B. I. BIRMAN, B. L. TIMAN

PHYSICS

1965

SovietRxiv

Abstract

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B. I. BIRMAN, B. L. TIMAN

ANALYSIS OF THE CONDITIONS FOR THE OCCURRENCE OF DIFFERENT DISTRIBUTIONS OF IMPURITIES IN CRYSTALS DURING DIRECTIONAL CRYSTALLIZATION

(Presented by Academician I. V. Obreimov, September 9, 1964)

PHYSICS

The distribution of impurities over the volume of a crystal, for a diffusion mechanism of transport in the liquid phase and under the assumption that the concentration depends only on the axial coordinate x and on time t, has been studied theoretically in many works ($^{1-4}$). In all these works, in order to solve the diffusion equation in the liquid phase,

$$\frac{1}{D}\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial x^2} \tag{1}$$

the same initial and boundary conditions were adopted:

$$C(x, 0) = c_0 = \text{const}; \tag{2}$$

$$j_L = -D\frac{\partial c}{\partial x}\bigg|_{x=L} = 0; \tag{3}$$

$$(1-k)v(t)C(y(t), t) + D\frac{\partial C}{\partial x}\bigg|_{x=y(t)} = 0. \tag{4}$$

The impurity concentration in the solid phase was found from the equation

$$C\ \ (x) = kC(x, t)\big|_{t=y^{-1}(x)} = kC_\phi(t)\big|_{t=y^{-1}(x)}, \tag{5}$$

where $C(x, t)$, $C\ \ (x)$, $C_\phi(t)$ are, respectively, the impurity concentrations in the melt, in the crystal, and at the crystallization front on the melt side; D is the diffusion coefficient in the melt; $y(t)$ is the distance of the crystallization front from the beginning of the container; L is the length of the container; k is the impurity distribution coefficient; j_L is the diffusion flux at the end of the container; $v(t) = dy/dt$ is the growth rate. The growth rate in these works was assumed either constant ([1–4]) or varying inversely proportional to the square root of time ([2]).

The character of the impurity distribution in the crystal must obviously be affected by the distribution law of the initial concentration in the melt, by the influx or removal of substance at the end of the container, and by a variable growth rate. For analyzing the influence of these factors, a direct search for solutions of equation (1) is associated with considerable mathematical difficulties. Therefore the inverse problem is more appropriate: finding solutions of the diffusion equation (1) when the balance condition (4) is satisfied at the crystallization front and the law $C_\phi(t)$ is known. The latter condition is analogous to a preassigned impurity distribution in the crystal. In this case, the initial distribution of impurity in the melt $C(x,0)$ and the diffusion flux $j_L(t)$, which ensure the realization of this distribution, are the unknowns.

In this formulation the problem can be solved by a method analogous to that used in works ([5,6]) for analyzing the distribution of thermal fields during crystallization of a flat plate. As a result, the following expression is obtained for $C(x,t)$:

$$C(x,t) = C_\phi(t) + \sum_{n=0}^{\infty} \frac{1}{D^{n+1}} \frac{d^n}{dt^n} \left\{ \frac{[y(t)-x]^{2n+2}}{(2n+2)!} \frac{dC_\phi}{dt} \right\} + \\ + \sum_{n=0}^{\infty} \frac{1}{D^{n+1}} \frac{d^n}{dt^n} \left\{ \frac{[y(t)-x]^{2n+1}}{(2n+1)!} (1-k) \frac{dy}{dt} C_\phi(t) \right\}. \quad (6)$$

It is applicable for any time dependence of the growth rate and of the distribution coefficient.

1. When the growth rate and the distribution coefficient are constant, the impurity concentration and the diffusion flux in the melt are determined by the formulas

$$C(x,t) = C_\phi(t) + \sum_{s=1}^{\infty} \frac{D^s}{v^{2s}} \frac{d^s C_\phi}{dt^s} H_s\left(\frac{v(x-vt)}{D}\right) - \\ -(1-k) \sum_{s=0}^{\infty} \frac{D^s}{v^{2s}} \frac{d^s C_\phi}{dt^s} K_s\left(\frac{v(x-vt)}{D}\right); \quad (7)$$

$$i(x,t) = v \left\{ (1-k) \sum_{s=0}^{\infty} \frac{D^s}{v^{2s}} \frac{d^s C_\phi}{dt^s} K_s^*\left(\frac{v(x-vt)}{D}\right) - \sum_{s=1}^{\infty} \frac{D^s}{v^{2s}} \frac{d^s C_\phi}{dt^s} H_s^*\left(\frac{v(x-vt)}{D}\right) \right\}, \quad (8)$$

where

$$H_s(z) = \sum_{l=0}^{\infty} \frac{(l+s-1)!}{l!(s-1)!} \frac{(-1)^l z^{l+2s}}{(l+2s)!}; \tag{9}$$

$$K_s(z) = \sum_{l=0}^{\infty} \frac{(l+s)!}{l!s!} \frac{(-1)^l z^{l+2s+1}}{(l+2s+1)!}; \tag{10}$$

$$H_s^*(z) = K_{s-1}(z); \tag{11}$$

$$K_s^*(z) = H_{s-1}(z) - K_{s-1}(z). \tag{12}$$

Series (9), (10) can be summed. We give their expressions for $s \leqslant 4$:

$$H_1(z) = z - 1 + e^{-z},$$

$$H_2(z) = (z^2/2 - 2z + 3) - (z+3)e^{-z}, \tag{13}$$

$$H_3(z) = (z^3/6 - \tfrac{3}{2}z^2 + 6z - 10) + e^{-z}(z^2/2 + 4z + 10),$$

$$H_4(z) = (z^4/4 - \tfrac{2}{3}z^3 + 5z^2 - 20z + 35) - \\ -e^{-z}(z^3/6 + \tfrac{5}{2}z^2 + 15z + 35);$$

$$K_0(z) = H_1^*(z) = 1 - e^{-z},$$

$$K_1(z) = H_2^*(z) = (z-2) + e^{-z}(z+2),$$

$$K_2(z) = H_3^*(z) = (z^2/2 - 3z + 6) - e^{-z}(z^2/2 + 3z + 6), \tag{14}$$

$$K_3(z) = H_4^*(z) = (z^3/6 - 2z^2 + 10z - 20) + \\ +e^{-z}(z^3/6 + 2z^2 + 10z + 20),$$

$$K_4(z) = H_5^*(z) = (z^4/24 - \tfrac{5}{6}z^3 + \tfrac{15}{2}z^2 - 35z + 70) - \\ -e^{-z}(z^4/24 + \tfrac{5}{6}z^3 + \tfrac{15}{2}z^2 + 35z + 70).$$

For many practical purposes it is necessary to grow crystals with a uniform distribution of impurity along their length. To ensure

this condition is necessary in order that, during the growth process, C_ϕ remain constant.

It follows from formula (7) that in this case the solution has the form

$$C(x,t) = C_\phi \left[k + (1-k)e^{-v(x-vt)/D}\right]. \tag{15}$$

It is seen from this that, in order to ensure uniform incorporation of the impurity into the crystal at a constant growth rate, it is necessary that $C(x,0)$ and $j_L(t)$ vary according to an exponential law:

$$C(x,0) = C_\phi \left[k + (1-k)e^{-vx/D}\right]; \tag{16}$$

$$j_L(t) = C_\phi v(1-k)e^{v(vt-L)/D}. \tag{17}$$

2. At a variable growth rate the treatment becomes more cumbersome; however, in principle it can be carried through to the end. For example, in the case where the growth rate increases proportionally to time,

$$v(t) = bt, \tag{18}$$

and the distribution coefficient is constant, the impurity concentration in the melt, under the condition $C_\phi = \text{const}$, is determined by the formula

$$C(x,t) = C_\phi \left[1 + (1-k)\sum_{s=1}^{\infty} \frac{(-1)^s (2s)!\, b^s \left(x - bt^2/2\right)^{3s}}{(3s)!\, s!\, 2^{s D^{2s}}}\right]. \tag{19}$$

The results obtained may be used for choosing conditions that ensure a prescribed impurity distribution in advance during directional crystallization, both at a constant and at a variable growth rate.

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Received
9 IX 1964

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Note: Figure translations are in progress. See original paper for figures.