# DIFFUSION OF IMPURITIES IN THE SOLID PHASE DURING ORIENTED CRYSTALLIZATION

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The one-dimensional problem of impurity diffusion in a variable-length solid rod is solved approximately by the integral method. Results are shown of typical calculations on the basis of the derived formulas.

When a crystal is grown by oriented pulling from a melt with alloyed impurities, then the impurity distribution will affect the process of impurity diffusion in the melt as well as in the solid phase. In most cases [1] diffusion in the solid phase is disregarded. This is not always permissible, however. In many cases the diffusivity of impurity in the solid phase is of the same order of magnitude as in the liquid phase. Thus, for instance, the diffusivity of copper in both silicon at 1200°C and in germanium at 850°C is $10^{-9}$ $m^2$/sec, i.e., of the same order as in the liquid phase. The diffusivity of lithium in silicon and in germanium under the same conditions is somewhat higher [2]. Evidently, analogous situations are encountered further in a wide range of technical applications for new materials.

We will consider the problem of impurity diffusion in the solid phase during oriented crystallization in a crucible of uniform cross section and height h. The problem will be treated in the one-dimensional formulation. The diffusivity of impurity in the solid phase will be assumed to be a second-degree parabolic function of the concentration. The crystallization front will be assumed to progress at a rate which is a known function of time. The impurity concentration at the crystallization front will be assumed known. It is determined from the solution to the problem of impurity diffusion in the melt. We will stipulate this concentration in the form of a third-degree polynomial in the length s of the solid phase.

We will formulate the problem in a movable system of coordinates, the origin of which is located on the crystallization front (Fig. 1):

$$\frac{\partial\rho}{\partial\tau} = \frac{\partial}{\partial x}\left[(m + n\rho + p\rho^2)\frac{\partial\rho}{\partial x}\right] - w\frac{\partial\rho}{\partial x}, \tag{1}$$

$$\rho(0,\ \tau) = b_0 + b_1 s + b_2 s^2 + b_3 s^3 = F(s), \tag{2}$$

$$\frac{\partial\rho(s,\ \tau)}{\partial x} = 0. \tag{3}$$

Since no solid phase exists yet at the first instant of time, there arise difficulties in formulating the initial condition – as is the case in many problems of mathematical physics [3]. Impurity diffusion in the solid phase will be considered from some instant of time $\tau_0$ on after crystallization has begun. The solid phase will then have a attained a definite length $s_0$. For a short time interval $\tau_0$ we will disregard diffusion in the solid phase. The initial condition will then be

$$\rho(x,\ \tau_0) = F(s_0 - x). \tag{4}$$

The location of the moving boundary will be determined from the expression

$$s = s_0 + \int_{\tau_0}^{\tau} w(\tau)\,d\tau. \tag{5}$$

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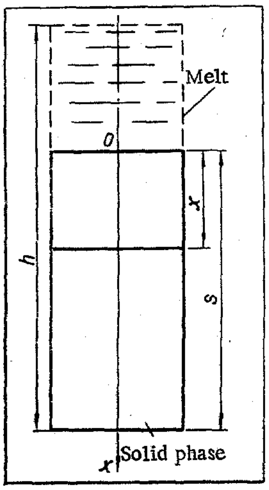

Fig. 1

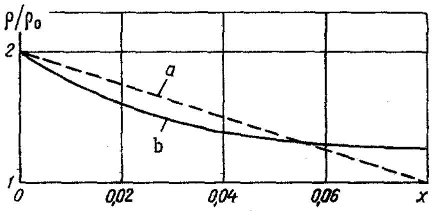

Fig. 2

Fig. 1. Schematic diagram for the problem.

Fig. 2. Relative concentration of impurity along the crystal height: a) without diffusion in the solid phase; b) with diffusion in the solid phase.

We solve the problem by the approximate integral method, which is since recently being used for the solution of problems in heat conduction and diffusion [4-7]. The solution to the problem will be sought in the form of a third-degree polynomial:

$$\rho = a_0 + a_1 x + a_2 x^2 + a_3 x^3. \tag{6}$$

For the solution we formulate an additional boundary condition:

$$\frac{\partial^2 \rho(s, \tau)}{\partial x^2} = 0. \tag{7}$$

Using the boundary conditions (2), (3), and (7), one can rewrite the equation of the concentration profile as

$$\rho(x, \tau) = F(s) + a_3(3s^2 x - 3sx^2 + x^3). \tag{8}$$

Coefficient $a_3$ will be determined from the integral of material balance.

For this purpose we multiply both sides of Eq. (1) by dx and integrate from 0 to s. As a result, we obtain

$$\frac{d\Theta}{d\tau} - \rho(s, \tau)\frac{ds}{d\tau} = m\left[\frac{\partial \rho(s, \tau)}{\partial x} - \frac{\partial \rho(0, \tau)}{\partial x}\right] + n\left[\rho(s, \tau)\frac{\partial \rho(s, \tau)}{\partial x} - \rho(0, \tau)\frac{\partial \rho(0, \tau)}{\partial x}\right]$$
$$+ p\left[\rho^2(s, \tau)\frac{\partial \rho(s, \tau)}{\partial x} - \rho^2(0, \tau)\frac{\partial \rho(0, \tau)}{\partial x}\right] - w[\rho(s, \tau) - \rho(0, \tau)]. \tag{9}$$

The quantity Θ is defined by the expression

$$\Theta = \int_0^s \rho dx = sF(s) + \frac{3}{4}a_3 s^4. \tag{10}$$

Equation (9) will be reduced to the form

$$\frac{da_3}{d\tau} + C(\tau)a_3 + D(\tau) = 0, \tag{11}$$

where

$$C(\tau) = \frac{4\{sw + m + nF(s) + p[F(s)]^2\}}{s^2}; \quad D(\tau) = \frac{4w}{3s^2}(b_1 + 2b_2 s + 3b_3 s^2).$$

In order to determine $a_3$, we solve Eq. (11).

Denoting the variable of integration by $\psi$, we obtain a solution to the given problem in the following form:

$$\rho(x,\ \tau) = F(s) + \left\{ a_3^0 \exp\left[-\int_{\tau_0}^{\tau} C(\psi)\,d\psi\right] - \int_{\tau_0}^{\tau} D(\psi) \exp\left[-\int_{\psi}^{\tau} C(\psi)\,d\psi\right] d\psi \right\} (3s^2x - 3sx^2 + x^3). \tag{12}$$

In order to determine $a_3^0$, we use the condition $\rho(s_0,\ \tau_0) = b_0$ obtained from (4)

$$a_3^0 = -\left(\frac{b_1}{s_0^2} + \frac{b_2}{s_0} + b_3\right).$$

Let us now examine how the term $a_3^0 \exp[-\int_{\tau_0}^{\tau} C(\psi)d\psi]$ varies when $s_0$ tends toward zero. For this purpose we consider the solution to the problem with D = const and w = const. Under the given conditions we have

$$\int_{\tau_0}^{\tau} C(\psi)\,d\psi = 4\left[\ln\frac{s_k}{s_0} + \frac{D}{w}\left(\frac{1}{s_0} - \frac{1}{s_k}\right)\right].$$

We then seek the limit

$$\lim_{\tau_0 \to 0} \left\{ a_3^0 \exp\left[-\int_{\tau_0}^{\tau} C(\psi)\,d\psi\right]\right\} = \lim_{s_0 \to 0} \frac{-\left(\frac{b_1}{s_0^2} + \frac{b_2}{s_0} + b_3\right)}{\exp\left\{4\left[\ln\frac{s_k}{s_0} + \frac{D}{w}\left(\frac{1}{s_0} - \frac{1}{s_k}\right)\right]\right\}} = \lim_{s_0 \to 0} \frac{f(s_0)}{\varphi(s_0)}.$$

This limit will be found by the application of l'Hopital's rule followed by a double differentiation of the numerator and the denominator with respect to $s_0$. The result is

$$\lim_{s_0 \to 0} \frac{f(s_0)}{\varphi(s_0)} = \lim_{s_0 \to 0} \frac{f''(s_0)}{\varphi''(s_0)} = 0.$$

It can be shown analogously that the integrand in formula (12), which contains $D(\psi)$, tends toward zero as $\psi \to 0$. In this way, the term with $a_3^0$ in (12) drops out and the lower limit of integration in the next term can be changed from $\tau_0$ to 0. These results will, evidently, be valid also in the case of variable front velocity and variable diffusivities. For numerical calculations one may use formula (12), assuming small values for $s_0$ (1.0-1.5% of the final crystal height). Such a procedure may simplify the evaluation of the integral which contains $D(\psi)$. Moreover, according to a special analysis, the numerical value of the term with $a_3^0$ is by a few orders of magnitude smaller than the next term and changing $s_0$ in one or another direction by a quantity smaller than $s_0$ has almost no effect on the results of computation.

These formulas were used for calculating the impurity concentration along the height of a crystal grown from a melt at a constant rate and with constant diffusivity D. The impurity concentration at the movable boundary was approximated by a first-degree polynomial in s:

$$\rho(0,\ \tau) = \rho_0(1 + 12.5s).$$

The velocity of the crystallization front was assumed equal to $1.388 \cdot 10^{-6}$ m/sec (5 mm/h) and the diffusivity $D = 10^{-9}$ m$^2$/sec, the latter value corresponding to the diffusivity of copper in germanium and in silicon. The impurity distribution in the solid phase was determined for a crystallized rod of length $s_c = 0.08$ m. The impurity distribution in the crystal, calculated according to formula (12), is shown in Fig. 2. The dashed line also shown on the same diagram represents the impurity concentration along the crystal height without diffusion in the solid phase. According to these graphs, impurity diffusion in the solid phase under the given conditions tends to equalize the impurity concentration along the crystal height. The procedure proposed here for solving the problem without an initial condition can also be used for determining the temperature distribution in the solid phase of a growing crystal, when the law of movement of the crystallization front is given.

## NOTATION

$\tau$ is the time;
$\rho$ is the partial density of impurities;
D is the diffusivity;
w is the velocity of crystallization front;
s is the position of movable boundary.

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