Features of binary melt solidification at variable crystal pulling rate

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The impurity diffusion in the melt, out of which the crystal is pulled into a cold zone, has been explained in the framework of one-dimensional non stationary solidification model in the second approximation by the amplitude of pulling speed oscillating term. It has been found that in the first approximation the crystallization and pulling rates have the same oscillation frequency, differing in phase shift φ_v. A dependence of φ_v on oscillation frequency has been obtained with following parameters: melt impurity diffusion coefficient, impurity distribution coefficient k and concentration overcooling coefficient, which value shows whether overcooling takes place in the melt. In the second approximation, along side with the second harmonic, the impurity diffusion is explained by the presence of time-independent admixture which makes the impurity concentration decrease on the interface border at $k<1$ at average time and increase at $k>1$. Thus, a crystal being pulled at variable rate has the effect of a partially mixed melt.

В рамках одномерной нестационарной модели затвердевания во втором приближении по амплитуде колебательной составляющей скорости вытягивания решена задача о диффузии примеси в расплаве, из которого кристалл вытягивают в холодную зону. Показано, что в первом приближении скорость кристаллизации колеблется с той же частотой, что и скорость вытягивания, но со сдвигом по фазе φ_v. Получена зависимость φ_v от частоты колебаний, в которую параметрически входят коэффициент диффузии примеси в расплаве, коэффициент распределения примеси k и коэффициент, по величине которого можно судить о наличии или отсутствии в расплаве зоны концентрационного переохлаждения. Во втором приближении, наряду со второй гармоникой, решение содержит независящую от времени добавку. Наличие этой добавки приводит к тому, что в среднем по времени концентрация примеси на межфазной границе при $k<1$ понижается, а при $k>1$ повышается. Таким образом, при вытягивании кристалла с переменной скоростью достигается эффект, наблюдаемый при частичном перемешивании расплава.

1. Introduction

The impurity striation is quite often observed in binary melt-grown crystals [1]. This defective structure being caused by discontinuous impurity distribution consists of layers perpendicular to the direction of crystal growth. Therefore it is also called cross striation [2]. The impurity striation considerably cuts down the production yield [3], indicating the loss in purification efficiency by the method of zone recrystallization.

The striation can be prevented by the decrease of crystal growth rate, under all other equal conditions. In fact, the distance between the bands increases under decrease of crystal growth rate [5]. So the speed can be decreased enough to make the period of striation larger than crystal's size. The periodicity of the bands in this structure [6] suggests an idea that its parameters can be controlled by periodical increasing or decreasing the growth rate with a proper frequency. However, it leads to the problem of

binary melt solidification under pulling the crystal with periodically varying rate. This work is devoted to theoretical investigation of the impurity distribution in the melt at crystal pulling rate containing a sinusoid-like oscillation component.

2. Computational procedure

Let us use the one-dimensional non-stationary model of binary melt solidification with assumptions that let take into account only impurity diffusion in the melt, excluding the temperature field. That is possible if we suppose [7] that heat spreading is instant in the crystal-melt system and the mass transfer takes place only in the melt and only by diffusion, the crystal melt temperature depends linearly on the impurity concentration, and the temperature field is described by linear function on coordinate.

Let us use the following designations: $C(x,t)$ – impurity concentration in the melting point at a certain moment of time. C_0 – impurity concentration in the melt at the infinite distance from the crystallization front. G – temperature gradient, D – impurity diffusion coefficient in the melt, m – liquidus line slope, k – impurity distribution coefficient.

Suppose a crystal being pulled out of the melt into the cold zone starting at $t = 0$ with the rate

$$w(t) = W + W_1 \sin \omega t \qquad (1)$$

where W, W_1 and ω are constants. In order to study the behavior of the interface border in such process, the problem on the impurity diffusion in the melt, which crystallizes at $V(t)$ rate has to be solved and the law of $V(t)$ alteration has to follow from this solution.

Let us use for the calculation the moving coordinate system with x starting from the position of crystallization front and pass to non-dimensional variables by formulas:

$$x \rightarrow \frac{Dx}{W}, \ t \rightarrow \frac{Dt}{W^2}, \ V(t) \rightarrow WV(t), \ \omega \rightarrow \frac{W^2\omega}{D},$$

$$C(x,t) \rightarrow C_0\left[1 + \frac{1-k}{k}C(x,t)\right], \ \delta = \frac{W_1}{W}. \quad (2)$$

and introduce a parameter

$$B_w = \frac{kGD}{(k-1)mC_0W}. \qquad (3)$$

Then the impurity concentration in the melt $C(x, t)$ will be the solution of the following equation:

$$C_{xx}(x, t) + V(t)C_x(x, t) = C_t(x, t), \quad (4)$$

$$C_x(0, t) + V(t)[(1 - k)C(0, t) + k] = 0, \ (5)$$

$$C(\infty,t) = 0, \ \ C(x,0) = 0, \qquad (6)$$

where

$$V(t) = 1 + \delta\sin\omega t - \frac{C_t(0,t)}{B_w}. \qquad (7)$$

Here, index designations of partial derivatives of C with respect of x and t are used. Eq. (4) describes the impurity diffusion in the medium, which covers interphase surface $x = 0$ with $V(t)$ rate. Eq (5) is the condition of impurity conservation on this surface. Eq (7) describes the dependence of the crystallization rate of binary melt on the crystal pulling rate (or in a general case, on the rate of temperature field movement along the growth axis) and impurity concentration degree rate on the phase boundary[8].

System of Eq (4)-(7) consists of four input parameters: δ, ω, k and B_w. The latter indicates the presence or absence of the overcooling zone (OZ) in the melt. OZ is absent at $B_w \geq 1$ (OZ criteria [9]). If $B_w < 1$, the difference $1 - B_w$ indicates the degree of such overcooling [10].

3. Results and discussion

The problem formulated is non-linear, but it can be made linear one, assuming the disturbance amplitude of pulling rate is small and the impurity distribution in the melt is almost stationary after a rather long period after crystallization start. Then the solution in the second approximation can be presented as follows:

$$C(x,t) = e^{-x} + C_1(x,t) + C_2(x,t), \qquad (8)$$

$$C_{n,xx}(x,t) + C_{n,x}(x,t) + \qquad (9)$$

$$+ \frac{e^{-x}}{B_w} C_{n,t}(0,t) + f_n(x,t) = C_{n,t}(x,t),$$

where the index at C means the order of correction to a stationary solution.

It is worth noting that practically a solution at a steady crystallization is of interest. Thus, we shall try a solution which at $t \rightarrow \infty$ does not depend on the initial condition.

Substituting (8) into (4)-(7) and grouping the values of same infinitesimal order, we

get two systems of equations for required corrections. The systems are of the same type; therefore they can be presented as follows:

$$C_{n,x}(0,t) + (1-k)C_n(0,t) - \qquad (10)$$
$$- (1/B_w)C_{n,t}(0,t) + g_n(t) = 0,$$

$$C_n(\infty,t) = 0, \quad n = 1, 2. \qquad (11)$$

here

$$f_1(x,t) = -e^{-x}\delta\sin\omega t, \quad g_1(t) = \delta\sin\omega t, \qquad (12)$$

$$f_2(x,t) = C_{1,x}(x,t)[\delta\sin\omega t - C_{1,t}(0,t)], \qquad (13)$$

$$G_2(t) = (1-k)C_1(0,t)[\delta\sin\omega t - C_{1,t}(0,t)]. \qquad (14)$$

The problems, which solutions do not depend on the initial condition, are usually solved by the method of undetermined coefficients [11]. As the solution being unknown a priori, we determine it by Laplace transformation method. Let use the initial condition $C_1(x,0) = -e^{-x}$ and put $B_w = 1$. The latter limitation is not expected to influence the general structure of solution, but it will considerably facilitate the calculation [12]. Laplace-image solution of the problem (9)-(11) at $n=1$ for the given case can be presented as follows:

$$\hat{C}_1 x,p) = -\frac{e^{-x}}{p+k} + \qquad (15)$$
$$+ \frac{2(p+k)e^{-\frac{x}{2}(1+\sqrt{1+4p}\,)} + (1-2k-\sqrt{1+4})e^{-x}}{2p(p+k)(p^2+\omega^2)}\,\omega\delta,$$

where p − Laplace transformation parameter. The first fraction in (15) is no other than an image of function $\exp(-xkt)$, disappearing at $t{\to}\infty$.

Asymptomatic behavior of the pre-image of the second fraction in the right part of (15) at $t{\to}\infty$ (that is exactly we are interested in) can be studied by a theorem on mutual correspondence of asymptotic decomposition of image and pre-image [13]. It is easy to check that in a point $p = 0$ this feature is eliminable. Then decomposing the given expression in the points $p = i\omega$ and $p = -i\omega$ neighborhood into power series, adding the first terms of these series and passing to the pre-image, we get the required view of solution:

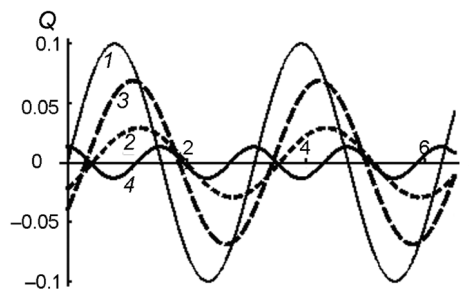$$C_1(x,t) = \delta[y_1(x)\sin\omega t + z_1(x)\cos\omega t], \quad (16)$$

Fig. 1. The dependence of amplitude Q (in relative units) of oscillating component of pulling rate (*1*), addition of the first order to the impurity concentration on the phase boundary (*2*), addition to the crystallization rate (*3*) and oscillating addition of the second order to the impurity concentration on the phase boundary (*4*) on dimensionless time time t for the distribution coefficient $k = 0.5$, non-dimensional frequency $\omega = 2$ and $B_w{=}1$ parameter. The amplitude of curve *4* is 20 times enlarged.

where $y_1(x)$ and $z_1(x)$ (for any value of B_w) are not determined yet.

Substituting (16) into (9)-(11) at $n=1$ and grouping summands with multiplier $\sin\omega t$ and $\cos\omega t$, we come to a boundary problem for $y_1(x)$ and $z_1(x)$ as an inhomogeneous system of two common differential equations. It is obvious that these function fit the system:

$$y_1(x) = \frac{y_0}{B_w}e^{-x} + \left\{y_0\left(1-\frac{1}{B_w}\right)\cos bx + \qquad (17)\right.$$
$$+ \left[z_0\left(1-\frac{1}{B_w}\right)-\frac{1}{\omega}\right]\sin bx\left\}e^{ax}\right.,$$

$$z_1(x) = \left(\frac{z_0}{B_w}+\frac{1}{\omega}\right)e^{-x} + \qquad (18)$$
$$+\left\{\left[z_0\left(1-\frac{1}{B_w}\right)-\frac{1}{\omega}\right]\cos bx - \right.$$
$$\left. - y_0\left(1-\frac{1}{B_w}\right)\sin bx\right\}e^{-ax},$$

where

$$y_0 \equiv y_1(0) = (B_w/s)[a_1(a-1)-b_1(b-\omega)], \quad (19)$$

$$z_0 \equiv z_1(0) = (B_w/s)[a_1(b-\omega)+b_1(a-1)], \quad (20)$$

$$a_1 = \omega + b(B_w-1), \qquad (21)$$
$$b_1 = kB_w + (a-1)(B_w-1), \quad s = \omega(a_1^2+b_1^2)$$
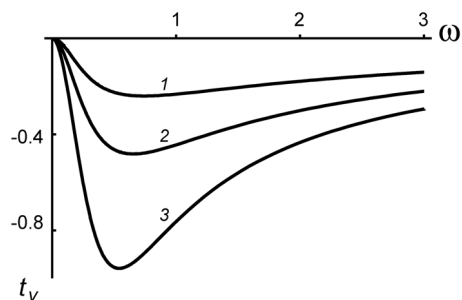$$a = \{1 + [1/2 + (1/4+4\omega^2)^{1/2}]^{1/2}\}/2,$$
$$b = \omega/(2a-1).$$

Fig. 2. The dependence of shift value between the oscillating phases of pulling rate and crystallization rate t_v on dimensionless time frequency ω for the distribution coefficient $k = 0.5$ and different values of B_w parameter: $1 - B_w = 1.5$, $2 - B_w = 1$, $3 - B_w = 0.5$.

Fig. 3 Dependence of the value of stationary addition to the impurity concentration on the phase boundary U (in units δ^2) on dimensionless pulling rate oscillation frequency ω for $B_w=1$ and different values of distribution coefficient k: $1 - k = 0.5$, $2 - k = 0.8$, $3 - k = 2$.

Here a and b parameters appear as material and imaginary parts of the roots of the characteristic equation for homogeneous system: $r^2(r+1)^2+\omega^2=0$ This equation has four roots, but only two of them $r_{1,2} = -a \pm b$i obey (11). The first correction to the impurity concentration on the phase boundary can be presented as:

$$C_1(0,t) = \delta(y_0^2 + z_0^2)^{1/2}\sin(\omega t + \varphi_c), \quad (22)$$

where $\varphi_c = arctg(z_0/y_0)$. Using (7) and (22) we obtain the correction to the crystallization rate;

$$V_1(t) = \quad (23)$$

$$= (\delta/B_w)[(\omega^2 y_0^2 + (\omega z_0 + B_w^2)]^{1/2}\sin[\omega(t + t_v)],$$

where

$$t_v = -(1/\omega)arctg[\omega y_0/(\omega z_0 + B_w)], \quad (24)$$

Thus, in the first approximation by δ the impurity concentration on the phase boundary (curve *2*, Fig.1) oscillates with the same frequency as the pulling rate $w(t)$ (curve *1*, Fig. 1), but shifted by phase. The same behavior has the component of the concentration gradient on the phase boundary $C_{1,x}(0, t)$ and the component of the crystallization rate $V_1(t)$ (curve *3*, Fig. 1).

Therefore in the first approximation, on average, neither the impurity concentration on the phase boundary nor its coordinate derivative differs from their values at constant crystallization rate. It would seem that the oscillation of crystal growth ought to deteriorate the situation because at $B_w=1$ every half-period of the melt will be in the state of the concentration overcooling which, according to numerous experimental
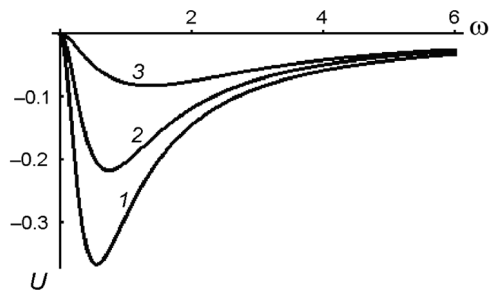
data, gives rise to bumps on the initially smooth phase surface [9]. However the analysis of the data shows that they have been obtained disregarding time factor [10]. And since this factor can be decisive in non-stationary conditions, one cannot predict the behavior of crystal-melt system at certain periods of time.

According to formula (24) we can determine important characteristics such as: impurity distribution coefficient k, impurity diffusion in the melt coefficient D and B_w parameter by the time shift between the maxima of crystallization and pulling rates. In fact, according to (2), (19)-(21) and (24) the value of t_v depends only on the parameters: W, ω, k, D and B_w. It is possible to calculate the values of k, D and B_w by measuring a period of time between the maxima of $w(t)$ and $V(t)$ at given values of W and ω during the steady crystallization. Fig. 2 shows that the amplitude of $t_v(\omega)$ curves is rather sensitive to the value of B_w. Therefore, the stationary oscillation at various pulling rate can be used for studying the concentration overcooling during crystal growth along with the decaying oscillation of the binary melt crystallization rate in the initial transitory process [6].

It is worth noting that CCD camera (sensicam qe) can be used for realization of the method of the shift between the oscillation phases of the pulling and crystallization rates. The characteristic breaks on the curves of dependences of the front crystallization on time $x_f(t)$ clearly determine the transition moments from a smooth phase surface to a cellular one [6]. It is obvious that when measuring t_v the the breaks on the curves $x_f(t)$ have to be prevented, as the theory given here is only applicable to a smooth boundary surface.

Substituting (17), (18) into (13), (14) and canceling the product of the first harmonics, we obtain expressions which contain a time-independent summand along with the second harmonics. Therefore, the second correction can be presented as follows:

$$C_2(x,t) = \qquad (25)$$
$$= \delta^2[u_2(x) + y_2(x)\sin2\omega t + z_2(x)\cos2\omega t],$$

where $u_2(x)$, $y_2(x)$ and $z_2(x)$ – still unknown functions. Substituting (24) into (9)-(11) at $n=2$ and grouping summands with multipliers 1, $\cos2\omega t$ and $\sin2\omega t$, we come to two boundary problems for function $u_2(x)$ and pair of function $y_2(x)$, $z_2(x)$. The latter two as well as $y_1(x)$, $z_1(x)$ are solved within the system of equations. The appearance of the second harmonic in the solution of crystallization problem (curve *4*, Fig.1) can serve as another illustration for non-linear system response to some influence (for example, frequency doubling in non-linear optics). It is obvious that all mentioned about the time factor with regard to the first harmonic is applicable to the second one.

It is especially worth noting a time-independent addition to impurity concentration in the melt $u_2(x)$, having a very simple form under $x = 0$:

$$u_2(0) \equiv U = -y_0\big/2. \qquad (26)$$

Fig. 3 shows U on ω dependences, plotted for various k. All of them lie below x axes with the minimum shifting towards low frequencies when k decreases. Thus, for $B_w=1$ and typical $k=0.5$ (curve 1, Fig. 3) the minimum is reached at $\omega_m=0.56$. In dimensional quantities at $D = 10^{-5}$ sm^2·sec^{-1} and $W = 10^{-3}$ sm·sec^{-1} it corresponds to frequency 0.056 sec^{-1} or period 112 sec.

However, passing to dimensional quantities according to formula (2) needs U value to be multiplied by $C_0(1-k)/k$. As the result, at $k > 1$ stationary addition to the impurity concentration on the interphase boundary is positive, that means that irrespective of $1-k$ sign the difference between $C(0, t)$ and C_0 decreases. Therefore, in order to preserve generality, let us focus on $k<1$ case, when the sings of dimensional and non-dimensional U coincide.

4. Conclusions

Thus, at oscillating regime of crystal pulling the average by time impurity concentration on the interphase boundary $\overline{C}(0)$ is lower, than in the case of stationary growth. That is more impurity is pushed in the melt, as it is observed at its partial mixing [9]. It is clear that under big amplitudes of oscillations (for example, at $\delta\sim1$) the effect of $\overline{C}(0)$ reduction favorable for crystal growth can be rather tangible. By other side, under large oscillation amplitudes of crystallization rate the probability of defects appearance on the interphase boundary in certain half-periods also increases. And again we come to the above mentioned time factor, which still remains uninvestigated neither experimentally nor theoretically.

The result of this paper has practical significance even with the assumptions adopted in this work. It is evident that the experiments needed for checking of our result will illuminate the problem of keeping smooth phase surface at the concentration overcooling of the melt.

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Особливості затвердіння бінарного розплаву при витягуванні кристалу зі змінною швидкістю

В.М.Каніщев, С.В.Баранник

У межах одномірної нестаціонарої моделі затвердіння у другому приближенні по амплитуді коливальної складової швидкості витягування розв'яна задача о дифузфії домішки у розплаві, з якого кристал витягують у холодну зону. Показано, що у першому наближенні швидкість кристалізації коливається з тією ж частотою, що і швидкість витягування, але зі здвижкою по фазі φ_v. Отримано залежність φ_v від частоти коливань, до якої параметрично входить коефіцієнт дифузії домішки у разплаві, коефіцієнт розподілення домішки k та коефіцієнт, за величиною якого можна скласти висновок про присутність або відсутність у розплаві зони концентраційного переохолодження. У другому наближенні, окрім другої гармоніки, рішення містить незалежний від часу додаток. Наявність цього додатку призводить до того, що в средньому за часом концентрація домішки межфазній границі при $k<1$ знижується, а при $k>1$ збільшується. Таким чином, при витягуванні кристала зі змінною щвидкістю досягається ефект, що можна наблюдати при частковому перемішуванні розплава.