On the transition criterion to the regular cellular structure of a binary melt crystallization front

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The effect of regular cellular structure formation at a binary melt crystallization has been considered in the frame of the bidimensional solidification model under account for the surface energy of the liquid/solid phase interface. The transition to the phase interface with bulges arranged periodically thereon takes place at the crystallization speed value exceeding twice that causing the formation of the concentration supercooling zone in the melt. The calculated results are compared with the experimental data taken from literature.

Вариационным методом в рамках двумерной модели затвердевания с учетом поверхностной энергии границы жидкой и твердой фаз исследован эффект образования регулярной ячеистой структуры при кристаллизации бинарного расплава. Показано, что переход к межфазной границе с периодически расположенными на ней выступами происходит при скорости кристаллизации, в два раза превышающей ее значение, при котором в расплаве появляется зона концентрационного переохлаждения. Проведено сравнение результатов расчета с имеющимися в литературе опытными данными.

It is known that as the crystal growth speed increases or the temperature gradient decreases, the initial smooth solid/liquid phase interface becomes at first "erupted" ("pox-like") and then chaotically arranged bulges arise thereon which form later a rather ordered periodical structure. Finally, the bulges grow into dendrites [1]. The rash formation on the phase interface has been shown to be due to the concentration supercooling zone (CSZ) in the melt [2]. Thus, the cellular structure becomes a regular one in conditions different from those predicted by the CSZ criterion. This work is aimed at elucidation of those conditions.

Let the bidimensional model of a binary melt solidification be used where the temperature field is set as a linear function of the coordinate x directed along the crystal growth axis and the surface energy of the phase interface is taken into account [3]. Let the problem be formulated at first in the differential form ant then its variational equivalent will be considered.

Let the following designations be used: $C(x,y)$, the impurity concentration in the melt; $x=\varphi(y)$, the phase interface equation; L, the cell half-width or the phase interface half-period; C_0, the impurity concentration in the melt at infinite distance from the crystallization front; D, the impurity diffusion coefficient in the melt; V, the crystallization speed; k, the impurity distribution coefficient; T_m, the pure melt solidification temperature; G, the temperature gradient; μ, the liquidus line slope in the phase diagram of the binary system; Γ, the capillary constant. Going to

dimensionless parameters

$$\kappa = \frac{D}{VL} \tag{1}$$

$$B = \frac{kGD}{(k-1)\mu VC_0}, \tag{2}$$

$$\gamma = \frac{kT_m V\Gamma}{(k-1)\mu DC_0} \tag{3}$$

and using the dimensionless variables in the (x, y, C) space, the problem of an impurity diffusion in a melt being crystallized at a constant speed can be presented [3] as

$$C_{xx} + C_x + \kappa^2 C_{yy} = 0, \tag{4}$$

$$C_x(\varphi) - \kappa^2 \varphi_y C_y(\varphi) + (1-k)C(\varphi) + k = 0, \tag{5}$$

$$C(\infty, y) = 0, \quad C_y(x,0) = C_y(x,1) = 0, \tag{6}$$

$$C(\varphi) = 1 - B\varphi + \gamma \kappa^2 \varphi_{yy} \left(1 + \kappa^2 \varphi_y^2\right)^{-3/2}. \tag{7}$$

Here, the partial derivatives $C(x,y)$ with respect to x and y as well as derivatives of φ with respect to y are designated using indices. Note that in the problem (4)-(7), the condition at the phase interface are presented by two equations (5) and (7) that are the boundary conditions of 3rd and 1st order, respectively. When formulating the second condition in (6), the experimentally established fact that the bulges on the crystallization front are symmetrical with respect to their centers.

Let the Eq. (7) be set aside meanwhile and the solution of the problem (4)-(6) be constructed at a fixed phase boundary. According to all the mathematical physics canons, a solution of such a problem exists and is the only one [4]. It is easy to check that if the first variation of the functional

$$I\{C(x,y), \varphi(y)\} = \int_0^1 dy \int_{(\varphi)}^{\infty} e^x \left(C_x^2 + \kappa^2 C_y^2\right) dx - \int_{(\varphi)} e^x [2k + (1-k)C] C dy. \tag{8}$$

(where (φ) denotes the line $x=\varphi(y)$ along which the line contour integral is taken) is set equal to zero, then both Eq. (4) and condition (5) are obtained simultaneously. Thus, the condition (5) can be set free [4] while the conditions (6) are easy to take into account when selecting the basis functions. The eigenfunctions of the corresponding boundary problem with flat interphase boundary are quite suitable as such basis functions. Then, the solution of the problem (4)-(6) can be presented as

$$C_n = \sum_{m=0}^{n} A_{mn} \exp(-q_{mn}x)\cos(\pi m y), \tag{9}$$

where n is the approximation order (0, 1, 2...);

$$q_{mn} = 0.5 + \sqrt{0.25 + (\pi m \kappa_n)^2}, \tag{10}$$

and A_{mn} are coefficients determined basing on the stationarity condition of the functional (8).

It is seen from the expression for the second variation of the functional (8)

$$\delta^2 I \;=\; 2\!\int\limits_{0}^{1} dx \int\limits_{\varphi}^{\infty} e^{z}\left(\delta C_{z}^{2} + \kappa^{2}\delta C_{x}^{2}\right) dz \;-\; 2\int\limits_{\{\varphi\}} e^{z}(1-k)\delta C^{2} dx \quad, \tag{11}$$

that at least at $k>1$, the solution of the problem (4)-(6) imparts not simply stationary but minimum value to that functional. The question if the latter is valid for any k requires a special consideration and falls outside the limits of this work. However, the study results of special cases where $k>1$ [5] suggest that the stationary value of the functional (8) is equivalent to its minimum within thew whole range of k values.

It was shown before that the double integral value in the Eq. (8) is in proportion to the energy being dissipated at the impurity diffusion within the melt volume [6]. This is evidences, in particular, by the dependence of its integrand on the squared concentration gradient. Using the boundary condition (5), the line contour integral in (8) can be presented as

$$\frac{k^{2}}{1-k}\int\limits_{(\varphi)} e^{x} dy \;-\; \frac{1}{1-k}\int\limits_{(\varphi)} e^{x}\left|C_{x} - \kappa^{2}\varphi_{y} C_{y}\right|^{2} dy \;. \tag{12}$$

It is seen that at fixed phase interface, the line part of the functional (8) consists of an item insignificant in variation and an integral with the integrand proportional to the squared concentration gradient but related to the phase interface. Thus, by analogy with the double integral, the minimum of the line contour integral in the functional (8) can be suggested to be defined by the minimum of energy being dissipated at the phase interface when the impurity particles go from the liquid phase to solid one.

Returning now to the problem (4)-(7), we obtain a system of equations where the function $\varphi(y)$ is not the set but to be sought. In the steady state conditions, the average impurity concentration at the phase interface should be 1, otherwise, the mass conservation law would not be met. Then, the equality

$$\int\limits_{0}^{1} C\big(\varphi(y), y\big) dy = 1, \tag{13}$$

restricting the selection of the sought-for $C(x,y)$ and $\varphi(y)$ functions is valid.

Thus, the variational problem equivalent to (4)-(7) is reduced to determination of $C(x,y)$ and $\varphi(y)$ functions that satisfy the conditions (5)-(7), (13) and impart the minimum value to the functional (8).

The periodical structure of crystallization front can be expected to be formed at a small amplitude of the cell bulges that will be designated as ξ. Then our task is to determine the conditions where the contribution to the dissipation energy due to such bulges changes its sign from plus to minus. Since that contribution value should be independent of the sign at ξ, it should be an even function of ξ, that is, at least proportional to ξ^2.

The solution of problem (4)-(7) at an accuracy to the 2nd smallness order with respect to ξ can be presented as

$$C(x,y) = e^{-x} + A_{1}\xi\exp(-q_{1}x)\cos\pi y + \xi^{2}[A_{0}e^{-x} + A_{2}\exp(-q_{2}x)\cos 2\pi y], \tag{14}$$

$$\varphi(y) = \xi\cos\pi y + \xi^{2}(\alpha_{0} + \alpha_{2}\cos 2\pi y). \tag{15}$$

Here q_{m} is defined by the Formula (10) where the index n equal to 2 is omitted and the parameters q_{1}, A and α can be found using a system of 6 equations composed by substituting those expressions into boundary conditions (5), (7) and equating to zero the coefficients at $\xi\cos\pi y$, ξ^{2} and $\xi^{2}\cos2\pi y$ [3]. Meanwhile, substituting (14), (15) into (8), we get the expression

$$I = -k + \xi^2 \frac{1}{2}\left[A_1^{\;2}\left(q_1 - 1\right) + k\left(A_1^{\;2} - 2A_1 - 2\alpha_0 + \frac{1}{2}\right)\right],\tag{16}$$

It is seen therefrom that half of the parameters mentioned are unnecessary. Substituting then the expression (7) into the condition (13) and taking into account (14), (15), it is easy to understand that $\alpha_0=0$. The remaining parameters q_1 and A_1 are rather easy to find from the system of two equations obtained by substituting the first in ξ approximations of $C(x,y)$ and $\varphi(y)$ and equating to zero the coefficients at $\xi\cos\pi y$. As a result, we get

$$q_1 = 1 + \frac{kB_\gamma}{1 - B_\gamma}\tag{17}$$

and $A_1 = 1 - B_\gamma$ where $B_\gamma = B + \pi^2\kappa^2\gamma$. Substituting those values into (16), we get finally

$$I = -k + \xi^2 \frac{k}{2}\left(B_\gamma - \frac{1}{2}\right).\tag{18}$$

It is seen from (18) that the additive to the functional due to bulges arranged periodically on the phase interface is negative at $B_\gamma < 1/2$. According to the variational principle for the solidification model under consideration, it is just this inequality that is the criterion of transition to a regular cellular structure of crystallization front. The transition will occur at critical values of the crystal growth parameters that are determined from the inequality

$$B + \pi^2\kappa^2\gamma = \frac{1}{2}.\tag{19}$$

It is to note a fundamental distinction of this expression from the formula used to determine the formation conditions of a concentration supercooling zone in a melt [1]. Using our notation, that formula is written as

$$B=1.\tag{20}$$

As will be seen from what follows, the "capillary additive" $\pi^2\kappa^2\gamma \ll 1$ within the range $B\approx1/2$ for real systems. Therefore, if an CSZ arises in the melt at a certain value of parameter $B=B_c$, the cellular structure becomes regular at $B=B_r\approx B_c/2$.

Now we have all the relationships enabling us to forecast within some limits the phase interface structure arising at specific crystallization conditions. The Figure shows the cell half-width L plotted versus the crystallization speed V calculated using (17) under account for (1)-(3) and (10). When plotting, the parameter values were used close to those indicated in [1] for lead containing tin impurity: $k=0.5$, $m=-3$ K/%, $D=10^{-4}$ cm^2/s, $C_0=0.1$%, $T_m=1000$ K, $G=7.5$ K/cm (curves *1, 2*), $G=12$ K/cm (curve *3*) and $G=15$ K/cm (curve *4*). The curve *1* is constructed with no account for capillary forces ($\Gamma=0$ cm), while those were taken into account for curves *2-4* ($\Gamma=10^{-8}$ cm [7]).

It is seen from the Fig.1 that the definition region of the curves is limited by a certain crystallization speed value, $V=V_0$. When the surface energy of phase interface is neglected (curve *1*), the V_0 value coincides with the crystal growth speed V_c corresponding to a CSZ formation in the melt. So, for the curve *1* $V_c=2.5\cdot10^{-3}$ cm/s while for the curve *2*, $V_0=2.83\cdot10^{-3}$ cm/s, and while $L=L_c=0$ cm and $B_\gamma=B_{\gamma c}=1$ correspond to the V_c value, it is $L=L_0=0.0173$ cm and $B_\gamma=B_{\gamma0}=0.922$ that correspond to V_0.

At $V>V_0$, the problem (4)-(7) has two solutions with two branches of the $L(V)$ curve corresponding thereto. In the lower branch of that curve, the B_γ values increase with V while dropping in the upper branch. According to (18), this means that the waves with $L>L_0$ will be more stable than those with $L<L_0$. In both cases, however, those will be damping ones till (according to (19)) the growth speed will exceed a certain value $V=V_r\approx2V_c$ to which $L=L_r$ and $B_\gamma=1/2$ values will correspond. The points in the curves answering to $V=V_r$ and $L=L_r$ are indicated by vertical strokes. For the curve *2*, $V_r=5.01\cdot10^{-3}$ cm/s and $L_r=0.0724$ cm.
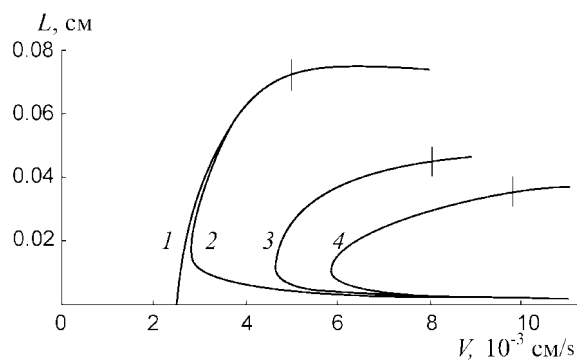
Fig: 1. Dependence of cell half-width L on crystallization speed V at temperature gradient G (K/cm) = 7.5 (*1*, *2*), 12 (*3*) , 15 (*4*) and capillary constant Γ (cm)=0 (*1*), 10^{-8} (*2-4*).

Table: dependence of the phase interface structure on the ratio of temperature gradient G to crystallization speed V predicted by theory and observed in experiment forthe Pb+0.1% Sn system [1].

	V, cm/s	G, K/cm	G/V, K·s/cm²	Phase interfacestructure
Theory	0.005	15	3000	Almost smooth surface (B=1)
	0.006	12	2000	Irregular structure (B=2/3)
	0.0075	7.5	1000	Regular cells (B=1/3)
Experiment	0.00466	15.0	3220	No cells or eruptions
	0.00567	12.0	2120	Irregular eruptions and cells
	0.00835	7.5	900	Regular cells

Comparing the curves *1* and *2* constructed at the same parameter values except for capillary constants (0 and 10^{-8} cm, respectively), it is seen that both curves are essentially merged long before the value B_{γ}=1/2. This points that in the parameter region where the crystallization front structure becomes regular, the surface energy of the phase interface can be neglected.

It is to note that, basing on the theory described here, the irregular violations of the phase interface smoothness cannot be judged, because its periodicity was initially set as the problem condition. It is reasonable to suppose that it is just the inequality 1/2<B<1 that encompasses the region of parameters where the crystal-melt system with an irregular crystallization front structure (chaotically scattered eruptions or bulges) has the least dissipation energy.

The Table summarizes the dependence of the phase interface structure on the G/V ratio predicted using (19) and (20) (see also Figure) as well as that obtained in [1] when growing lead single crystals with tin impurity. The results obtained evidence at least qualitative agreement between the theory and experiment.

The problem of the cell size is of a certain interest. The problem is, however, so extensive that it requires a special consideration.

To conclude this study, the following can be stated. The $L(V)$ dependence plot similar to the curve *1* of the Figure is a kind of phase diagram for the phase interface within the parameter region where no dendrites are still observed. From that diagram, coordinates of two characteristic points can be determined, $V=V_c$ and $V=V_r\approx2V_c$. The first of those corresponds to transition from a smooth phase interface to that with irregular bulges, while the second is related to the transition to periodic structure. While the V_c dependence on the crystallization conditions was studied in many works [2], the similar dependence for V_r has been considered in this work for the first time and mainly due to the used variational method.

References

1. W.A. Tiller, J.W. Rutter, *Can. J. Phys.*, **34**, 96 (1956).
2. W.A.Tiller, Crystal Growth from a Melt, in: The Art and Science of Growing Crystals, John Wiley & Sons,

Inc., New York – London (1963).
3. V.N. Kanischev, *Crystallografiya,* **49**, 1151 (2004).
4. L.V.Kantorovich, V.I.Krylov, Approximate Methods of Higher Analysis, Fizmatgiz, Moscow (1962) [in Russian].
5. V.N.Kanischev, S.V.Barannik, *Functional Materials,* **13**, 558 (2006).
6. V.N.Kanischev, S.V.Barannik, *Crystallografiya,* **51**, 124 (2006).
7. W.W. Mullins, R.F. Sekerka, *J. Appl. Phys.,* **35**, 444, (1964).

Про критерій переходу до регулярної комірчастої структури фронту кристалізації бінарного розплаву

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Варіаційним методом в рамках двовімірної моделі твердіння с урахуванням поверхневої енергії межі рідкої та твердої фаз досліджено ефект утворення регулярної комірчастої структури при кристалізації бінарного розплаву. Показано, що перехід до міжфазної межі з періодично розташованими на ній виступами відбувається при швидкості кристалізації, яка вдвічі перевищує її значення, при якому в розплаві з'являється зона концентраційного переохолодження. Проведено зіставлення результатів обчислення з наявними в літературі експериментальними даними.