

On transition criterion from flat crystallization front in binary melt to cellular one

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The impurity diffusion problem in a melt solidifying at a constant speed has been solved taking into account the surface energy of phase interface under linear approximation in deviation amplitude from the flat crystallization front. It has been shown that the transition criterion from flat crystallization front to cellular one can be obtained from that solution. A clear evidence has been obtained that the concentration overcooling of the melt is not a sufficient condition of the growth cell formation.

С учетом поверхностной энергии межфазной границы в линейном приближении по амплитуде отклонения от плоского фронта кристаллизации решена задача по диффузии примеси в затвердевающем с постоянной скоростью расплаве. Показано, что из этого решения можно получить критерий перехода от плоского фронта кристаллизации к ячеистому. Получено наглядное свидетельство того, что концентрационное переохлаждение расплава не является достаточным условием образования ячеек роста.

The transition from flat crystallization front (CF) to cellular one is known to occur under certain critical values of growth parameters [1, 2]. In the cellular crystal growth (CCG) theory, a criterion of that transition is obtained in two stages. First, a solution of the binary melt solidification is searched for and then the solution obtained is tested for stability [3, 4]. However, as it follows from the solution of impurity diffusion problem in a melt solidifying at a constant speed obtained in [5], all information on critical parameter values could be obtained already at the first stage. In [5], a simplest solidification model was used where, in particular, the surface energy of phase interface (PI) was neglected. The purpose of this work is to take the latter into account when considering the transition to the cellular growth.

Let a solidification model be used differing from that used before [6] only in that the PI surface energy is not neglected. The impurity concentration in the melt $C(x,y)$ will be expressed in $C_0(1-k)/k$ unit pro-

ceeding from the C_0 level, where C_0 is the impurity concentration at an infinite distance from the crystallization front; k , the impurity distribution coefficient. The x coordinate will be measured in D/v units, where D is the impurity diffusion coefficient in the melt; v , the crystallization speed; the initial point being the position that the CF would occupy if it would be flat. The y coordinate will be measured in l units, where l is the cell halfwidth or the half-period of the CF line defined by the equation $x = \varphi(y)$.

Let dimensionless coefficients be introduced

$$\kappa = \frac{D}{vl}, \quad B = \frac{kGD}{(k-1)mvC_0}, \quad \gamma = \frac{kT_m v \Gamma}{(k-1)mDC_0}, \quad (1)$$

where G is the temperature gradient; m , the liquidus line slope; T_m , the pure melt solidification temperature; Γ , the capillary constant being in proportion to the PI surface energy. Note that the $1/\kappa$ is the same cellu-

lar structure half-period but expressed in the units of characteristic diffusion length; coefficients B and γ may take only positive values, since $(k - 1)$ and m quantities are of the same sign. It is expedient also to bear in mind that the parameter B can be selected independently of γ , that, in a real experiment, corresponds to the case when it is just the temperature gradient G that is selected as a parameter to be varied.

Then the bidimensional diffusion problem for an impurity in a melt crystallizing at a constant speed can be formulated in the form

$$C_{xx} + C_x + \kappa^2 C_{yy} = 0, \quad (2)$$

$$C_x(\varphi(y)) - \kappa^2 \varphi_y C_y(\varphi(y)) + (1 - k)C(\varphi(y)) + k = 0, \quad (3)$$

$$C(\varphi(y)) = 1 - B\varphi(y) + \gamma \kappa^2 \varphi_{yy} (1 + \kappa^2 \varphi_y^2)^{-3/2}, \quad (4)$$

$$C(\infty, y) = 0, \quad C_y(x, 0) = C_y(x, l) = 0. \quad (5)$$

Here, the partial derivatives of $C(x, y)$ with respect to x and y as well as derivatives of $\varphi(y)$ with respect to y are denoted using indices. The Eq.(3) is the impurity conservation equation at the CF. The Eq.(4) relates the impurity concentration at the PI to thermodynamic characteristics of the latter. It follows from the phase diagram under condition that the temperature field is flat and depends linearly on x [6] as well as from the Gibbs-Thomson condition.

When being confined to small amplitudes of the cell projections, δ , then the solution of the above problem as a first approximation in δ can be presented [5] as

$$C(x, y) = e^{-x} + A\delta \exp(-qx) \cos \pi y, \quad (6)$$

$$\varphi(y) = \delta \cos \pi y,$$

where

$$q = 0.5 + \sqrt{0.25 + \pi^2 \kappa^2}. \quad (7)$$

Let the solution (6) be substituted into each condition at the PI, the exponents be expanded into Taylor series, and sums of the common factors at $\delta \cos \pi y$ be set to zero. Thus, a system of two equations arises from which we obtain

$$B + \pi^2 \kappa^2 \gamma = \frac{q-1}{q+k-1}, \quad (8)$$

$$A = 1 - B - \pi^2 \kappa^2 \gamma. \quad (9)$$

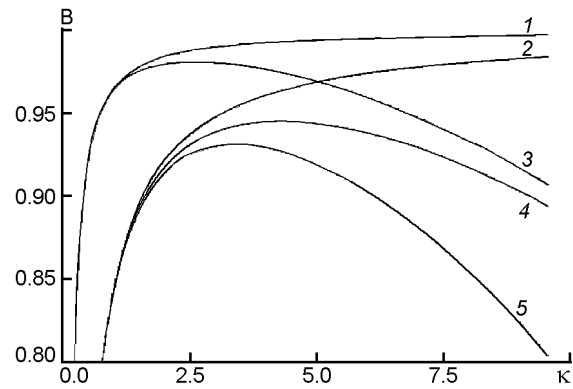


Fig. 1. B parameter as a function of κ coefficient at different distribution coefficients, k , and γ parameter values: $k = 0.1, \gamma = 0$ (1); $k = 0.1, \gamma = 10^{-4}$ (2); $k = 0.5, \gamma = 0$ (3); $k = 0.5, \gamma = 10^{-4}$ (4); $k = 0.5, \gamma = 2 \cdot 10^{-4}$ (5).

It follows from the solution presented that in the problem (2)–(5), the coefficient κ is a dependent parameter and can be determined from Eq.(8) at fixed κ and γ from the preset B , of course if the roots of Eq.(8) have a physical sense in this case.

Fig. 1 presents the plots of $B(\kappa)$ function defined by Eq.(8) at various κ and γ values. The γ values were selected taking into account typical values of crystallization parameters [1] and $\Gamma = 10^{-8}$ cm [3]. It is seen from Fig. 1 that there is a certain value $B = B_c$ coincident with the maximum of the $B(\kappa)$ function at which the Eq.(8) loses its sense at $B > B_c$. In other words, at $1/B < 1/B_c$, or in the pre-critical region of parameters, the problem (2)–(5) may have a planar solution ($\delta = 0$). If $1/B > 1/B_c$, that is, in the over-critical regime, the solution may be also a bidimensional one ($\delta \neq 0$) with a cellular interface. The period of the latter can be determined from the κ value found from Eq.(8).

It is seen from Fig. 1 that the B_c value is shifted towards smaller ones as the capillary constant increases. According to (1), this means that critical values of the crystallization speed and the impurity concentrations increase while the temperature gradient decreases. This result obtained in one pioneering work on CCG theory [3] using another method. It is easy to explain by the trend of surface tension forces to maintain a smooth PI [2]. Nevertheless, it allows also a geometric interpretation similar to that presented in literature on solidification the-

ory for the case when the interface surface energy is neglected [1, 2].

First of all, it is to note that according to the condition (4), at the first approximation in δ , the limiting values of the impurity concentration, $C(\varphi)$, must be within a plane defined in the space with C, x, y coordinates by the equation

$$C = 1 - B_\gamma x, \quad (10)$$

where $B_\gamma = B + \pi^2 \kappa^2 \gamma$. Let this plane be denoted as (L_{B_γ}) . At $\gamma = 0$, it coincides with the plane (let it be referred to as (L_B)) that is a bidimensional analogue of the liquidus line presented in C and x coordinates [6]. From the family of (L_{B_γ}) planes, the (L_1) one defined by $C = 1 - x$ is to be considered individually. It is just straight lines 2, 3, and 4 presented in Fig. 2 that answer to (L_1) , (L_B) , and (L_{B_γ}) planes. In the same Figure, the impurity distribution curve in a melt is shown at flat CF (1 curve). In the scale selected by us (see above), its shape ($C = e^{-x}$) as well as slope of the tangent thereto, 2, are independent of any problem parameters.

Now let us trace how the pattern presented in Fig. 2 will change as the B parameter decreases. First, let the more simple case be considered when $\gamma = 0$. As is seen from Fig. 2a, at $B > 1$, the (L_B) plane has a steeper slope than (L_1) . It follows from the above, however, that there is no planar solution of the problem (2)–(5) at such B values. Only if the slope parameter of the (L_B) plane, or the B parameter, is smaller than 1 (Fig. 2b), a solution with cellular PI ($\delta \neq 0$) becomes possible. In this case, a part of the (C_p) surface appears below the (L_B) plane. The projection of that surface on the XY plane is known in the CCG theory as the concentration overcooling (CO) zone and the transition condition to the cellular growth is referred to as the CO criterion.

When $\gamma \neq 0$, the existence of a non-planar solution depends on the mutual arrangement of (L_{B_γ}) and (L_1) planes. At $B_\gamma > 1$, the former plane has a steeper slope than the latter (Fig. 2c) and the solution may be a planar only. If $B_\gamma < 1$, there is an opposite case, so that a solution with a cellular PI becomes possible. At $\gamma \neq 0$, the planes (L_B) and (L_{B_γ}) are rotated to one another at an angle depending on the γ value. In this case, a situation may appear when $B < 1$, that is,

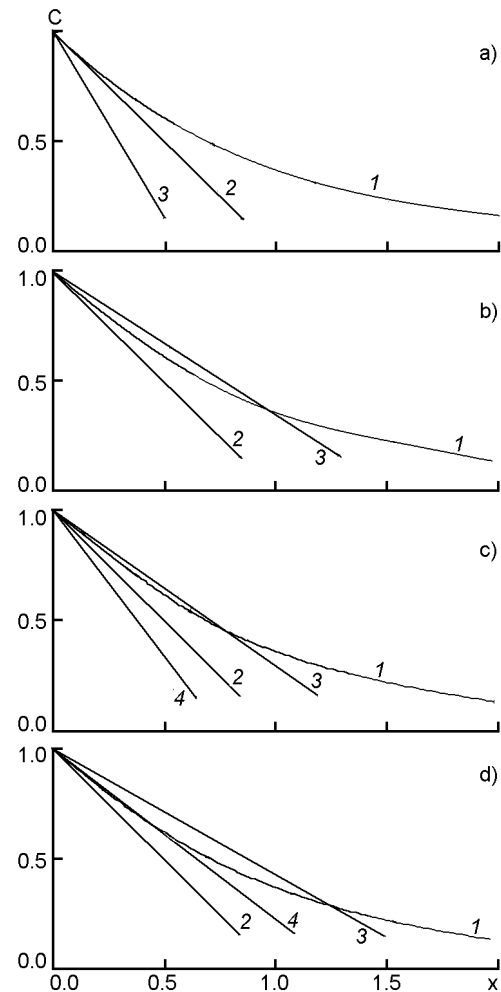


Fig. 2. Impurity concentration C dependences on x coordinate. 1, the impurity distribution curve in melt at flat crystallization front; 2, tangent to the impurity distribution curve in its vertex; 3, liquidus line in C and x coordinates; 4, a straight line with slope depending on B and γ . In a), c) cases, the problem solution is planar only: in b), d) ones, the phase interface may be cellular.

the condition of CO zone existence is met, but the (L_{B_γ}) plane has a steeper slope than (L_1) , i.e., there is no non-planar solution. Thus, the statement that a CO of a melt is not a sufficient condition of a cellular PI structure formation [3] is confirmed evidently.

It is to note that any solution of the problem (2)–(5) within the over-critical region of parameters cannot be unique in principle. The point with $1/B_c$ coordinate in the plot of the CF curvature as a function of $1/B$ is only a bifurcation point. As this point is approached, the crystal-melt system is "before a choice": either the interface

will remain flat or it will be subdivided into cells. As it has been noted in the introduction, the system behavior can be forecast only using additional studies.

It is of interest that when $\gamma \neq 0$ and $B < B_c$, one more choice alternative arises along with the above-mentioned one. In fact, it is seen from Curves 2, 4, and 5 of Fig. 1 that as the B parameter decreases, the cells may be developed in two trends: either with decreasing κ coefficient (left-hand branch) or with increasing one (the right-hand one), that is, either the cell width will increase or decrease. It is just the further studies that will indicate what trend shall be preferred. It is to note that the variation approach to the CCG problem developed in [4, 6, 7] is highly effective when such dilemmas are to be solved.

The results obtained in this work indicate that the relatively simple solution of the impurity diffusion problem in a melt crystallizing at a constant speed at small deviations from the flat PI is a very informative and visual one. It is obvious also that additional studies within the frame of

the same solidification model but involving other methods, in particular, integral functionals with unknown integration domain, will provide a better understanding of the transition nature from flat crystallization front to cellular one.

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Про критерій переходу від плоского фронту кристалізації бінарного розплаву до комірчастого

В.М.Каніщев

З урахуванням поверхневої енергії міжфазної межі у лінійному наближенні за амплітудою відхилення від плоского фронту кристалізації вирішено задачу про дифузії домішки у розплаві, що твердіє з постійною швидкістю. Показано, що з цього рішення можна одержати критерій переходу від плоского фронту кристалізації до комірчастого. Отримано наочне свідчення того, що концентраційне переохолодження розплаву не є достатньою умовою утворення комірок росту.