Journal of Engineering Physics and Thermophysics, Vol. 65, No. 3, 1993

A MODEL OF GROWTH OF AN INTERMEDIATE PHASE IN BI- AND POLYCRYSTALS

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UDC 539.219.3

An analytically solvable model of the growth of an intermediate phase between low-soluble components on diffusion at grain boundaries involving outflow is suggested. Criteria for a transition from the Fisher regime $t^{1/4}$ *to a parabolic one are established. The formalism suggested is extended to the case of the growth of a solid-state solution with an exponential concentration dependence of the diffusion coefficient.*

Although the Fisher solution for the impurity diffusion in a bicrystal and its modification for polycrystals have long been known [1-4], an analogous problem for the growth of intermediate phases in systems with limited solubility has been analyzed, as far as we known, only in [5] for the case where the diffusion coefficients for a solid-state solution are well in excess of those for a phase. In [5], solutions analogous to a conventional Fisher solution have been obtained on the assumption that the diffusion process is quasistationary:

$$\frac{\partial C_b(t,\ y)}{\partial t}=0, \tag{1}$$

where C_b is the grain boundary concentration of component B in the phase, and the Y axis runs along a grain boundary (GB). In the form of Eq. (1) this assumption is not fulfilled; it is inexact since at a fixed y the quantity $C_b(y)$ changes from C_1 to $C_1 + \Delta C_1$ (within the limits of the homogeneity interval) and incorrectly predicts the form of the phase wedge. The assumption

$$\frac{\partial C_b(\xi)}{\partial t}=0, \tag{2}$$

is more exactly fulfilled, where $\xi = y/y_0(t)$, $y_0(t)$ is the maximum length of the phase wedge. For instance, in the middle of the phase wedge C_b is virtuelly unchanged throughout the period of phase growth (the homogeneity interval is from C_1 to $C_1 + \Delta C_1$). Use of assumption (2), as shown below, leads to correct prediction of the form of the phase wedge.

Our developed model is rather simple, and it may be generalized to the case of growth of several phases and allows prediction of the phase composition and sufficiently easy calculation of diffusion coefficients.

The model is based on the following assumptions:

1. An intermediate phase forms at first on the basis of the GB; the latter, transforming from the boundary A-A to the boundary I-I, remains, due to easy influx with a diffusion coefficient D_b and having a thickness of $\delta \approx 1$ nm (i.e., the GB is not overgrown with a new phase and does not bifurcate).
2. Formed phase I broadens normal to the GB due to volume diffusion with a diffusion coefficient D.
3. At all thee points of the formed I-A phase boundary between the broadening phase I and the matrix A the concentration of the component B is C_1 on the side of phase I and is zero on the side of phase A (solubility of B in A is ignored).
4. Consideration is given to the following variants:

a) following [5], we assume that outflow from the GB is the same at all GB points:

Cherkassy Engineering-Technological Institute, Cherkassy Pedagogical Institute. Institute of Metallurgy, Russian Academy of Sciences, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 65, No. 3, pp. 311-316, September, 1993. Original article submitted May 22, 1992.

$$\frac{\partial C}{\partial x}=\frac{\Delta C'}{x(t,\ y)}=\frac{\Delta C_1}{x_0};\ x_0=x(t,\ 0); \tag{3}$$

b) following [5], in which a linear approximation for $C_b(y)$ is shown to be a permissible one for a rigorous solution, we also assume here that $C_b(y)$ changes approximately linearly with y.

Conditions 4a) and 4b) will be considered independently and then the results obtained will be compared.

5. A flow in the volume of a phase wedge normal to the GB is constant along x (a corresponding property is proved in [6]) in a reference system associated with the moving nose of the wedge.

At first, we employ assumption 4a).

The balance equation of the flows at the nose of the growing phase wedge is as follows

$$C_1\frac{dy_0}{dt}=\frac{D_b\Delta C_1}{y_0}-\frac{2}{\delta}\int\limits_0^{y_0(t)} D\frac{\partial C(t,\ x/y)}{\partial x}\,dy, \tag{4}$$

where the second term on the r.h.s. accounts for the decrease of the flow, reaching the nose, due to lateral outflow into the volume of the phase.

Taking into consideration assumption (3) on the outflow being the same, we obtain from (4)

$$C_1\frac{dy_0}{dt}=\frac{D_b\Delta C_1}{y_0}-\frac{2y_0(t)}{\delta}\,\frac{D\Delta C_1}{x_0(t)}. \tag{5}$$

The dependence $x_0(t)$ is determined from the usual equation for transverse motion of the phase boundary

$$C_1\frac{dx_0}{dt}=\frac{D\Delta C_1}{x_0},$$

so that $x_0(t)$ grows according to the parabolic law

$$x_0(t)=\left(\frac{2D\Delta C_1}{C_1}\,t\right)^{1/2}.$$

Thus, the equation for $y_0(t)$ has the simple form

$$\frac{dy_0}{dt}=\frac{A}{y_0}-B\frac{y_0}{t^{1/2}};\ A=\frac{D_b\Delta C_1}{C_1},\ B=\frac{1}{\delta}\left(\frac{2D\Delta C_1}{C_1}\right)^{1/2}. \tag{6}$$

Its general solution is as follows:

$$y_0^2=\frac{A}{B}\,t^{1/2}-\frac{A}{4B^2}\left(1-e^{-4Bt^{1/2}}\right).$$

In the case of frozen outflow ($(D\Delta C_1 t)^{1/2} << \delta$, i.e., $Bt^{1/2} << 1$), this gives the parabolic law (regime A)

$$y_0^2=2At.$$

On passing to large times of annealing, $t >> 1/B^2$, we arrive at the Fisher regime of diffusion (regime B):

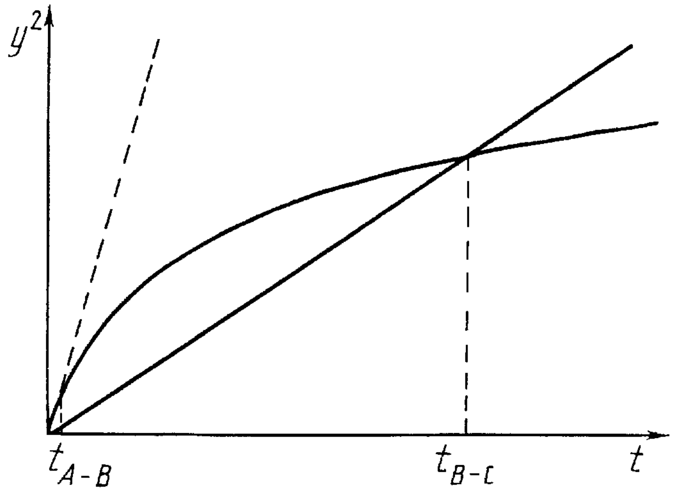
$$y_0^2=\frac{A}{B}\,t^{1/2}\left(1-\frac{1}{Bt^{1/2}}\right)\approx\frac{A}{B}\,t^{1/2},$$

i.e., $y_0 \sim t^{1/4}$. The characteristic time of the transition from A to B is

$$t_{A-B}\approx C_1\delta^2/2D\Delta C_1,$$

which agrees with an analogous estimate for tracer diffusion [4]. Here the corresponding length of the phase wedge is

$$y_{A-B}\sim\delta\,(D_b/2D)^{1/2}. \tag{7}$$



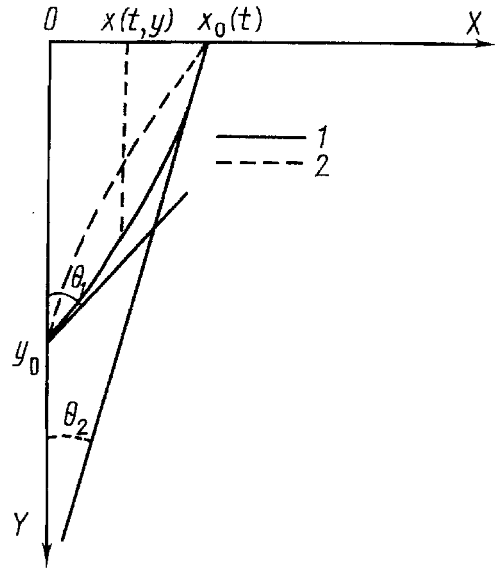


Fig. 1. Kinetics of phase growth along a GB, comparison with the kinetics of purely GB growth, and phase growth by volume diffusion.

Fig. 2. Form of the phase wedge calculated in the present work (1) and in [5] (2).

Since $D_b/D \cong 10^3$- 10^5 [7], $y_{A-B} \cong 0.03$-$0.3\,\mu$m. Obviously the phase layer grows not only in the form of a wedge along the GB but also through diffusion in the direction parallel to the GB according to the law $kt^{1/2}$. We may determine y_{A-B} at which the parabolic volume diffusion surpasses the boundary diffusion, i.e. ,when $kt^{1/2} \cong \gamma t^{1/4}$ (Fig. 1):

$$y_{B-C} \simeq \frac{\delta}{2} D_b/D \cong 0{,}5 - 50 \ \mu\mathrm{m}. \tag{8}$$

thus, the phase wedge grows in the Fisher regime within the length range

$$\delta \left(\frac{D_b}{2D}\right)^{1/2} < y_0 < \delta \frac{D_b}{2D}.$$

Now we use assumption 4b). Then

$$\partial C_b/\partial y = -\Delta C_1/y_0(t), \ C_b(t, \xi) = C_1 + \Delta C' = C_1 + (1-\xi)\Delta C_1, \tag{9}$$

$$\partial C(x, \xi)/\partial x = (1-\xi)\Delta C_1/x(t, \xi), \tag{10}$$

where $x(t, \xi)$ is the profile of the phase boundary.

With the assumptions made, the balance equations for the diffusion along the GB and for the motion of the phase boundaries normal to the GB are of the form

$$C_1 \frac{dy_0}{dt} = \frac{D_b \Delta C_1}{y_0} - \frac{2}{\delta} D y_0 \int_0^1 \frac{\Delta C_1 (1-\xi)}{x} d\xi, \tag{11}$$

where the r.h.s. is the flow outgoing along the boundary, the first term in it is the incoming flow, while the last term accounts for outflow from the GB into the volume of the growing phase:

$$C_1 \frac{\partial x(t, y)}{\partial t} = -D \frac{\partial C}{\partial x} = \frac{D \Delta C_1}{x(t, y)} \left(1 - \frac{y}{y_0}\right). \tag{12}$$

Now passing to the new variable ξ, we obtain from (12)

$$C_1 \frac{\partial x(t,\ \xi)}{\partial t} = C_1 \xi \frac{1}{y_0} \frac{dy_0}{dt} \frac{\partial x}{\partial \xi} + \frac{D \Delta C_1}{x} (1 - \xi). \tag{13}$$

Solving the system of differential equations (11)-(13) is a complicated problem. But as has been shown above, in a wide range of y values we may use the Fisher law $y_0 = \gamma t^{1/4}$ in Eq. (13), too. Then it will acquire the form

$$\frac{\partial x(t,\ \xi)}{\partial t} = \frac{\xi}{4t} \frac{\partial x}{\partial \xi} + \frac{D \Delta C_1}{C_1 x} (1 - \xi),\ 0 < \xi < 1, \tag{14}$$

$$x(t,\ \xi \to 1) = 0. \tag{15}$$

It is easy to verify that a solution of Eq. (14), satisfying boundary condition (15), is the function

$$x(t,\ \xi) = \left[\frac{2 D \Delta C_1}{C_1} t \left(1 - \frac{4}{3} \xi + \frac{1}{3} \xi^4 \right) \right]^{1/2}. \tag{16}$$

The profile of the phase wedge $x(\xi) \to x(y)$ calculated according to Eq. (16) is shown in Fig. 2. The vertex angle θ_1 is determined from the formula

$$\begin{aligned} \operatorname{tg} \theta_1 = -\left.\frac{\partial x}{\partial y}\right|_{y=y_0} &= -\frac{1}{y_0} \left.\frac{\partial x}{\partial \xi}\right|_{\xi \to 1} = -\frac{1}{\gamma t^{1/4}} \left.\frac{\partial x}{\partial \xi}\right|_{\xi \to 1} = \\ &= \left(\frac{8 D \Delta C_1}{3 C_1 \gamma_1^2} \right)^{1/2} t^{1/4} \end{aligned} \tag{17}$$

It increases with time analogously to the Fisher solution [7].

In order to determine the coefficient γ_1, we substitute the dependence found into Eq. (11) for the growth $y_0(t)$. The law $y_0 = \gamma t^{1/4}$ must be obtained asymptotically in a quasi-stationary regime when the overwhelming portion of the incoming flow $D_b \Delta C_1 / y_0$ is used for drawing-off and only a negligible part is employed for bringing the wedge nose into motion. Then instead of (11) we have

$$\frac{D_1 \Delta C_1}{y_0} \approx \frac{2}{\delta} y_0 D \Delta C_1 \int_0^1 \frac{1 - \xi}{x(t,\ \xi)} d\xi. \tag{18}$$

Substituting the function from (10) and $y_0 = \gamma t^{1/4}$, we first make sure that the time t is shortened, which proves self-consistency of the scheme, and secondly determine γ_1:

$$\gamma_1 = \left(\frac{\frac{\delta D_b}{2D} \sqrt{\frac{D \Delta C_1}{C_1}}}{\int_0^1 \frac{(1 - \xi)\, d\xi}{\sqrt{2 - 8/3 \xi + 2/3 \xi^4}}} \right)^{1/2} \approx \left(\frac{D_b^2 \delta^2 \Delta C_1}{2 D C_1} \frac{1}{0{,}72} \right)^{1/4}. \tag{19}$$

Here the volume of the intermediate phase per unit length grows according to the law

$$\Delta V = \int_0^{y_0} x(t,\ y)\, dy = y_0 \int_0^1 x(t,\ \xi)\, d\xi = \text{const}\, t^{3/4}. \tag{20}$$

Now we compare the results obtained using assumptions 4a) and 4b). If assumption 4b) is made, the outflow from the GB is not constant but changes by no more than 30%. Indeed, the quantity

$$\frac{\Delta C'}{x(t,\ \xi)} = \frac{\Delta C_1 (1 - \xi)}{\sqrt{\frac{2 D \Delta C_1}{C_1} t \left(1 - \frac{4}{3} \xi + \frac{1}{3} \xi^4 \right)}}$$

differs from (3) by the factor $(1-\xi)/\sqrt{1-4/3\xi + 1/3\xi^4}$. This factor changes from unity at $\xi = 0$ to 0.71 at $\xi \to 1$, with γ_1 differing from γ by approximately 8%.

In Fig. 2 the profile of the phase calculated in [5] is shown by a dashed line. As is seen, our solution demonstrates that the profile must be convex and not concave. It is just a convex profile that has been experimentally determined in [5] for In diffusion in an Sn-Ge bicrystal and in [8] for Zn diffusion in an Fe + 5 at. % Si bicrystal at a temperature near 900°C. The authors of [12] have succeeded in reproducing the "ideal" Fisher regime, i.e., without "spurious" volume flows along the Y axis. Experimental data of [8] show that $\theta_1 > \theta_2$, and not the reverse, which confirms the validity of our model.

After attaining the critical thickness $y_{B\text{-}C}$, the regime of phase growth must change since the assumptions of the model are no longer valid, i.e. the concentration profile along X has a more gentle slope than along Y and the flow through the phase will be directed along the Y axis. Eventually the phase will grow along the Y axis like a parabola. The angle θ continues to increase, the front becomes almost flat, and the phase grows according to a parabolic law as if no grain boundary existed at all. Indeed, such a result has been observed in [8] for diffusion of tin in an Fe + 5 at % Si bicrystal at a temperature of about 800°C. The thickness of the diffusion layer amounted to approximately 30 μm. As is obvious, even for the bicrystal at $y_0 \gtrsim 100\,\mu$m the phase will grow like a parabola.

For polycrystals, this result is valid if $y_{cr} < R$, where R is the radius of a crystal grain. If $R < y_{cr}$, then the criterion for passage from the law $y \sim t^{1/4}$ to $y \sim t^{1/2}$ is as follows [4]:

$$y_{cr} \approx (D_b \delta R / D)^{1/2}. \tag{21}$$

At $R \approx 10\,\mu$m $y_{cr} \approx 3-30\,\mu$m, at $R \approx 1\,\mu$m $y_{cr} \approx 1-10\,\mu$m, and at $R \approx 0.1\,\mu$m $y_{cr} \approx 0.3-3\,\mu$m. Therefore in experiments on the phase growth in flat samples of the Cu-Zn system [9, 10] the parabolic law of phase growth is fulfilled although the samples were polycrystalline, since $R \approx 1\,\mu$m and $y > 10\,\mu$m.

Under definite conditions the scheme suggested above may be employed to describe the growth of the solid-state solution of B in A. From the experiment in [11] it is known that in many cases the diffusion coefficient of B in a solid-state solution based on A abruptly (often exponentially) increases with the concentration of B. In this case, as shown in [12], the concentration profile has a characteristic Γ-shape that resembles a concentration drop at the grain boundary, passing into a plateau corresponding to a phase layer. Although the separation of the solid-state solution into a "phase" with the boundaries of "existence" C_1 and $C_1 + \Delta C_1$ and the pure component A is somewhat ambiguous, the ambiguity does not affect the results of calculation of the kinetics of growth of the solid-state solution layer.

The ambiguity in determination of C_1 exists for phases with a wide homogeneity region as well which are also characterized by a strong concentration dependence D(C). In particular, γ-brass Cu_5Zn_8 also exhibits a Γ-shaped profile [9, 10]. However the ambiguity in determination of C_1 has not affected at all the accuracy of calculations performed in [9, 10].

In the case D(C) = const (when a solution is close to ideal and the melting points of A and B are almost the same) one may employ the Fisher model for bicrystals or the model of spheres for polycrystals [4].

To sum up, it can be said that:

1) the problem of phase growth in a bicrystal with constant outflow along the grain boundary is solved analytically;

2) the time of transition from the A regime to the B regime and the corresponding length of the phase wedge are determined;

3) it is shown that the assumptions on the linearity of the concentration profile along the grain boundary and on the constant outflow from the grain boundary do not contradict each other and may be equally employed to describe phase growth along the grain boundary;

4) the phase wedge is shown to have a convex, and not a concave, as is common to assume, form;

5) the time of transition from the B regime to the C regime and the corresponding length of the phase wedge are determined;

6) it is shown that with a large time of annealing a front of the phase layer flattens and the phase grows without "perceiving" the grain boundary.

NOTATION

t, annealing time; C_b, atomic concentration of the diffusant at the grain boundary (GB); y_0, maximum length of the phase wedge; y, coordinate along the GB; D_b, GB diffusion coefficient; δ, GB thickness; D, volume diffusion coefficient of the growing phase; C_1, $C_1 + \Delta C_1$, boundary concentrations of component B in intermediate phase I; γ, constant of the velocity of motion of the phase wedge vertex; θ_1, vertex angle of the wedge of phase I; θ_2, base angle of the wedge.

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