EFFECT OF THERMAL CONDITIONS ON THE STABILITY OF A CRYSTALLIZATION PROCESS FROM A MELT

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The stability of a crystallization process from a melt is considered in the approximation of the one-dimensional thermal problem in relation to random displacements of the liquid and solid phase interface as a function of the crystallization conditions.

At the present time, the production of crystals and methods of crystallization from the melt are receiving the most widespread popularity (fused zone methods of Chokhral'skii, Verneille [1], and Stepanov [2]). The absence of a strict configuration formation unifies them and, therefore, the form of the crystal is determined by the growing mechanism. Disturbances of any kind of the stability of the growth parameters lead to a change of the transverse dimensions and are the main cause of the appearance of defects in a crystal.

A change of dimensions of a growing crystal is due to a change of position of the crystallization front. Usually, the automatic maintenance of the crystallization front by determining the level leads to an improvement of the shape and quality of the crystal. It will be interesting to carry out an analysis of the thermal conditions of crystal growth for the purpose of choosing crystallization conditions which will ensure stability of the position of the crystallization front in relation to random perturbations. The application of these conditions permits the growth process to be used as an automatic control system and crystals of improved quality and constant cross section to be obtained.

A study of the nonsteady-state equation of thermal conductivity, taking account of the special features of the structure of the thermal zone, will be a direct solution of the problem posed. However, it appears that in the investigation of crystallization from a melt data about the stability of the process can be obtained as a result of solving the quasi-steady-state problem. As demonstration of the validity of this approach to crystallization processes the excellent agreement between the theoretical [3] and experimental [4] results obtained during the investigation of the shape stability of the liquid and solid phase interface can be used.

We shall judge the behavior of the system by the sign of the ratio $\eta = \delta'/\delta$ (δ is the amplitude of the random displacement of the crystallization front and δ' is the speed of displacement of the front as a result of the reaction of the system to the perturbation). If $\eta < 0$ (there is a negative feedback), the system is stable. If $\eta > 0$ (there is a positive feedback in the system), the system is unstable. We shall consider the problem in the system of coordinates shown in Fig. 1. For this, we shall assume the isotherms to be planes, we shall substitute the actual liquid column by a vertical cylinder, and we shall not take into account thermal convection in the melt. The temperature distribution in the melt and in the crystal will be found as the result of solving the boundary-value problem for the one-dimensional thermal conductivity equations, taking into account the movement of the substance and the heat exchange at the surface [5]:

$$\frac{d^2T_1}{dx^2} - \frac{V}{\varkappa_1} \cdot \frac{dT_1}{dx} - \frac{2\mu}{R\lambda_1}(T_1 - T_m) = 0, \quad 0 \leqslant x \leqslant X, \tag{1}$$

$$\frac{d^2T_2}{dx^2} - \frac{V}{\varkappa_2} \cdot \frac{dT_2}{dx} - \frac{2\mu}{R\lambda_2}(T_2 - T_m) = 0, \quad X \leqslant x \leqslant L. \tag{2}$$

Obviously, the first boundary condition is

$$T_1|_{x=X} = T_2|_{x=X} = T_0. \tag{3}$$

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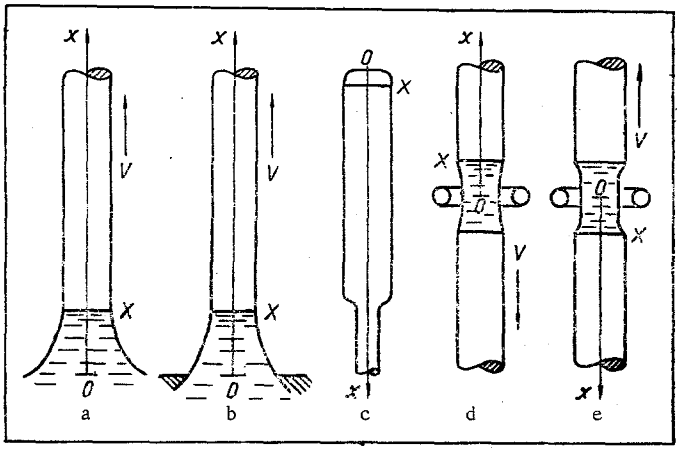

Fig. 1. Diagram of crystallization by the method of: a) Chokhral'skii; b) Stepanov; c) Verneille; d) fused zone (zone moving downward); e) fused zone (zone moving upward).

For the melt, we shall assume a known temperature at a fixed point of the liquid column, which we shall use as the origin of the coordinates,

$$T_1|_{x=0} = T_f \,. \tag{4}$$

For the crystal, we shall consider the problem for two types of boundary conditions.

I. Temperature at the end of the crystal is fixed

$$T_2|_{x=L} = T_3 . \tag{5}$$

II. Heat removal through seeding is fixed

$$\left.\frac{dT_2}{dx}\right|_{x=L} = k. \tag{6}$$

Equations (1) and (2), in which the heat exchange is given by Newton's law, can be used for high temperatures, if it is assumed that

$$\mu = \mu_c + \mu_r , \tag{7}$$

where

$$\mu_r = \sigma f_{b.s} \frac{T_{cr}^4 - T_m^4}{T_{cr} - T_m} \,. \tag{8}$$

A similar linearization of the law of radiation by a radiation coefficient leads to results which coincide with experiment during the crystallization of such a high-temperature substance as ruby [6].

An additional condition associated with the distribution of temperatures in the liquid and solid phases is the equation of thermal balance at the crystallization front:

$$-\lambda_2 \left.\frac{dT_2}{dx}\right|_{x=X} + \lambda_1 \left.\frac{dT_1}{dx}\right|_{x=X} = \mathcal{L}\rho V. \tag{9}$$

If the position of the crystallization front receives a small perturbation δ, for example, as the result of a brief change of displacement of the crystal, conditions (3) and (9) must be fulfilled for the new position of the crystallization front, taking into account the difference between the actual rate of crystallization and the rate of displacement of the crystal, by the amount of the rate of movement of the crystallization front as a result of the reaction of the system to the perturbation.

$$T_1|_{x=X+\delta} = T_2|_{x=X+\delta} = T_0 , \tag{10}$$

$$-\lambda_2 \left.\frac{dT_2}{dx}\right|_{x=X+\delta} + \lambda_1 \left.\frac{dT_1}{dx}\right|_{x=X+\delta} = \mathcal{L}\rho (V - \dot{\delta}). \tag{11}$$

Expressions for the temperature gradients in the liquid and solid phases with the new position of the crystallization front can be expanded in Taylor series and, by using the smallness δ, can be limited to the linear terms of the expansion

$$-\lambda_2 \frac{dT_2}{dx}\bigg|_{x=X} - \lambda_2\delta \frac{d}{dX}\left(\frac{dT_2}{dx}\bigg|_{x=X}\right) + \lambda_1 \frac{dT_1}{dx}\bigg|_{x=X} + \lambda_1\delta \frac{d}{dX}\left(\frac{dT_1}{dx}\bigg|_{x=X}\right) = \mathcal{L}\rho\,(V-\dot{\delta}).$$

Taking Eq. (9) into account, we obtain

$$\eta = \frac{\dot{\delta}}{\delta} = \frac{\lambda_2}{\mathcal{L}\rho}\cdot\frac{d}{dX}\left(\frac{dT_2}{dx}\bigg|_{x=X}\right) - \frac{\lambda_1}{\mathcal{L}\rho}\times\frac{d}{dX}\left(\frac{dT_1}{dx}\bigg|_{x=X}\right). \tag{12}$$

The temperature gradients in the liquid and solid phases, in the presence of a perturbation of the crystallization front, can vary because of a change in the following parameters: a) extension of the liquid zone; b) temperature of the outside medium; and c) the heat-exchange coefficient of the crystal surface. We shall not take into account a change in length of the crystal. The length of the crystal is changing continuously during crystallization and, therefore, we shall consider the case when L ≫ X. Expression (12) can now be transformed in the following way:

$$\eta = -\frac{\lambda_1}{\mathcal{L}\rho}\left[\frac{d}{dX}\left(\frac{dT_1}{dx}\bigg|_{x=X}\right) + \frac{d}{dT_{\mathrm{m}}}\left(\frac{dT_1}{dx}\bigg|_{x=X}\right)\frac{dT_{\mathrm{m}}}{dX} + \right.$$

$$\left. + \frac{d}{dY}\left(\frac{dT_1}{dx}\bigg|_{x=X}\right)\frac{dY}{dX}\right] + \frac{\lambda_2}{\mathcal{L}\rho}\left[\frac{d}{dT_{\mathrm{m}}}\left(\frac{dT_2}{dx}\bigg|_{x=X}\right)\frac{dT_{\mathrm{m}}}{dX} + \frac{d}{dY}\left(\frac{dT_2}{dx}\bigg|_{x=X}\right)\frac{dY}{dX}\right]. \tag{13}$$

Let us consider, first of all, the contribution to the stability of a change of the extent of the liquid zone and the temperature of the surrounding medium, on the assumption that the crystal size does not change and that the heat-exchange coefficient remains constant, and then we shall consider a change of crystal size and a nonconstant heat-exchange coefficient of the surface. This approach is justified in that the problem will be considered in linear approximation and the contribution of all factors to the stability can be assumed to be additive.

Suppose that the temperature distribution of the medium is specified by the linear function

$$T_{\mathrm{m}} = T_{\mathrm{m}0} - kx. \tag{14}$$

We introduce the scaled temperatures

$$T_i^* = T_i - T_{\mathrm{m}} \quad (i = 1,\ 2,\ T_{\mathrm{m}} = \mathrm{const});$$

$$T_i^* = T_i - T_{\mathrm{m}0} + kx - \frac{k\lambda_i RV}{2\mu\varkappa_i} \quad (T_{\mathrm{m}} \neq \mathrm{const});$$

$$T_{0i}^* = T_0 - T_{\mathrm{m}0} + kX - \frac{k\lambda_i RV}{2\mu\varkappa_i};$$

$$T_{\mathrm{f}}^* = T_{\mathrm{f}} - T_{\mathrm{m}0} - \frac{k\lambda_1 RV}{2\mu\varkappa_1};$$

$$T_3^* = T_3 - T_{\mathrm{m}0} + kL - \frac{k\lambda_2 RV}{2\mu\varkappa_2}.$$

Equations (1) and (2) and the boundary conditions (3)-(6) assume the form

$$\frac{d^2T_i^*}{dx^2} - \frac{V}{\varkappa_i}\cdot\frac{dT_i^*}{dx} - \frac{2\mu}{R\lambda_i}T_i^* = 0; \tag{15}$$

$$T_1^*|_{x=0} = T_{\mathrm{f}}^*; \tag{16}$$

$$T_i^*|_{x=X} = T_{0i}^*; \tag{17}$$

$$T_2|_{x=L} = T_3^*; \tag{18}$$

$$\frac{dT_2^*}{dx}\bigg|_{x=L} = 0. \tag{19}$$

The last condition is obtained on the assumption that the seeding area is much less than the area of the crystal and that the removal of heat from the crystal is effected in consequence of the nonconstant temperature of the outside medium. We denote

$$\xi_i = \sqrt{\frac{V^2}{4\varkappa_i^2} + \frac{2\mu}{R\lambda_i}}.$$

We find

$$T_1^* = \operatorname{csch}(\xi_1 X) \left\{T_f^* \exp\left(\frac{V}{2\varkappa_1}\, x\right) \operatorname{sh}[\xi_1 (X - x)] + T_{01}^* \exp\left[\frac{V}{2\varkappa_1}\, (x - X)\right] \operatorname{sh}(\xi_1 x)\right\};$$

$$\left.\frac{dT_1^*}{dx}\right|_{x=X} = -T_f^* \xi_1 \exp\left(\frac{V}{2\varkappa_1}\, X\right) \operatorname{csch}(\xi_1 X) + T_{01}^* \left[\frac{V}{2\varkappa_1} + \xi_1 \operatorname{cth}(\xi_1 X)\right]. \qquad (20)$$

We expand exp [(V/2$\varkappa_1$)X] in series and, using the smallness (V/2$\varkappa_1$)X, we limit ourselves to two terms of the expansion

$$\left.\frac{dT_1}{dx}\right|_{x=X} = -T_f^* \xi_1 \left(1 + \frac{V}{2\varkappa_1}\, X\right) \operatorname{csch}(\xi_1 X) + T_{01}^* \left[\frac{V}{2\varkappa_1} + \xi_1 \operatorname{cth}(\xi_1 X)\right]. \qquad (21)$$

For the boundary conditions (17) and (18)

$$T_2^* = \operatorname{csch}[\xi_2 (L - X)] \left\{T_{02}^* \exp\left[\frac{V}{2\varkappa_2}\, (x - X)\right] \operatorname{sh}[\xi_2 (L - x)]\right\} + T_3^* \exp\left[\frac{V}{2\varkappa_2}\, (x - L)\right] \operatorname{sh}[\xi_2 (x - X)]; \qquad (22)$$

$$\left.\frac{dT_2^*}{dx}\right|_{x=X} = T_{02} \left\{\frac{V}{2\varkappa_2} - \xi_2 \operatorname{cth}[\xi_2 (L - X)]\right\} + \xi_2 T_3^* \exp\left[\frac{V}{2\varkappa_2}\, (X - L)\right] \operatorname{csch}[\xi_2 (L - X)]. \qquad (23)$$

For boundary conditions (17) and (19)

$$T_2^* = T_{02}^* \frac{\frac{V}{2\varkappa_2} \operatorname{sh}[\xi_2 (L - x)] + \xi_2 \operatorname{ch}[\xi_2 (L - x)]}{\frac{V}{2\varkappa_2} \operatorname{sh}[\xi_2 (L - X)] + \xi_2 \operatorname{ch}(\xi_2 (L - X)]} \exp\left[\frac{V}{2\varkappa_2}\, (x - X)\right], \qquad (24)$$

$$\left.\frac{dT_2^*}{dx}\right|_{x=X} = T_{02}^* \left\{\frac{V}{2\varkappa_2} - \xi_2 \frac{\frac{V}{2\varkappa_2} \operatorname{ch}[\xi_2 (L - X)] + \xi_2 \operatorname{sh}[\xi_2 (L - X)]}{\frac{V}{2\varkappa_2} \operatorname{sh}[\xi_2 (L - X)] + \xi_2 \operatorname{ch}[\xi_2 (L - X)]}\right\}. \qquad (25)$$

If the heat-exchange coefficient or the diameter of the crystal (liquid column) depends on the coordinates (T_m = const), Eq. (1) and (2) can be written as

$$\frac{d^2 T_i^*}{dx^2} - \frac{V}{\varkappa_i} \cdot \frac{dT_i^*}{dx} - \frac{2}{\lambda_i} Y(x) T_i^* = 0. \qquad (26)$$

By the substitution of $T_i^* = \tau_i \exp[(V/2\varkappa_i)x]$, Eq. (26) is converted to the form

$$\frac{d^2 \tau_i}{dx^2} - \left[\frac{V^2}{4\varkappa_i^2} + \frac{2}{\lambda_i} Y(x)\right] \tau_i = 0. \qquad (27)$$

The theory of the approximate solution of equations of the type (27) has been well developed [7]. In the vicinity of the point X, an approximation can be obtained for Y(x) from the power series

$$Y(x) = Y(X) + (x - X) Y'(X) + \frac{1}{2} (x - X)^2 Y''(X) + \cdots. \qquad (28)$$

If, in expression (28), the expansion is limited to three terms, the function Y(x) will be approximated by a considerable segment in the vicinity of the point X, and the solution of Eq. (27) can be represented approximately in terms of a Beber function [7]. If, in expression (28), the term containing $(x - X)^2$ can be neglected, Eq. (27) will be the standard form of the equation for the Airy integral. Neglecting terms with (x − X) and subsequent ones in the right-hand side of Eq. (28) we obtain the equation

$$\frac{d^2 \tau_i}{dx^2} - \left[\frac{V^2}{4\varkappa_i^2} + \frac{2}{\lambda_i} Y(X)\right] \tau_i = 0, \qquad (29)$$

the solution of which has the form

$$\tau_i = C_1 \exp[\xi_i (X) x] + C_2 \exp[-\xi_i (X) x]. \qquad (30)$$

This expression is the approximation to the solution of Eq. (27) in the interval $|x - X|$ of a quite small quantity. By choosing another starting point, $x = X_1$, an approximation can be obtained which is valid in the interval $|x - X_1|$ of a quite small quantity, etc. The constants C_1 and C_2 are determined in each interval by means of the values found in the adjacent intervals, and the quantities τ_i and τ_i' are compared at the points defining the two intervals. Thus, we approximate Y(x) by a power function for which it can be assumed $T_m \neq$ const. This process is effective if Y'/Y is small.

The cause of a change of the heat-exchange coefficient at the surface can be, for example, a forced "blowing" of the crystal in a localized zone [8], and the cause of a change of the diameter is a change of the thermal mechanism of growing in the case of displacement of the crystallization front, which is characteristic of Verneille's method [9], or capillary effects at the crystal — melt boundary in the case of crystal pulling by Chokhral'-skii's or Stepanov's method [10]. In these cases, the crystal is a cylinder with a step at the crystallization front, originating as a result of the perturbation. The diameter of the melt column also is changed. Let us consider the region immediately adjacent to the crystallization front, assuming that the shape of the step, together with the change of the heat exchange coefficient, determines the form of the function Y(x). We obtain from Eq. (29)

$$T_i^* = \exp\left(\frac{V}{2\varkappa_i}\,x\right)\{C_1\exp[\xi_i(X)\,x] + C_2\exp[-\xi_i(X)\,x]\}, \tag{31}$$

$$\left.\frac{dT_i^*}{dx}\right|_{x=X} = \frac{V}{2\varkappa_i}\exp\left(\frac{V}{2\varkappa_i}\,X\right) + \{C_1\exp[\xi_i(X)\,X] + C_2\exp[-\xi_i(X)\,X]\} +$$
$$+\exp\left(\frac{V}{2\varkappa_i}\,X\right)\{\xi_i C_1\exp[\xi_i(X)\,X] - \xi_i C_2\exp[-\xi_i(X)\,X]\}. \tag{32}$$

If other intervals of change of Y(x) are not considered, only one boundary condition can be used:

$$T_i^*|_{x=X} = T_0^*. \tag{33}$$

Whence

$$\left.\frac{dT_i^*}{dx}\right|_{x=X} = \frac{V}{2\varkappa_i}\,T_0^* + \exp\left(\frac{V}{2\varkappa_i}\,X\right)\xi_i(X)\,\{C_1\exp[\xi_i(X)\,X - C_2\exp[-\xi_i(X)\,X]\}. \tag{34}$$

By using expressions (21), (34), and (23), the criterion of stability (13) can be obtained in explicit form

$$\eta = -\frac{\lambda_1}{\mathscr{L}\rho}\,\xi_1^2\,\frac{T_f^*\,\mathrm{ch}(\xi_1 X) - T_{01}^*}{\mathrm{sh}^2(\xi_1 X)} - \frac{c_1 T_f^*\xi_1 V\,[\xi_1 X\,\mathrm{ch}(\xi_1 X) - \mathrm{sh}(\xi_1 X)]}{2\mathscr{L}\,\mathrm{sh}^2(\xi_1 X)} - \frac{\lambda_1 k}{\mathscr{L}\rho}\left[\frac{V}{2\varkappa_1} + \xi_1\,\mathrm{cth}(\xi_1 X)\right] +$$
$$+\frac{1}{\mathscr{L}\rho R}\left[\frac{1}{\xi_2^2}\cdot\left.\frac{dT_2}{dx}\right|_{x=X} - \frac{1}{\xi_1^2}\cdot\left.\frac{dT_1}{dx}\right|_{x=X} + \frac{T_0^* V}{2}\left(\frac{1}{\varkappa_1\xi_1^2} - \frac{1}{\varkappa_2\xi_2^2}\right)\right]\left.\frac{d\mu}{dx}\right|_{x=X} - \frac{1}{\mathscr{L}\rho R^2}\left[\frac{1}{\xi_2^2}\cdot\left.\frac{dT_2}{dx}\right|_{x=X} -\right.$$
$$\left. - \frac{1}{\xi_1^2}\cdot\left.\frac{dT_1}{dx}\right|_{x=X} + \frac{T_0^* V}{2}\left(\frac{1}{\varkappa_1\xi_1^2} - \frac{1}{\varkappa_2\xi_2^2}\right)\right]\left.\frac{dR}{dx}\right|_{x=X} - \frac{\lambda_2 k}{\mathscr{L}\rho}\left\{\xi_2\,\mathrm{cth}[\xi_2(L - X)] - \frac{V}{2\varkappa_2}\right\}. \tag{35}$$

When using expression (25) in place of Eq. (23), the last term in Eq. (35) is replaced by

$$-\frac{\lambda_2 k}{\mathscr{L}\rho}\left\{\xi_2\,\frac{\frac{V}{2\varkappa_2}\,\mathrm{ch}[\xi_2(L - X)] + \xi_2\,\mathrm{sh}[\xi_2(L - X)]}{\frac{V}{2\varkappa_2}\,\mathrm{sh}[\xi_2(L - X)] + \xi_2\,\mathrm{ch}(\xi_2(L - X)]} - \frac{V}{2\varkappa_2}\right\}. \tag{36}$$

The contribution to the stability of the process of crystallization introduces the negative terms of expression (35). The first term is negative if $T_f^*\cosh(\xi_1 X) > T_{01}^*$, the second term is negative always; the third and subsequent terms if $k > 0$; the fourth if $(d\mu/dX) > 0$; the fifth if $(dR/dX) < 0$. In order to estimate the quantities $(dT_1/dx)|_{x=X}$ and $(dT_2/dx)|_{x=X}$, formulas (21), (23), or (25) can be used.

The relative contribution of the different terms of expression (35) to the stability depends on the nature of the crystallization process and of the substance being crystallized. For example, during pulling of a thin aluminum ribbon by Stepanov's method, for the thermal mechanisms described in [11], by using the data of [12], we obtain

$$\eta = -1{,}0 - 0{,}6 - 0{,}02 - 0.3 - 5.6 - 0{,}02 = -7.5\ \mathrm{sec}^{-1}.$$

When pulling a sapphire fiber, $\eta = -65\ \mathrm{sec}^{-1}$, so that the term related with change of diameter also plays a principal role, which confirms the validity of the conclusions drawn in [13], where the estimate of the stability in Stepanov's method is carried out by a similar scheme.

NOTATION

T_i, temperature; λ_i, coefficient of thermal conductivity; $\varkappa_i$, coefficient of thermal diffusivity; c_i, specific heat ($i = 1$ for the melt and $i = 2$ for the crystal); x, running coordinate; X, coordinate of the crystallization front; T_f, temperature of the melt at a fixed point; T_0, crystallization temperature; V, speed of travel of crystal (melt); ρ, density (change of density during crystallization is not taken into account); R/2, ratio of area of cross section of the crystal to its perimeter (for a cylinder, one-half of the radius, for a plate, one-half of the thickness); μ, heat-exchange coefficient (μ_c, convective; μ_r, radiative); σ, Stefan—Boltzmann constant; T_m, temperature of the surrounding medium (gas, screens); T_{cr}, temperature of the crystal; $f_{b.s}$, factor taking account of the blackness and shape of the crystal and the wall receiving the emission; T_e, temperature of the end of the crystal; $\mathscr{L}$, specific heat of fusion; L, length of the crystal; k, temperature gradient of the medium; $Y = \mu/R$.

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