + \sigma_{yy} + \sigma_{zz}$.

where E is Young's modulus, ν is Poisson's ratio. The second term in the brackets determines the "reflection" field, which provides the zero values of the normal components of the stress tensor on the free surface. The total stress field around the wedge of the growing phase can be obtained by integrating (23), taking into account (22). The result can be shown to be

$$\sigma = \sigma_0 \cdot f(x/L, y/L) , \tag{24}$$

where

$$\sigma_0 = \frac{2E\varepsilon_0 w_0}{3\pi(1-\nu)L} \tag{25}$$

and

$$f(x,y) = \tag{26}$$

$$2 + x\cdot \mathrm{arctg}\frac{y}{x} - x\cdot \mathrm{arctg}\frac{y-1}{x} - 3x\cdot \mathrm{arctg}\frac{x}{x^2+y(y+1)} -$$

$$-0.5y\cdot\ln\frac{x^2+(y-1)^2}{x^2+(y+1)^2} - 2y\cdot\ln\frac{x^2+(y+1)^2}{x^2+y^2} - \frac{2(y+1)}{x^2+(y+1)^2}$$

The stress distribution around the wedge of the growing phase is shown in Fig. 2. One can see fields of significant tensile stresses at the wedge tip and compression stresses at its basis. The stresses decrease with the distance from the grain boundary. On the whole surface compressive stresses appear having a maximum

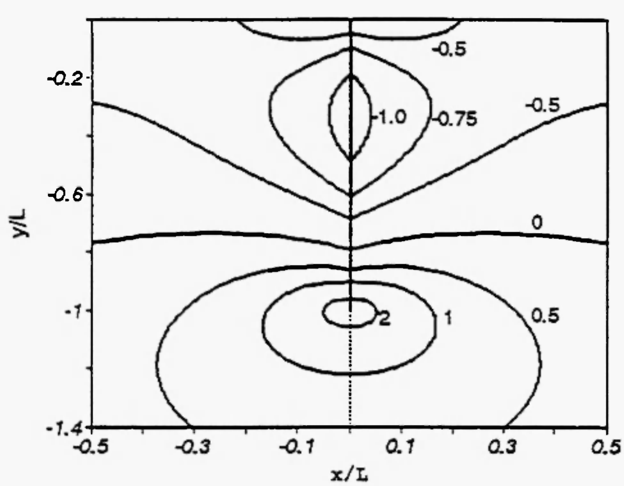

Fig. 2: Stress distribution in the vicinity of a new phase wedge. The figure shows the σ/σ_0 value for the iso-stress line.

$0.71\sigma_0$ for $x = 0.548L$. In the region $y > 0.5L$ the stresses are tensile and are maximum on the grain boundary ($x = 0$).

In accordance with eq. (26) the stress distribution along the wedge and the grain boundary is given by

$$f(0,y) = \frac{2y}{y+1} - y \cdot \ln\frac{|y-1|(y+1)^3}{y^4} \quad . \qquad (27)$$

The maximum of the comparative stresses is located at $y = 0.331L$ and equals $1.117\sigma_0$. The tensile stresses grow logarithmically as the wedge tip is approached. These results differ from those obtained in /2/, where stresses were finite at all points. The reason for this difference is to be seen, as already mentioned, in the shape of the wedge which in the present case has a finite angle at the tip. Assuming $w_0/L \sim 10^{-2}$ and $\varepsilon_0 \sim 10^{-2}$, σ_0 is estimated at $10^{-4}E$. These results indicate that at the tip of the wedge of the growing phase a region of plastic deformation should appear, in analogy to the situation that exists at the tip of a growing crack. In certain cases the tensile stresses near the tip of the wedge may cause cracking and even fracture of the material.

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