

Crystallization of a binary melt under the sample spontaneous cooling-down

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The impurity diffusion problem in a melt being crystallized in a uniformly accelerated moving temperature field with temperature gradient decreasing in time has been solved using the net model within the frame of unidimensional nonsteady solidification model. The temperature gradient decrease in the process mentioned has been shown to result in a nonmonotonous time dependence of the crystallization speed, that is in agreement with the literature experimental data.

Методом сеток в рамках одномерной нестационарной модели затвердевания решена задача о диффузии примеси в расплаве, который кристаллизуется в равноускоренно перемещающемся температурном поле с уменьшающимся во времени градиентом температуры. Показано, что уменьшение градиента температуры в указанном процессе приводит к немонотонному поведению зависимости скорости кристаллизации от времени, что согласуется с известными экспериментальными данными.

1. Introduction

When a crystal is grown from the melt, it is possible that the growth regime stationarity may be disturbed for any reason. This case may result, e.g., in a transition from the smooth phase interface to the cellular one, that is known to be accompanied by a sharp deterioration of the crystal quality.

Although the problems related to the transient effects during the crystallization are obviously of great importance, those are discussed in literature mainly in connection with the high-speed solidification problem [1]. At the same time, the use of modern equipment providing the observation of the phase interface small displacements evidences the necessity of a detailed study of the crystal growth transient regimen [2]. This is true, e.g., for the solidification stages under a smooth temperature lowering of the melted tail part of a crystal when growing sapphire using the HDC method. This work is aimed at the consideration of a binary melt

crystallization under uniformly accelerated displacement of the temperature field with temperature gradient decreasing in time.

First of all, it is to note that the derivation of the formula defining the crystallization speed $V(t)$ in a nonstationary regime [3] does not assume a constant temperature gradient G . Thus, in a general case, that quantity may be a function of time, $G(t)$. It is assumed that:

- (a) the heat propagation in the crystal-melt system is instantaneous,
- (b) the mass transfer takes place in the melt only and is due to diffusion only,
- (c) the crystal melting temperature is a linear function of the impurity concentration,
- (d) the latent heat of melting is negligible,
- (e) the heat conductivity factors in the liquid and solid phases are the same,
- (f) temperature T is a linear function of the distance to the phase interface x

$$T = T_0 + G(t)(x - x_0), \quad (1)$$

where T_0 is the melting point of the crystal with the impurity concentration C_0 .

Then the impurity diffusion problem in the melt in the coordinate system moving together with the crystallization front can be presented as

$$DC_{xx}(x,t) + V(t)C_x(x,t) = C_t(x,t), \quad (2)$$

$$DC_x(0,t) = V(t)(k-1)C(0,t), \quad (3)$$

$$C(\infty,t)=C_0, \quad C(x,0)=C_0, \quad (4)$$

$$V(t) = a_w t + \frac{m}{G(t)} C_t(0,t). \quad (5)$$

Here, $C(x,t)$ is the impurity concentration in the x point of the melt at the time moment t (indices at C denote the partial derivatives with respect to x and t); k , the impurity distribution coefficient; D , the impurity diffusion coefficient in the melt; m , the liquidus line slope in the phase diagram; C_0 , the impurity concentration far from the interphase boundary; a_w , the acceleration of the temperature field displacement.

The Eq. (2) describes the impurity diffusion in a medium oncoming the phase interface $x = 0$ at the speed $V(t)$. The equality (3) is the condition of the impurity conservation at that interface. The crystallization speed of the binary melt, according to (5), depends in this case on variations in three quantities, namely, the temperature field (TF) displacement speed, the impurity concentration at the phase interface, and the temperature gradient.

Results and discussion

The problem is nonlinear, moreover, the coefficient in the boundary condition is time-dependent. The problem was solved using the net method at values of parameters corresponding to Sn + 1% In alloy studied in experiment in [4]: $C_0 = 1\%$, $k = 0.56$, $m = -1.8$ K/%. A typical value $D = 5 \cdot 10^{-5}$ cm²/s and initial temperature gradient value $G_0 = 10$ K/cm were also used. The acceleration value of the TF displacement was varied in certain limits, thus, it served as a fitting parameter.

The calculations were done according to the implicit scheme on the net $\{x_i = ih, t_j = j\tau; i = 0, 1, \dots, 100; j = 0, 1, \dots, 120\}$ where $h = 13.6$ μm and $\tau = 1$ s are the space and time variable steps, respectively. The number of space steps exceeding 100 did not

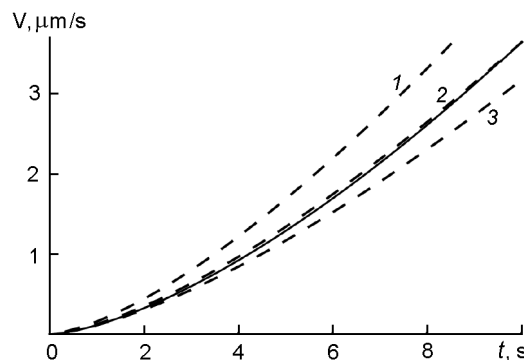


Fig. 1. The crystallization speed V as a function of time t calculated by the net method for the time step $\tau = 0.33$ s and different values of the space step h (μm): 5.5 (1), 8.3 (2), 12 (3). The solid line presents the analytical calculation results.

provide any appreciable change in the calculation results. The number of time steps was defined by the time (120 s) during which the crystallization front of the tin-indium alloy remained flat, according to the data from [4].

It is known [5] that it is rather difficult to prove the convergence of numerical solutions for equations in partial derivatives, particularly if those are nonlinear. That is why the following considerations were taken into account when selecting the τ and h values.

It has been shown [6] that at small t values, the crystallization speed at accelerated TF displacement with constant temperature gradient is described as

$$V(t) = \frac{4a_w G_0 \sqrt{D}}{3\sqrt{\pi} (k-1)mG_0} t^{3/2} \quad (6)$$

The $V(t)$ curve calculated from (6) at $a_w = 1.72$ $\mu\text{m/s}^2$ passes the experimental point obtained in [4] with coordinates 14 s and $V = 6.1$ $\mu\text{m/s}$. That curve for the 10 s interval is shown in Fig. 1 as the solid line. It is seen from the same Figure that at the specified time step value, the slope of $V(t)$ curves calculated by the net method depends on the space step value. By selecting h , it is possible to attain the coincidence of numerically and analytically determined crystallization speed values at the end of the interval mentioned. The curve 2 constructed in that manner coincides practically with the analytical one. But for all that, there are small distinctions between those curves, the largest difference (referred to as deviation

Table 1. Deviation of the crystallization speed ΔV_{10} on 10 s interval depending on the time (τ) and space (h) step values.

τ , s	1	0.77	0.5	0.33	0.2	0.1
h , μm	13.6	12.1	9.91	8.26	6.56	4.78
ΔV_{10} , $\mu\text{m/s}$	0.0642	0.0581	0.0531	0.0517	0.0532	0.0571

and denoted as ΔV_{10}) being about the middle of the interval. The deviations for different time step values obtained in that manner and the space step valued corresponding thereto are presented in Table 1. It is seen therefrom that the function $\Delta V_{10}(\tau)$ has a minimum at $\tau = 0.33$ s and $h = 8.3$ μm .

The elucidation of reasons for such behavior of $\Delta V_{10}(\tau)$ as well as the question about the solution convergence of our difference problem are outside the frames of this investigation. Nevertheless, it can be supposed that the minimum error in the numerical calculations was attained just at the step values where the ΔV_{10} attained a minimum. However, the analysis has shown that the results calculated for $\tau = 1$ s and $h = 13.6$ μm differ from those for $\tau = 0.33$ s and $h = 8.3$ μm only by few per cent. That is, when using the value $\tau = 1$ s, the expected error loss is small, but calculations with 1 s step are much easier than with any other one.

If the curve 2 of Fig. 1 is continued into the time region where the approximation used in the analytical calculation are known to be unsuitable, it can be noticed (Fig. 2a) that the $V(t)$ dependence remains monotonous within the whole time interval of interest. A weak maximum more similar to the saturation plateau (Fig. 2c) is revealed only at high a_w values. For such acceleration values, however, the solidification model used here seems to require a modification [7].

Thus, the impurity accumulation in the melt in front of the phase interface under an uniformly accelerated temperature field displacement is not a sufficient condition for nonmonotonous behavior of the crystallization speed.

When initiating the solution of the problem (2)-(5) with time-dependent coefficient G , its numerical solution error can be supposed to be approximately the same as in the case $G = \text{const}$. On the one hand, it is obvious that to define the law for the temperature field variation during the spontaneous cooling-down of a melted sample is a separate rather complex problem. On the other hand, using the net method, it is pos-

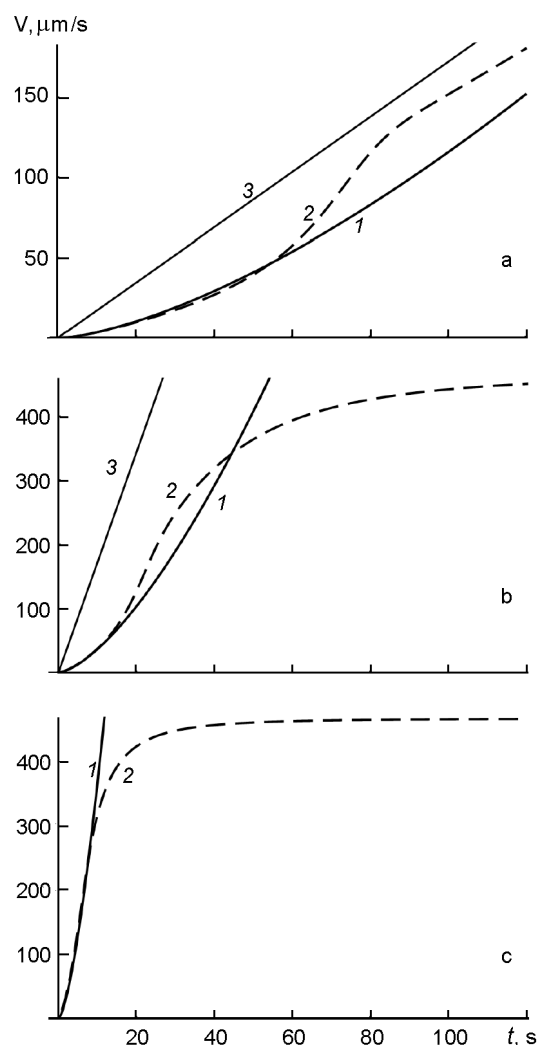


Fig. 2. The crystallization speed V as a function of time t for different values of the temperature field displacement acceleration a_w ($\mu\text{m/s}^2$): 1.72 (a), 17.2 (b), 172 (c). Lines 1, 2 present the analytical and numerical calculations, respectively; 3, the temperature field displacement speed.

sible to select a function $G(t)$ which, being substituted into the problem statement, would provide the solution agreeing satisfactorily with experimental data.

As a trial function, very efficient is found to be the linear in time one

$$G(t) = G_0 - bt, \quad (7)$$

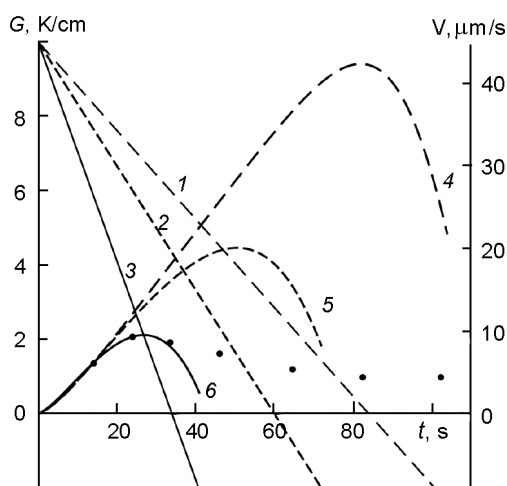


Fig. 3. Temperature gradient G at the phase interface (1-3) and crystallization speed V (4-6) as functions of time t at different values of temperature gradient reduction speed, b [K/(cm·s)]: 0.119 (1, 4), 0.167 (2, 5), 0.295 (3, 6). The individual points refer to the experimental $V(t)$ dependence [4].

where $G_0 = 10$ K/cm and b is a certain rate of temperature gradient decrease. Here, two adjustable parameters are available, namely, a_w and b . However, using the condition the calculated $V(t)$ curves should pass the first experimental point (Fig. 3), the number of parameters to be varied can be reduced to one.

It is seen from Fig. 3 that the uniform reduction of the temperature gradient at the crystallization front (curves 1-3) results in a dome-shaped $V(t)$ dependence (curves 4-6). In this case, the $V(t)$ maximum for each specific b value is approximately above the intersection point of the $G(t)$ curve with the abscissa axis. It follows therefrom that to attain the nonmonotonous behavior of the crystallization speed, not a simply reduction but a rather significant reduction of the temperature gradient is necessary.

By fitting the $G(t)$ line slope, it is possible to provide that the calculated $V(t)$ curve will pass the first two experimental points (curve 6 in Fig. 3, curve 3 in Fig. 4). In this case, the parameters will take the values $a_w = 2.49$ $\mu\text{m}/\text{s}^2$ and $b = 0.295$ K/(cm·s). If the temperature gradient at the next section (between the 2nd and 3rd points) will be presented by the same formula (7) but with other coefficients, the $V(t)$ curve will pass three experimental points (with abscissas 14, 24, and 34 s). In this case, the temperature gradient takes the form of a continuous piecewise linear function:

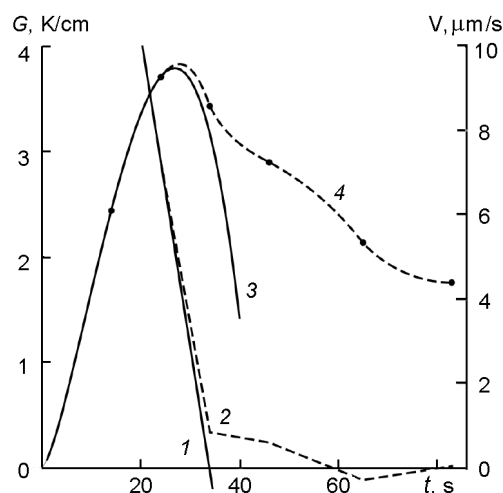


Fig. 4. The crystallization speed V (3, 4) as a function of time t calculated using the linear (1) and piecewise linear (2) time dependence of temperature gradient G . Individual points refer to the experimental $V(t)$ dependence [4].

$$G(t) = \begin{cases} 10 - 0.295t & \text{at } 0 \leq t \leq 24, \\ 2.92 - 0.258(t - 24) & \text{at } 24 \leq t \leq 34. \end{cases} \quad (8)$$

Here, the time and temperature gradient are presented in seconds and K/cm units, respectively. It is obvious that any number of points can be joined in that manner, what is demonstrated in Fig. 4. A knee in curve 2 answers to each experimental point in curve 4 (Fig. 4), beginning from the 2nd one.

It is seen from Fig. 4 that the broken line of the temperature gradient time dependence curve 2, Fig. 4) constructed using the experimental results drops in the region of negative values and behaves nonmonotonously. Such a behavior of the calculated $G(t)$ function may be connected first of all with imperfection of the model selected. In fact, when formulating the problem, we have assumed that the heat conductivity coefficients are the same in the liquid and solid phases, while such an assumptions may be too rough at small temperature gradients.

Fig. 5 presents the distribution curves of indium impurity in tin melt calculated for different moments of crystallization. The binary system liquidus lines in C - x coordinates are presented for the same moments [3]. With regard to the temperature field (1), taking (8) into account, those lines answer to the expression

$$C_L = C(0, t) + \frac{G(t)}{m}x. \quad (9)$$

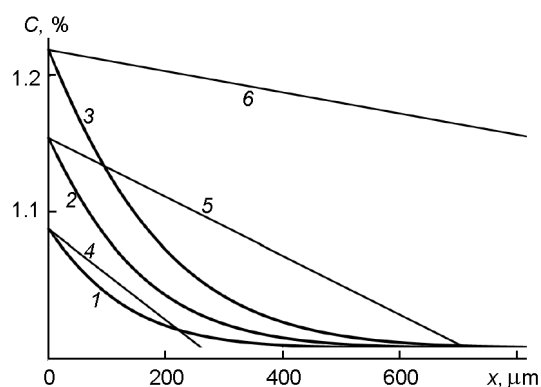


Fig. 5. Dependences of indium concentration C in the tin melt on the distance x from the phase interface for different time moments t after the crystallization onset (s): 14 (1), 21 (2), 30 (3). 4, 5, 6 are the liquidus lines in C - x coordinates.

Since the slope of lines (9) reduces in time, the concentration overcooling (CO) zone width x_c increases, and faster than at constant temperature gradient [6] at that. That width for each time moment is seen to be defined by the intersection of $C(x,t)$ and C_L lines.

In a different way, the x_c value can be estimated only by comparing the instantaneous crystallization speed with a certain speed at which the CO zone arises in the melt. It is known [8] that in the steady crystallization regime, that speed is so-called critical speed

$$V_c = \frac{kGD}{(k-1)mC_0}. \quad (10)$$

It is determined in experiment from the first violation (pox-like) of the phase interface smoothness. The V_c value as a certain reference seems to have sense in the case of non-stationary crystallization, too. In that case, however, it is a function of time (due to the $G(t)$ dependence) (Table 2). In general, the moment t_c when the CO arises in the melt can be determined using the equality

$$C_x(0, t_c) = \frac{G(t_c)}{m}. \quad (11)$$

In a transient process with accelerated temperature field displacement, it is just the crystallization speed V_{ca} (Table 2) (exceeding the V_c by a factor of about $1/k$) [6] that corresponds to the above-mentioned moment.

Table 2. The crystallization speed V , indium concentration at the phase interface at the melt side $C(0,t)$, temperature gradient G , critical crystallization speeds V_c , V_{ca} and the concentration overcooling zone width x_c calculated for the time moment t after the solidification onset of the tin-indium melt.

t , s	V , $\mu\text{m/s}$	$C(0,t)$ %	G , K/cm	V_c , $\mu\text{m/s}$	V_{ca} , $\mu\text{m/s}$	x_c , $\mu\text{m/s}$
0	0	1	10	3.54	5.90	0
8	3.20	1.04	7.64	2.70	4.62	0
11	4.70	1.06	6.76	2.39	4.12	67
24	9.28	1.18	2.92	1.03	1.85	1108
30	9.47	1.22	1.37	0.484	0.882	2867

It is seen from Table 2 that the crystallization speed in the example under consideration becomes higher than V_c at 8th second after the solidification begins. The CO zone, however, arises at the 11th second only, when $V(t) > V_{ca}$. At $t = 24$ s, the crystallization speed exceeds the critical value V_{ca} by a factor of 5; according to data from [8] (though obtained in steady regime) that must result in a developed cellular structure of the phase interface. Taking into account the fact that the interface of the solidifying tin-indium alloy remained smooth for 120 s, the importance of the result obtained in [4] is well understandable.

The following conclusions can be drawn from the calculations carried out here. The transition from the smooth interface to another structure requires a certain energy barrier to be overcome. Indeed, the formation of a more developed structure causes an additional interface area. Thus, when studying the binary melt solidification problem, the time factor is to be taken into account among others. By the way, the contradictions in literature data on the problem may be connected to the fact that the time factor was not taken into account when the data were obtained.

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Кристалізація бінарного розплаву при спонтанному охолодженні частково розплавленого зразка

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Методом сіток у рамках одновимірної нестационарної моделі твердіння розв'язано задачу про дифузію домішки у розплаві, який кристалізується у температурному полі, яке переміщується рівномірно-прискорено з градієнтом температури, що зменшується з часом. Показано, що зменшення градієнта температури у згаданому процесі спричиняє немонотонну поведінку часової залежності швидкості кристалізації, що узгоджується з відомими експериментальними даними.