

## Critical parameter calculation of a binary melt crystallization in stationary regime

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Taking into account the latent melting heat and the heat conductivity differences between the solid and liquid phases, the stationary heat and mass transfer problem in a bounded domain region of a crystal/melt system has been solved under linear approximation with respect to the crystallization front non-flatness. The region of the problem input parameters has been shown to be subdivided into two sub-regions, a subcritical (where the solution can be a flat one only) and a supercritical one (where the crystallization front can take a cellular structure). The derived condition of the transition to the supercritical crystallization regime corresponds exactly to the modified criterion of concentration overcooling that is known in the cellular crystal growth theory.

С учетом скрытой теплоты плавления и различия между теплопроводностями твердой и жидкой фаз в линейном приближении по амплитуде отклонения от плоского фронта кристаллизации (ФК) решена стационарная задача по тепломассопереносу в ограниченной области системы кристалл — расплав. Показано, что область значений входных параметров задачи разбивается на две области: докритическую, когда решение может быть только плоским, и закритическую, когда ФК может принимать ячеистую структуру. Полученное условие перехода к закритическому режиму кристаллизации в точности соответствует известному в теории ячеистого роста кристаллов модифицированному критерию концентрационного переохлаждения.

It has been shown [1, 2] that the critical values of the crystallization parameters for a binary melt can be obtained from the stationary problem solution without considering the solution stability. In this case, the criterion of the crystallization front (FC) transition from the flat shape to the cellular one is obtained as the existence condition of a non-flat solution for the corresponding problem. Thus, the approach to the cellular crystal growth (CCG) problem applied in [1, 2] differs in principle from the method proposed by Mullins and Sekerka [3], although is much similar thereto due to the stationary approximation used by those authors. In our previous studies, the latent melting heat was neglected as well as the heat conductivity difference between

the solid and liquid phases. The purpose of this work is to obtain the critical crystallization parameters for a binary melt in stationary regime taking into account the mentioned characteristics of the crystal/melt system.

It is obvious that to that end, it is sufficient to use the solidification model proposed by Mullins and Sekerka [3] (the MS model) where the heat propagation domain is assumed to be unbounded [4]. The studies in the frame of a model considering a bounded heat transfer domain are, however, of interest. The selection of that model is justified at least by the fact that the MS model is a limiting case thereof. At the same time, the bounded domain model does not result in any appreciable complication

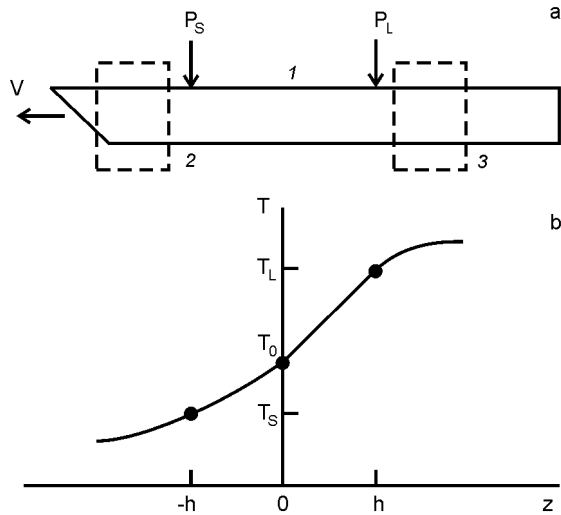


Fig. Scheme of crystal growing (a) and temperature  $T$  distribution at the flat phase interface crystal-melt (b). Crucible with a substance being crystallized at a rate  $v$  (1); furnaces (2, 3);  $P_S$ ,  $P_L$ , the temperature observation points in the crystal ( $T_S$ ) and the melt ( $T_L$ ), respectively.

of calculations as compared to the MS model.

The selected solidification model is illustrated by the Fig. presenting a quite real crystal growing scheme [6] using the two-furnace principle proposed in [3] providing easily the stationary crystallization regime. The crucible 1 containing the substance to be crystallized is pulled at a constant speed (from right to left in the Figure) through two furnaces 2 and 3 forming the crystal and melt zones, respectively. The model is based on the assumption that the furnaces do not influence the phase interface (PI) domain itself. Let this domain (restricted by the  $P_S$  and  $P_L$  points in the Figure) be defined as a  $2h$  wide band where  $h$  is a certain characteristic dimension (discussed below). The part played by the furnaces in our model is reduced to the maintaining of the temperature values  $T_S$  and  $T_L$  at the  $P_S$  and  $P_L$  points, respectively. Thus, it is supposed that there are no heat sources in the PI domain, except for the CF itself. Note that the same assumption is the basis of the MS model, however, the PI domain is of infinite size therein and  $T_S \rightarrow -\infty$  [4]. It obvious that, by regulating the power applied to the furnaces and thus selecting the  $T_S$  and  $T_L$  values, we could attain always that the CF (providing of course it is flat) will be positioned at the middle of the above-mentioned band.

Let the orthogonal coordinate system  $x, z$  be chosen where the  $Oz$  axis is directed towards the melt and  $z$  is counted starting from the flat CF position. The following notation will be used from here on:

- $z = \varphi(x)$  is the CF line equation;
- $C(x, z)$  is the impurity concentration in the  $(x, z)$  point of the melt ( $z \geq \varphi$ );
- $C_\infty$  is the impurity concentration in the melt at infinity from the CF;
- $v$  is the crystallization speed;
- $D$  is the impurity diffusion coefficient in the melt;
- $m$  is the liquidus line slope in the phase diagram of the binary system under consideration;
- $k$  is the impurity distribution coefficient;
- $T(x, z)$  is the temperature in the  $(x, z)$  point of the melt ( $z \geq \varphi$ ) or the crystal ( $z \leq \varphi$ );
- $T_0$  is the solidification temperature of the melt at the impurity concentration  $C_\infty/k$ ;
- $K_L(K_S)$  is the heat conductivity coefficient of the melt (crystal);
- $L$  is the specific latent melting heat per unit volume.

Let the solution definition domain  $\Omega$  be set by the inequalities  $0 \leq x \leq l$  and  $-h \leq z \leq h$  where  $l$  is the cellular structure half-period. Let the  $h$  value be selected so that the condition  $D/v \ll h \ll D_T/v$  is met where  $D_T$  is the temperature conductivity coefficient in the crystal or in the melt. This condition is easy to met, since in actual systems,  $D_T$  exceeds  $D$  by several decimal orders [4]. Then we can take  $C(x, h) = C(x, \infty) = C_\infty$ . If we take into account that it is the cases where  $l \ll D_T/v$  that are of a practical interest [3], then we can make use of Laplacian equation to find out the temperature field in the  $\Omega$  domain. The convection in the melt and the diffusion in the crystal are assumed to be negligible and the equilibrium is assumed to exist at the phase interface.

The concentration and temperature distribution in the domain  $\Omega$  at the stationary regime can be determined by solving the following problem:

$$D\nabla^2 C + vC_z = 0, \tag{1}$$

$$D[C_z(\varphi(x)) - \varphi_x C_x(\varphi(x))] + v(1-k)C(\varphi(x)) = 0, \tag{2}$$

$$C(x, \infty) = C_\infty, C_x(0, z) = C_x(l, z) = 0, \tag{3}$$

$$\nabla^2 T = 0, \tag{4}$$

$$T(x, -h) = T_S, T(x, h) = T_L, \quad (5)$$

$$T_x(0, z) = T_x(l, z) = 0, \quad (6)$$

$$K_S[T_z(\varphi - 0) - \varphi_x T_x(\varphi - 0)] - K_L[T_z(\varphi + 0) - \varphi_x T_x(\varphi + 0)] = \nu L, \quad (7)$$

$$T(\varphi - 0) = T(\varphi + 0) = T_0 + m[C(\varphi(x)) - C_\infty/k]. \quad (8)$$

Here, indices are used to denote the partial derivatives of  $C$  and  $T$  with respect to  $x$  and  $z$  as well as the usual derivative of  $\varphi$  with respect to  $x$ ;  $\nabla$ , the two-dimensional nabla operator. Note that, taking into account that there is a stationary state and the surface energy of the phase interface is negligible as well as some insignificant details, the problem (1)–(8) differs from that formulated in [4] only in the boundary conditions (5).

For the flat case ( $\varphi = 0$ ), the solution of the problem (1)–(8) has the form

$$C(z) = (C_\infty/k)[k + (1 - k)\exp(-\nu z/D)], \quad (11)$$

$$T(z) = T_0 + G_S z \text{ at } z \leq 0, \quad (12)$$

$$T(z) = T_0 + G_L z \text{ at } z \geq 0.$$

Here,  $G_S = (T_0 - T_S)/h$  and  $G_L = (T_L - T_0)/h$ . It is just the polygonal section of the  $T(z)$  plot presented in the Fig. 1(b) that answers to the temperature distribution (12) in the  $-h \leq z \leq h$  region.

Substituting the distribution (12) into (7), we obtain the expression

$$K_S G_S - K_L G_L = \nu L, \quad (13)$$

where from it is seen that at preset non-varying parameters  $K_S$ ,  $K_L$ , and  $L$ , one of the parameters  $G_S$ ,  $G_L$ , or  $\nu$  that can be varied is the dependent one. This is to be taken into account when carrying out the experiments on the CCG as well in the crystal growth practice. For example, when varying the crystallization speed, it is impossible to fix the averaged heat conductivity coefficient used in the CCG theory [7, 8]

$$\bar{G} = \frac{K_S G_S + K_L G_L}{K_S + K_L}, \quad (14)$$

but either  $G_S$  or  $G_L$  can be remained constant. From the standpoint of the CCG prob-

lem, it is the  $G_L$  constancy that is of more importance, thus, when varying  $\nu$ , it is desirable to correct  $G_S$ . So, when increasing  $\nu$  and maintaining  $T_S$  and  $T_L$  at constant levels (Fig. b), it is natural to expect that the CF will be displaced from the  $z = 0$  position to left, i.e., both  $G_S$  and  $G_L$  will change. It is obvious that to restore the former  $G_L$  value, the CF should be returned to the  $z = 0$  position by lowering the  $T_S$  value, i.e. the power applied to the furnace 2 should be lowered (see Fig. a). The  $G_S$  in this case will increase by the value that can be calculated using Eq.(13).

It is to note that the right-hand side of inequality (13) can be neglected in many cases of practical importance. In fact, as  $L/(K_L + K_S) \approx 100 \text{ K}\cdot\text{s}/\text{cm}^2$  [3], then at  $G_L \sim 10 \text{ K}/\text{cm}$  and  $\nu \sim 10^{-4} \text{ cm}/\text{s}$  (corundum, YAG, AHC, etc.), the  $\nu L/(K_L G_L)$  value is of the order of  $10^{-3}$ , so the above-mentioned FC displacement remains unappreciable even if the crystallization speed is changed by one decimal order.

It is more convenient to carry out the further calculations in dimensionless variables, that are defined as

$$C' = \frac{k(C - C_\infty)}{C_\infty(1 - k)}, \quad T' = \frac{T - T_0}{T_L - T_0}, \quad l' = \frac{\nu l}{D}, \quad (15)$$

where  $l$  is any of linear dimensions ( $x$ ,  $z$ ,  $l$ ,  $h$ ). Let the dimensionless coefficients be introduced defined as

$$\theta = \frac{T_0 - T_S}{T_L - T_0}, \quad \eta = \frac{K_L}{K_S}, \quad \lambda = \frac{LD}{K_S(T_L - T_0)}, \quad (16)$$

$$M = \frac{(k - 1)mC_\infty}{K(T_L - T_0)}, \quad B = \frac{kG_L D}{(k - 1)\nu C_0}.$$

As a result of such a replacement, the 11 input parameters of the initial problem are reduced down to five ones ( $k$  and first four parameters of (16)). The parameter  $l'$  is one to be sought while  $h'$  is expressed in terms of other ones as

$$\theta - \eta = \lambda h', \quad (17)$$

that is equivalent to (13). The coefficient  $B$  is not an independent one ( $B = 1/(Mh')$ ) but it is very convenient in considerations of the CCG problem [1, 5] because in unites all the parameters that are possible to be varied in experiment.

Let a perturbation (18) be imposed onto a flat PI ( $\varphi' = 0$ )

$$\varphi' = \delta \cos \omega x', \quad (18)$$

where  $\delta$  is the perturbation parameter and  $\omega = \pi/l'$ . In the first approximation with respect to  $\delta$ , it is the perturbed concentration field

$$C' = e^{-z'} + A\delta \exp(-qz') \cos \omega x', \quad (19)$$

that answers to the perturbation. In (19),  $q$  is calculated as

$$q = 0.5 + \sqrt{0.25 + \omega^2} \quad (20)$$

while the constant  $A$  is to be determined. Proceeding from (2) and taking into account (15), we obtain

$$A = \frac{k}{q + k - 1}. \quad (21)$$

Substituting (18) into (19), we obtain in the same approximation

$$C'(\varphi') = 1 - \frac{q-1}{q+k-1} \delta \cos \omega x'. \quad (22)$$

Using the formulae (8), (15), (16), and (22), we obtain the condition

$$T'(\varphi') = M \frac{q-1}{q+k-1} \delta \cos \omega x', \quad (23)$$

that makes it possible to obtain the heat conductivity part of the problem in the first approximation:

$$T' = \theta \frac{z'}{h'} + \left( M \frac{q-1}{q+k-1} - \frac{\theta}{h'} \right) \times \delta \frac{\text{sh}\omega(h'+z')}{\text{sh}\omega h'} \cos \omega x', \quad -h' \leq z' \leq \varphi'. \quad (24)$$

$$T' = \frac{z'}{h'} + \left( M \frac{q-1}{q+k-1} - \frac{1}{h'} \right) \times \delta \frac{\text{sh}\omega(h'-z')}{\text{sh}\omega h'} \cos \omega x', \quad \varphi' \leq z' \leq h'. \quad (25)$$

Substituting (24) and (25) into (7) under account for (15) and (16), in the zero approximation we obtain the expression (17). Taking into account the items proportional to  $\delta \cos \omega x'$ , we obtain

$$\frac{q-1}{q+k-1} = B \frac{\theta + \eta}{1 + \eta}. \quad (26)$$

According to (20), the left-hand side of (26) cannot exceed 1. Thus, the non-flat solution of the problem may exist only under condition

$$B < \frac{1 + \eta}{\theta + \eta}. \quad (27)$$

It is the upper limit of that inequality that will determine the critical values of the crystallization parameters.

The parameter  $B$  is convenient in that if it is less than 1, a concentration overcooling (CO) zone appears in the melt [1]. Thus, if the right-hand side of the inequality (27) is larger or smaller than 1, this evidences the existence of a non-flat problem solution prior to the CO zone appearance or when it exists already, respectively. So, at  $\theta = \eta = 1$  (the simplest 2D solidification model), we obtain from (27) the classical CO criterion [7]. If we take  $\theta = \eta = 1/2$  for simplicity sake, that is equivalent to  $K_S = 2K_L$  (relation close to the reality for metals [3]), and  $L = 0$ , then in the  $1 \leq B < 3/2$  the non-flat solution will exist in the absence of the CO in the melt. If  $K_S = K_L$  and  $L \neq 0$ , then at  $2/(2 + \lambda h') \leq B < 1$ , the solution will be still flat although the melt will contain already a CO zone.

Using (16) it is easy to check that the inequality (27) answers exactly to the so-called modified CO criterion [3]:

$$\frac{\bar{G}}{v} < \frac{(k-1)mC_\infty}{kD}, \quad (28)$$

where  $\bar{G}$  is given by (14). It is to note that the expression (28) is very elegant and easy to remember but is impractical in use. Taking into account (13), it is better to write it in the form

$$\frac{G_L}{v} < \frac{1}{2K_L} \left[ (K_S + K_L) \frac{(k-1)mC_\infty}{kD} - L \right]. \quad (29)$$

The latter inequality shows how the  $L$ ,  $K_L$  and  $K_S$  parameters introduced in the model effect the  $G_L$  and  $v$  critical values; but it does not produce an illusion of significance of the  $G_S$  parameter.

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## **Розрахунок критичних значень параметрів кристалізації бінарного розплаву в стаціонарному режимі**

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З урахуванням прихованої теплоти плавлення та різниці між теплопровідностями твердої та рідкої фаз у лінійному наближенні вздовж амплітуди відхилення від плоского фронту кристалізації (ФК) вирішено стаціонарну задачу з тепломасопереносу в обмеженій області системи кристал-розплав. Показано, що область значень вхідних параметрів задачі розбивається на дві області: докритичну, коли рішення може бути тільки плоским, та закритичну, коли ФК може утворювати коміркову структуру. Одержана умова переходу до закритичного режиму кристалізації точно відповідає відомому в теорії комірчастого росту кристалів модифікованому критерію концентраційного переохолодження.