

On the binary melt crystallization in temperature field advancing with acceleration

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The time dependence of the crystallization speed in transient process arising at the uniformly accelerated movement of the temperature field towards the melt is considered theoretically in the frame of nonstationary model of binary melt solidification. It has been shown that the crystallization speed in such process grows in time according to $t^{3/2}$ law. It is established that the crystallization speed at which the melt concentration overcooling (CO) arises in the transient process may differ noticeably from that at which the melt concentration overcooling appears under steady-state conditions.

В рамках одномерной нестационарной модели затвердевания бинарного расплава теоретически исследована зависимость скорости кристаллизации от времени в переходном процессе, возникающем при равноускоренном перемещении температурного поля в сторону расплава. Показано, что скорость кристаллизации во времени в таком процессе нарастает по закону $t^{3/2}$. Установлено, что скорость кристаллизации, при которой концентрационное переохлаждение (КП) расплава возникает в переходном процессе, может заметно отличаться от скорости кристаллизации, при которой КП расплава появляется в стационарном режиме.

It is known that a certain critical growth rate exists at crystal growing from the melt. Its exceeding, other conditions being the same, results in a transition from smooth phase interface to cellular one and, as a result, in a sharp crystal quality loss [1]. Since numerous growth characteristics are uncertain, this growth rate is defined in experiment, following in this case (as fifty years ago) the correlation [2]:

$$V_c = \frac{kGD}{(k-1)mC_0}, \quad (1)$$

This correlation follows from the condition of concentration overcooling zone appearance in the melt (CO criterion). Here, k is the impurity distribution coefficient; G – temperature gradient near the phase interface; D – the impurity diffusion constant in the melt; m – the liquidus line slope on the phase diagram; C_0 – the impurity concen-

tration in the melt at a significant distance from the phase interface.

It is to note that the formula (1) was derived for the constant speed crystallization [3]. That is why the V_c determination even for one C_0 value requires a series of crystallization operations with analysis of defect content in every crystal. In real conditions (e.g., at the development of large crystal growing technology), this may results in a series of rather expensive experiments.

The melt crystallization in the accelerated moving temperature field (TF) is more effective for the determination of critical growth rate [4]. This method makes it possible to specify exactly the moment of the mentioned transition in just one experiment. However, it is obvious that, because of difference between the TF travel velocity and crystallization speed in time-varying process [5], the so obtained critical growth

rate value will differ from the V_c value. This research is aimed at estimation of the mentioned difference at uniformly accelerated movement of temperature field.

Let us avail of one-dimensional nonstationary model of binary melt solidification and suppose that:

- a) in the crystal-melt system, the heat extends instantly;
- b) the mass transfer is realized only in the melt and just only due to diffusion;
- c) the crystal melting temperature depends linearly on the impurity concentration;
- d) the latent heat of melting is negligibly small;
- e) the heat conductivity coefficients for liquid and solid phases are identical.

All this assumptions are common for the problems like this [6]. Temperature would be considered to be linear function of the coordinate x :

$$T = T_0 + G(x - x_0), \quad (2)$$

where T_0 is the crystal melting temperature with impurity concentration C_0 ; x_0 – the phase boundary position.

Let us represent that at the time instant $t = 0$, the temperature field in the crystal-melt system starts to be moved towards the melt at a velocity $W = a_w t$, where a_w is the uniform acceleration. Because of the impurity forcing out into the melt (at $k < 1$) or its capturing by the crystal (at $k > 1$), the phase interface, according to the phase diagram, will begin to lag behind the isotherm $T = T_0$. To find out how the phase interface will behave in such a process, it should to solve a problem of the impurity diffusion in the melt being crystallized at a velocity of $V(t)$, and the law of such velocity variation should follow from the solution itself.

For calculation, we shall use the moving coordinate system where the position of crystallization front will be defined as $x=0$. Then the impurity concentration in the melt $C(x, t)$ will be determined by the solution of the following problem:

$$DC_{xx}(x, t) + V(t)C_x(x, t) = C_t(x, t), \quad (3)$$

$$DC_x(0, t) = V(t)(k - 1)C(0, t), \quad (4)$$

$$C(\infty, t) = C_0, \quad C(x, 0) = C_0, \quad (5)$$

where

$$V(t) = a_w t + \frac{m}{G}C_t(0, t) \quad (6)$$

Here, the index notation of partial derivatives on x and t is used. Equation (3) describes the impurity diffusion in a medium which covers the phase interface $x = 0$ at the velocity $V(t)$. Equation (4) represents the guard condition for the impurity on this surface. Expression (6) reflect the fact that the crystallization speed of a binary melt depends on both temperature field travel velocity along the growth axis and on changing speed of impurity concentration at the interphase boundary [5].

The formulated problem is nonlinear, but at moderate time values, it can be linearized presenting the solution in the form

$$C(x, t) = C_0 + C_1(x, t), \quad (7)$$

where $C_1(x, t)$ is the disturbing additive. Substituting (7) in (3)-(6) and taking away summands of the second infinitesimal order, we will come to linear problem which can be solved rather simple using Laplace transformation. The solution image of such a problem looks like this:

$$\hat{C}_1(x, p) = -\frac{a_w(k-1)GC_0 \exp(-x\sqrt{p}/D)}{p^2[m(k-1)C_0p + G\sqrt{Dp}]}, \quad (8)$$

where p is the transformation parameter.

Since it is just the asymptotic behavior of function $C_1(x, t)$ at $t \rightarrow 0$ that is of interest, so it is sufficient to analyze the asymptotic behavior of its image at $p \rightarrow \infty$, and then to use the theorem about correspondence of asymptotic expansions of image and original [7]. Limiting by two expansion terms (8), we get:

$$\hat{C}_1(x, p) = -\frac{a_w G}{m} \left(\frac{e^{-\alpha\sqrt{p}}}{p^3} - \beta \frac{e^{-\alpha\sqrt{p}}}{p^{7/2}} \right), \quad (9)$$

where designations are included:

$$\alpha = \frac{x}{\sqrt{D}}, \quad \beta = \frac{G\sqrt{D}}{(k-1)mC_0}.$$

The simplest way to move from the image (9) to its original is to use the ready tables of inverse Laplace transformation [8]. The only restriction for this is too high exponents at p in denominators of fractions (9): images with such exponents are absent in the tables. By differencing (9) with respect to parameter α the necessary number of times, we get to images available in [8] from which we can move to originals with following integration with respect to α the same number of times. As a result, we get:

$$C_1(x, t) = -\frac{a_w G}{m} \left[\operatorname{erfc} \left(\frac{\alpha}{2\sqrt{t}} \right) - g \sqrt{\frac{t}{\pi}} \exp \left(-\frac{\alpha^2}{4t} \right) \right] \quad (10)$$

where

$$f = \frac{60t^2(1 + \alpha\beta) + 20t\alpha^2(3 + \alpha\beta) + \alpha^4(5 + \alpha\beta)}{120},$$

$$g = \frac{32t^2\beta + 2t\alpha(25 + 9\alpha\beta) + \alpha^3(5 + \alpha\beta)}{60}.$$

It can be shown that in the case $W=W_0=\text{const}$ [5], the image of linearized task solution $\hat{C}_{01}(x, p)$ is obtained from (8) by changing W_0 for a_w/p , and its original $C_{01}(x, t)$, by substitution of a_w in (10) by W_0 and, respectively, of f, g by

$$f_0 = \frac{6t(1 + \alpha\beta) + \alpha^2(3 + \alpha\beta)}{6},$$

$$g_0 = \frac{4t\beta + \alpha(3 + \alpha\beta)}{3}.$$

At $x = 0$, the formula (10) becomes essentially simpler:

$$C_1(0, t) = -\frac{a_w G}{m} \left(\frac{t^2}{2} - \frac{8G}{15(k-1)mC_0} \sqrt{D/\pi} t^{5/2} \right). \quad (11)$$

Differentiating (7) with respect to x taking (10) into consideration, we get an important characteristic of impurity distribution in the melt:

$$C_x(0, t) = \frac{a_w G}{m} \left(\frac{Gt^2}{2(k-1)mC_0} - \frac{4t^{3/2}}{3\sqrt{\pi D}} \right). \quad (12)$$

While using (6), (7) and (10), we find a formula suitable for moderate values t :

$$V(t) = \frac{4a_w G \sqrt{D}}{3\sqrt{\pi}(k-1)mC_0} t^{3/2} \quad (13)$$

Thereby, in contrast to the case of temperature field moving uniformly when $V \sim t^{1/2}$ at the start of solidification process [5], at uniformly accelerated TF movement, the crystallization speed grows according to $t^{3/2}$ law.

Let the obtained expressions to the case of Sn+1% In melt crystallization which was examined by authors of [9]. According to the time dependence of crystallization speed for pure tin presented in that work, the temperature field movement in those experiments can be supposed to be approximately uniformly accelerated.

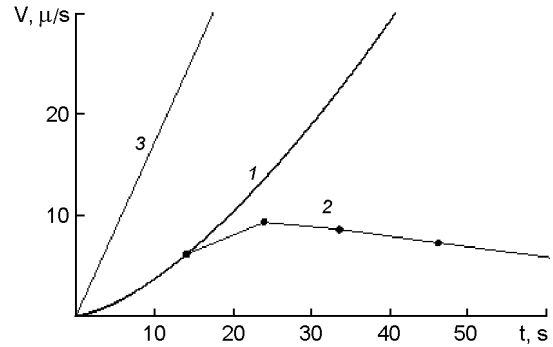


Fig. 1. Dependences crystallization speed of the binary melt from time t : 1 – modelling; 2 – experimental [4]; 3 – TF movement acceleration rate.

Calculations were done for the following parameters values: $C_0=1\%$, $k=0.56$ [9], $m=-1.8$ K/% [10]. The typical value $G=10$ K/cm [1] was also used as well as the value $D=5 \cdot 10^{-5}$ cm²/s averaged over different tin alloys [11]. The TF movement acceleration rate was accepted to be of $1.72 \mu\text{m/s}^2$. It was selected so that function graph $V(t)$ defining by expression (13) (curve 1) will pass the point with coordinates $t=14$ s and $V=6.1 \mu\text{m/s}$. This is the first point in the $V(t)$ diagram (curve 2, Fig. 1) which was get in the experiment for tin-indium alloy [9]. In Fig.1, it is seen well that in the course of time, the crystallization speed of binary melt (curve 1) lags behind of TF travel velocity (straight line 3).

It is to say that the value a_w calculate in the same way for tin-bismuth alloy ($k=0.22$, $m=-2.2$ K/% [12], point with coordinates $t=20$ s, $V=4.7 \mu\text{m/s}$ [9]) amounted $1.70 \mu\text{m/s}^2$. The closeness of a_w values got for different alloys shows that the solidification process of each alloy is laying well in model accepted by us.

Distribution curves of indium in tin melt $C(x, t_f)$ calculated by formula (7) under account for (9) for a fixed time point t_f is shown in Fig. 2. Presented is also the straight line $C_L = C(0, t) + (G/m)x$ which is liquidus line in coordinates C and x [13]. Judging from amplitudes of $C(x, t_f)$ curves, the approximation (7) used at least for the first 20-30 s interval can be considered quite suitable.

The look of Fig. 2, shows an analogy with scheme of the concentration overcooling appearance in binary melt presented usually in the literature on crystal growth [1]. In fact, up to the time point $t=t_c$, the distribution curve $C(x, t_f)$ lies higher than

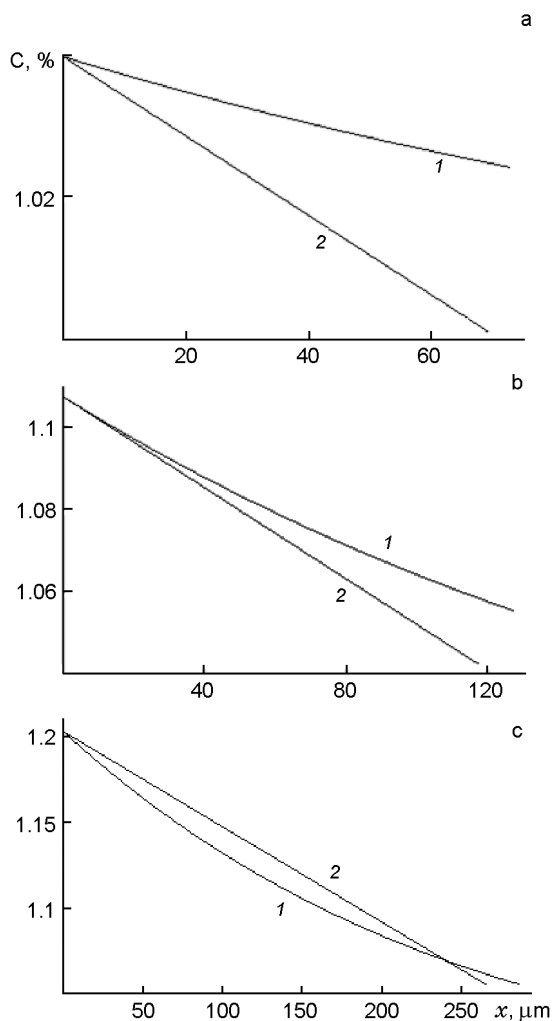


Fig. 2. Dependences of concentration overcooling appearance \ln in binary melt of Sn defined by distance from the phase interface x_c (1) for various t after beginning crystallization at constant temperature gradient: $a - t = 10$ s, $b - t = 17$ s, $c - t = 30$ s. 2 - liquidus line in C and x .

liquidus line CL (Fig. 2a) what is indication to the CO absence. After the CO zone appears in the melt at $t > t_c$, its width x_c defined by distance from the phase interface to concurrence point of $C(x, t_f)$ and CL lines (Fig. 2c), grows in time because the TF travel speed grows, too.

The critical moment $t = t_c$ can be determined from the condition of contact between $C(x, t_c)$ and C_L lines in the point $x=0$ (Fig. 2b). This, taking into account (12), leads to equation:

$$\frac{4t_c^{3/2}}{3\sqrt{\pi D}} - \frac{Gt_c^2}{2(k-1)mC_0} = \frac{1}{a_w} \quad (14)$$

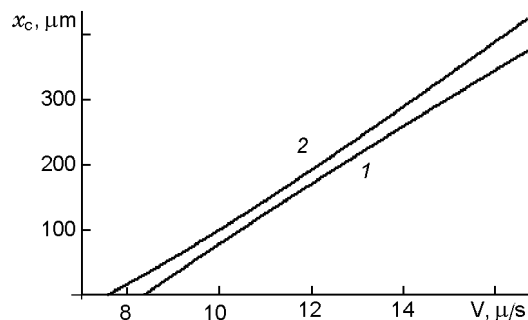


Fig. 3. Dependences $x_c(V)$ with acceleration (1) and with constant speed (2).

In the first approximation, the subtrahend in (14) can be neglected (for example, in our case its value with respect to minuend takes 25%). Then, at uniformly accelerated temperature field movement, the appearance time of concentration overcooling in the melt after the solidification onset can be defined as:

$$t_c \approx \left(\frac{9\pi D}{16a_w^2} \right)^{3/2} \quad (15)$$

According to (13), this time corresponds to critical crystallization speed:

$$V_{ca} \approx \frac{GD}{(k-1)mC_0} = \frac{V_c}{k} \quad (16)$$

The difference between V_c and V_{ca} is connected with the fact that the distribution curves in the melt in stationary and transient states may differ essentially at the same crystallization speed. In the first case, the distribution is described by simple exponent [1], while in the second case, by complex expression including a special function [see (10)]. Under some conditions (for example, at low acceleration) this difference may be insignificant. But it surely cannot be neglected a priori.

Substituting the parameter points used by us in formulas (1), (15), (16) we get $V_c = 3.5 \mu\text{m/s}$, $t_c = 14$ s and $V_{ca} = 6.3 \mu\text{m/s}$. More exact calculation of the latter two quantities gives 17 s and 8.4 $\mu\text{m/s}$, respectively. If the fact is taken into account that the phase interface at tin-indium melt crystallization in [9] stay flat during 120 s, it can be expected that the concentration overcooling at this case reached a considerable value.

Obviously the x_c zone width could be a measure for CO, if a method of its experimental determination would be available. On the other hand, the CO value could be

judged from the positive difference between the crystallization speed and its critical value. Fig. 3 shows the dependence $x_c(V)$ calculated for two transitional processes arising at the TF movement with acceleration $a_w = 1.72 \mu\text{m/s}$ (curve 1) and with constant speed $W_0 = 10V_c = 35 \mu\text{m/s}$ (curve 2). It is to note that in both cases, the dependence $x_c(V)$ is almost linear and also that in the second case, as in the first one, the crystallization speed at which a CO zone appears in the melt (abscissa of curve 2 initial point) exceeds noticeably the V_c value.

It is seen from Fig. 1 that the time dependence of crystallization speed experimentally got in [9] does not follow the $t^{3/2}$ law and behaves nonmonotonously. It is naturally to suppose that the nonmonotonous dependence $V(t)$ at accelerated temperature field movement is connected not only with impurity accumulation at the phase interface but with temperature gradient decreasing during the crystallization, too. In fact, in experiments described in [9], the melt was solidified in due to spontaneous cooling-down. To check the assumption, it is necessary to put into equation (6) a time-dependent quantity G . That is, to solve the nonlinear boundary problem with changeable coefficients. The most rational approach to this problem solving is to

use the numerical method and it will be done in our next work.

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Про кристалізацію бінарного розплаву у температурному полі, яке переміщується прискорено

В.М.Каніщев

У рамках одновимірної нестационарної моделі твердіння бінарного розплаву теоретично досліджено залежність швидкості кристалізації від часу у перехідному процесі, який виникає при рівномірно-прискореному переміщенні температурного поля у напрямі розплаву. Показано, що швидкість кристалізації за часом у такому процесі зростає за законом $t^{3/2}$. Встановлено, що швидкість кристалізації, при якій концентраційне переохолодження (КП) розплаву виникає у перехідному процесі, може помітно відрізнятися від швидкості кристалізації, при якій КП з'являється у стаціонарному режимі.