

IMPURITY DIFFUSION IN THE MELT IN CRYSTAL
PRODUCTION BY BRIDGMAN'S METHOD

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An approximate solution is derived for the one-dimensional diffusion of impurities in a melt in directional crystallization within a restricted volume and motion of the interface and constant speed. Results are given for the position of the diffusion layer and the impurity concentration.

The material is melted in a crucible with the dope in production of single crystals by Bridgman's method; then the crucible is removed from the hot zone and the material crystallizes. The dope distribution in the crystal is substantially dependent on diffusion in the melt.

Consider the dope distribution in the melt in crystallization for a cylindrical crucible of length l . The speed of the shunt w is assumed to be constant, while the initial distribution ρ_0 of the dope in the melt is uniform. The diffusion coefficient D and the equilibrium partition coefficient k are constant, with $k < 1$. The problem is considered as one-dimensional. It is difficult to obtain an exact solution of this problem, because it is formulated for a finite region of variable length (one of the boundaries is mobile). The integral method [1-3] allows one to derive separately for two periods an approximate solution to the diffusion problem for crystallization in a restricted volume (Fig. 1). The problem is formulated in a mobile coordinated system ox with the origin at the crystallization front.

In the first period, a diffusion layer of thickness δ is formed at the crystallization front, in which the impurity concentration varies from maximal at the front itself down to ρ_0 ; this period ends when the upper boundary of the diffusion layer reaches the end of the crucible. Then the condition for the first period is $l - w\tau > \delta$.

The equations for the first period take the form

$$\frac{\partial \rho}{\partial \tau} = D \frac{\partial^2 \rho}{\partial x^2} + w \frac{\partial \rho}{\partial x}, \quad (1)$$

$$\rho(x, 0) = \rho_0, \quad (2)$$

$$\frac{\partial \rho(0, \tau)}{\partial x} = \frac{(k-1)w}{D} \rho(0, \tau), \quad (3)$$

$$\rho(\delta, \tau) = \rho_0, \quad (4)$$

$$\frac{\partial \rho(\delta, \tau)}{\partial x} = 0, \quad (5)$$

$$\frac{\partial^2 \rho(\delta, \tau)}{\partial x^2} = 0; \quad (6)$$

boundary conditions (4)-(6) are the mathematical formulation for the boundary layer; the dope distribution within the diffusion layer is represented as a polynomial of third degree:

$$\rho = a_0 + a_1x + a_2x^2 + a_3x^3. \quad (7)$$

From (3)-(6) we find the coefficients in (7):

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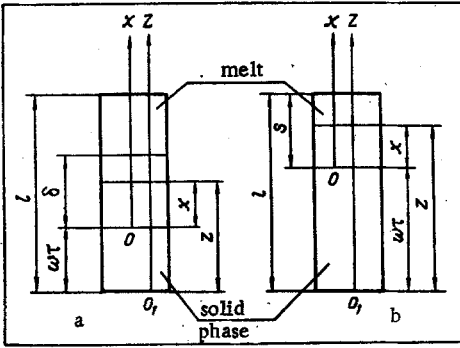


Fig. 1. Scheme: A) for the first period; B) for the second one, $s < \delta$.

and integrate with limits 0 and δ :

$$\int_0^{\delta} \frac{\partial \rho}{\partial \tau} dx = D \int_0^{\delta} \frac{\partial^2 \rho}{\partial x^2} dx + w \int_0^{\delta} \frac{\partial \rho}{\partial x} dx. \quad (10)$$

Integration gives

$$\frac{\partial \theta}{\partial \tau} = D \left[\frac{\partial \rho(\delta, \tau)}{\partial x} - \frac{\partial \rho(0, \tau)}{\partial x} \right] + w \left[\rho(\delta, \tau) - \rho(0, \tau) \right], \quad (11)$$

where $\theta = \int_0^{\delta} \rho dx$; the expression for θ is found from (8):

$$\theta = \frac{3\rho_0 N}{3 + \delta N} \left(\frac{\delta}{N} + \frac{\delta^2}{4} \right). \quad (12)$$

We rewrite (11) as

$$3 \frac{d}{d\tau} \left(\frac{\frac{\delta}{N} + \frac{\delta^2}{4}}{3 + \delta N} \right) = \frac{w\delta - 3D}{3 + \delta N}. \quad (13)$$

We differentiate the left side of this expression and take δ as a function of τ ; we separate the variables and get

$$3 \frac{\frac{3}{N} + \frac{3}{2} \delta + \frac{N\delta^2}{4}}{(3 + \delta N)(w\delta - 3D)} d\delta = d\tau. \quad (14)$$

We transform (14) and integrate:

$$3 \int \frac{\frac{3}{N} + \frac{3}{2} \delta + \frac{N\delta^2}{4}}{a\delta^2 + b\delta + c} d\delta = \tau + K, \quad (15)$$

where $a = wN$, $b = 3(w - ND)$, $c = -9D$, and K is an arbitrary constant, which is found from the initial condition

$$\delta = 0 \text{ for } \tau = 0. \quad (16)$$

We integrate this expression and find the arbitrary constant as

$$A \frac{1}{\sqrt{b^2 - 4ac}} \ln \frac{(2ax + b - \sqrt{b^2 - 4ac})(b + \sqrt{b^2 - 4ac})}{(2ax + b + \sqrt{b^2 - 4ac})(b - \sqrt{b^2 - 4ac})} + B \ln \left| \frac{ax^2 + bx + c}{c} \right| + Mx = \tau, \quad (17)$$

where

$$a = \frac{w^2(k-1)}{D}; \quad b = 3w(2-k); \quad c = -9D;$$

$$A = \frac{3D}{w(k-1)} \left(\frac{3}{4} + \frac{9}{8} k^2 \right); \quad B = \frac{9}{8} \frac{Dk}{w^2(k-1)}; \quad M = \frac{3}{4w}.$$

$$a_0 = \frac{3\rho_0}{3 + \delta N}; \quad a_1 = \frac{3\rho_0 N}{3 + \delta N}; \quad a_2 = -\frac{3\rho_0 N}{\delta(3 + \delta N)}; \quad a_3 = \frac{\rho_0 N}{\delta^2(3 + \delta N)},$$

where $N = (k-1)w/D$.

Then the above polynomial gives (7) as

$$\rho = \frac{\rho_0 N}{3 + \delta N} \left(\frac{3}{N} + 3x - \frac{3x^2}{\delta} + \frac{x^3}{\delta^2} \right) \quad (8)$$

or

$$\frac{\rho}{\rho_0} = 1 - \frac{N\delta}{3 + \delta N} \left(\frac{x}{\delta} - 1 \right)^3 \quad (9)$$

We derive the motion of the diffusion layer from the equation of conservation of matter; we multiply both parts of (1) by dx

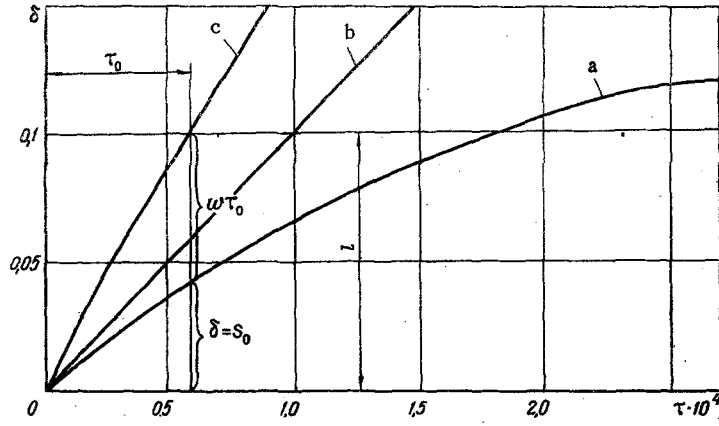


Fig. 2. Thickness and position of upper boundary of diffusion layer in the system of coordinates ox and o_1x .

As $b^2 - 4ac = 9w^2k^2$, $\sqrt{b^2 - 4ac} = 3wk$, $b + \sqrt{b^2 - 4ac} = 6w$, and $b - \sqrt{b^2 - 4ac} = 6w(1-k)$, we get that (17) simplifies to

$$L \ln \left[\frac{6 - 2 \frac{\omega}{D} \delta}{6 - 2 \frac{\omega}{D} (1-k)\delta} \right] + B \ln \left[\frac{\omega^2 (1-k)}{9D^2} \delta^2 - \frac{\omega}{3D} (2-k)\delta + 1 \right] + \frac{3}{4w} x = \tau, \quad (18)$$

where

$$L = \frac{A}{3wk} = \frac{3D}{4w^2k(k-1)} \left(1 + \frac{3}{2} k^2 \right).$$

Equation (18) gives the τ dependence of δ in inexplicit form.

The expression in the logarithm is meaningful if it is greater than zero; if the quantities become zero, then $\tau \rightarrow \infty$, since coefficients L and B are negative for $K < 1$; then the thickness of the diffusion layer does not increase without limit but tends to a certain finite value, which is found by equating to zero the quantity in the logarithm:

$$6 - 2 \frac{\omega}{D} \delta = 0,$$

which gives

$$\delta_{\max} = 3D/w; \quad (19)$$

if $\delta = 3D/w$, the quantity in the logarithm in the second term on the left in (18) also becomes zero.

Then the thickness of the diffusion layer varies during the growth from 0 to $3D/w$; we determined the dope concentration at the crystallization front for $\delta = \delta_{\max}$, for which purpose in (8) we put $x = 0$ and $\delta = \delta_{\max} = 3D/w$:

$$\rho = \frac{3\rho_0}{3 + \frac{\omega}{D}(k-1) \frac{3D}{w}} = \frac{\rho_0}{k}.$$

From (18) we get that $\delta = \delta_{\max}$ for $\tau = \infty$; we can assume approximately that the impurity that the dope distribution in the melt is steady when a time τ_1 has passed such that the thickness of the diffusion layer differs by only 1% from its maximal value; we put $\delta = 0.99 \cdot 3D/w$ in (18) to get

$$\tau_1 = L \ln \left| \frac{0.06}{0.06 + 5.94k} \right| + B \ln |0.01k| + 0.7425 \frac{D}{w^2}. \quad (20)$$

The equations for the second period are

$$\frac{\partial \rho}{\partial \tau} = D \frac{\partial^2 \rho}{\partial x^2} + \omega \frac{\partial \rho}{\partial x}, \quad \tau > \tau_0, \quad 0 < x < l - \omega\tau_0, \quad (21)$$

$$\rho(x, \tau_0) = f_1(x), \quad (22)$$

$$\frac{\partial \rho(0, \tau)}{\partial x} = \frac{(k-1)\omega}{D} \rho(0, \tau), \quad (23)$$

$$\frac{\partial \rho(s, \tau)}{\partial x} = 0. \quad (24)$$

Condition (24) is given at the mobile boundary, whose coordinate is defined by

$$s = s_0 - \omega(\tau - \tau_0) = l - \omega\tau. \quad (25)$$

The initial distribution $f_1(x)$ is obtained from the solution for the first part of the problem.

We seek a solution in the form of (7) and do this via the additional boundary condition

$$\frac{\partial^2 \rho(s, \tau)}{\partial x^2} = 0. \quad (26)$$

We use (23), (24), and (26) to express all the coefficients in (7) in terms of a_3 ; then the concentration distribution in the melt is

$$\rho = a_3 \left(\frac{3}{N} s^2 + 3s^2x - 3sx^2 + x^3 \right). \quad (27)$$

To find a_3 we use the integral for the conservation of matter for the dope; both sides in (21) are multiplied by dx and integrated with limits 0 and s , which gives

$$\frac{d\theta}{d\tau} = D \left[\frac{\partial \rho(s, \tau)}{\partial x} - \frac{\partial \rho(0, \tau)}{\partial x} \right] + \omega [\rho(s, \tau) - \rho(0, \tau)], \quad (28)$$

where $\theta = \int_0^s \rho dx$; we use (27) to get an expression for θ :

$$\theta = a_3 \left[\frac{3D}{(k-1)\omega} s^3 + \frac{3}{4} s^4 \right]. \quad (29)$$

Substitution of (27) into (28) gives

$$\frac{d\theta}{d\tau} = a_3(\omega s^3 - 3Ds^2). \quad (30)$$

Differentiation of θ with respect to τ , with s taken as a function of τ , gives with substitution into (30) that

$$\frac{da_3}{d\tau} \left[\frac{3D}{(k-1)\omega} s^3 + \frac{3}{4} s^4 \right] + a_3 \left[\frac{9D}{(k-1)\omega} s^2 + 3s^3 \right] \frac{ds}{d\tau} = a_3(\omega s^3 - 3Ds^2). \quad (31)$$

This expression is of the form

$$\frac{da_3}{d\tau} + C(\tau)a_3 = 0, \quad (32)$$

where

$$C(\tau) = \frac{[9D + 3s(k-1)\omega] \frac{ds}{d\tau} - (k-1)(\omega s + 3D)\omega}{3Ds + \frac{3}{4}s^2(k-1)\omega}. \quad (33)$$

The general solution to (32) is

$$a_3 = P \exp \left[- \int_{\tau_0}^{\tau} C(\tau) d\tau \right]. \quad (34)$$

The constant P is determined from the initial condition

$$\tau = \tau_0 \quad \rho = \rho(0, \tau_0). \quad (35)$$

We find $\rho(0, \tau)$ from (8) by putting $x = 0$ and $\delta = \delta(\tau_0) = s_0$:

$$\rho(0, \tau_0) = \frac{3\rho_0}{3 + s_0N}. \quad (36)$$

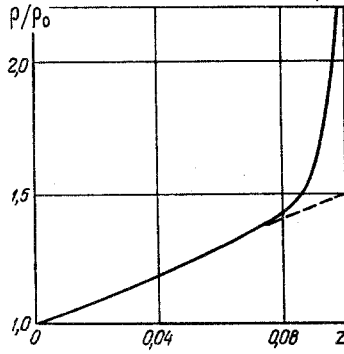


Fig. 3. Relative concentration of impurities at crystallization for various positions in the o_1z coordinate system.

We find $\rho(0, \tau)$ by putting $x = 0$ in (39):

$$\rho(0, \tau) = \frac{3\rho_0}{3 + \frac{\omega(k-1)}{D} s_0} \cdot \frac{s_0^2}{s_0^2} \exp \left[- \int_{\tau_0}^{\tau} C(\tau) d\tau \right]. \quad (40)$$

To calculate $\int_{\tau_0}^{\tau} C(\tau) d\tau$ it is convenient to convert from the variable τ to s ; in the present case $s < s_0$, so we alter the limits of integration to get

$$- \int_{\tau_0}^{\tau} C(\tau) d\tau = \frac{1}{\omega} \int_s^{s_0} C(s) ds. \quad (41)$$

Note that the density distributions described by (8) and (27) coincide for $\tau = \tau_0$.

These solutions have been used to calculate the dope distribution in the melt in a cylindrical crucible with $l = 100$ mm; the crystallization rate was taken as 10^{-5} m/sec (36 mm/h), with $D = 5 \cdot 10^{-7}$ m²/sec and $k = 0.2$. Figure 2a shows δ as a function of τ as derived from (18); this was found by setting δ and determining τ . Curve b characterizes the position of the crystallization front in the coordinate system o_1z , which is related to the form. We add the ordinates of lines a and b to get curve c, which characterizes the upper boundary of the diffusion layer in the o_1z coordinate system.

The first period comes to an end when $\delta + w\tau_0 = l$, i.e., when line c intersects the horizontal straight line with ordinate l ; in the case of Fig. 2 we get $\delta = 0.042$ m and $\tau_0 = 5800$ sec, where $\delta < \delta_{\max}$, since

$$\delta_{\max} = \frac{3D}{\omega} = \frac{3 \cdot 5 \cdot 10^{-7}}{10^{-5}} = 0.15 \text{ m.}$$

Figure 3 shows the relative dope concentration at the front for various positions of the latter in the o_1z coordinate system; this was calculated from (9) for $\tau < \tau_0$, $z < 0.058$ m from the solution for the first part of the problem with $x = 0$, while for $\tau > \tau_0$, $z > 0.058$ m it was calculated from (40) via the solution for the second part; $\tau = \tau_0$, $\rho/\rho_0 = 1.29$. The figure also shows for $z > 0.058$ m the dope concentration (broken line) derived from (9) on the assumption that the crystallization occurs in a crucible of length $l > w\tau + \delta$ for $z < 0.1$ m (in the general case for crystallization in a crucible of semiinfinite length).

It is clear that the restriction on the crucible length must be taken into account, because otherwise one would get considerable error in determining the concentration at the crystallization front when this approaches the end of the crucible. If we can neglect diffusion in the solid state in Bridgman's method, the relative dope distribution in the finished crystal will be determined by the curve of Fig. 3; here $\rho|_{z=0} = \rho_0 k$; if one cannot neglect solid-state diffusion, one has to solve also for the distribution in the solid phase for a region with mobile boundary on the basis of the solutions obtained here for diffusion of the dope in the melt.

NOTATION

δ is the thickness of diffusional layer;
 D is the diffusivity;

From (27) and (34)

$$P = a_3^0 = \frac{\rho_0 N}{s_0^2 (3 + s_0 N)} \quad (37)$$

and further

$$a_3 = \frac{\rho_0 N}{s_0^2 (3 + s_0 N)} \exp \left[- \int_{\tau_0}^{\tau} C(\tau) d\tau \right]. \quad (38)$$

Finally, we put the solution to the second part in the form

$$\rho(x, \tau) = \frac{\rho_0 \omega (k-1)}{s_0^2 [3D + \omega(k-1)s_0]} \exp \left[- \int_{\tau_0}^{\tau} C(\tau) d\tau \right] \times \left[\frac{3Ds^2}{(k-1)\omega} + 3s^2 x - 3s x^2 + x^3 \right]. \quad (39)$$

- ρ is the partial density of admixtures;
 w is the rate of crystallization;
 k is the equilibrium distribution coefficient;
 τ is the time;
 s is the position of moving boundary.

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