OSCILLATORY CRYSTALLIZATION OF A BINARY MELT

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A study is made of slightly nonlinear oscillations resulting from dynamic instability of a steady-state solidification process.

The physical properties of solids are determined to a significant extent by macroscopic irregularities in their structure. The presence of such irregularities depends, in turn, mainly on features of the solidification process by which the material was obtained. Different types of irregularities may be connected with spontaneous oscillatory regimes of crystallization or with the presence of fluctuations in realization of the solidification process (such as with instability of the electrical regime of remelting furnaces, periodic stoppages of the solidification front, fluctuations in ambient temperature, etc.). Occupying a special place is so-called "layered segregation" (a transverse laminated structure), when the composition of the solid changes periodically in the direction normal to the crystallization front. Meanwhile, the form of the layers reflects the configuration of the phase boundary at the moment of their formation. Depending on the technical requirements established for the material, it is desirable either to generally avoid such layering by maximizing the homogeneity of the composition or (as in the production of certain types of semiconductors) to ensure some preassigned properties in the structure (the thickness of the layers, the amplitude of the fluctuations in composition). Thus, it is very important to determine the causes of transverse layered structures and to formulate a physical model which will make it possible to evaluate their characteristics under different conditions and to implement specific measures to obtain structures with specified properties.

In the absence of ordered fluctuations in the external conditions, laminated segregation is usually related to the development of a zone of concentrated supercooling ahead of the crystallization front [1-5]. However, the construction of detailed models is still at the rudimentary stage, and there is as yet no single point of view of the process. We should note two directions being taken in theoretical studies in this area. The first is examination of the generation of an oscillatory crystallization regime as a result of specific features of the two-phase zone ahead of the front, these features in turn being attributable to the morphological instability of the front (see [6], for example). However, in this case one might also expect the appearance of "dendritic" inhomogeneity along individual structural layers — which is far from always actually being the case. The second direction of study focuses on the connection between the formation of the transverse structure and the capacity of a solid solution to layer into isomorphic phases (see [7], for example). However, transverse lamination is also seen in materials which are incapable of such layering.

In most cases, it is natural to regard laminated segregation as the result of the development of dynamic instability of steady-state crystallization in regard to perturbations of the velocity of the front. Randomly occurring small perturbations increase exponentially with time but later stabilize as a result of nonlinear effects. This leads to the establishment of stable fluctuations in velocity which are periodic with a slight degree of nonlinearity. These fluctuations necessarily lead to fluctuations in the diffusion and heat flows, concentration of impurities at the front, and, ultimately the occurrence of transverse lamination.

The first hypothesis on the possibility of instability of this nature was evidently made in [1]. Experimental data on the general character of such instability and considerations on the presence of a direct link between compositional irregularities and front-velocity fluctuations were presented in [5, 8, 9], for example. Proof of the existence of dynamic instability was given in [10]. We note that from the point of view being discussed

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it is not difficult, in principle, to also understand certain important features of how laminated segregation is affected by convective motions in the melt near the crystallization front and several factors which alter the properties of the material (rotation of the crystallization bath, change in the intensity of external body forces, application of an external electromagnetic field, etc.). In fact, convective motions have a significant effect on the magnitude and character of heat and diffusion flows near the front. These flows, in turn, affect the stability of the front.

Below we examine the crystallization of a binary melt occupying an infinite half-space $\xi > \Sigma(\tau)$, where $\Sigma(\tau)$ is dependent on the time coordinate of the crystallization front. Ignoring convection and adopting the simplifying assumption that the density, diffusion coefficient, and thermophysical properties of the melt are independent of its composition, we have the following equations for the concentration of an impurity σ and the temperature θ

$$\frac{\partial\sigma}{\partial\tau} = D\frac{\partial^2\sigma}{\partial\xi^2}, \quad \frac{\partial\theta}{\partial\tau} = a\frac{\partial^2\theta}{\partial\xi^2}, \quad \xi > \Sigma(\tau). \tag{1}$$

For simplicity, we describe heat removal from the front by means of specially introduced constants – the heat-transfer coefficient α and the temperature of an external thermostat θ_ℓ; this allows us to write the condition of heat balance on the front in the same form as in [10]. With increasing distance from the front and toward the center of the melt, the temperature asymptotically approaches the constant value θ_∞. Since heat conduction processes take place in the melt considerably more rapidly than diffusion processes, it will suffice to use a quasisteady representation for the temperature field. In particular, this allows us to examine the heat conduction problem separtely from the diffusion problem. As a result, we have the relation [10]

$$\theta_s = \theta|_{\xi=\Sigma(\tau)} = \left(1 + \frac{\rho C\dot{\Sigma}}{\alpha}\right)^{-1}\left[\theta_l + \left(\theta_\infty + \frac{L}{C}\right)\frac{\rho C\dot{\Sigma}}{\alpha}\right], \tag{2}$$

which connects the temperature on the front with the velocity of the front; henceforth, a superimposed dot denotes differentiation with respect to τ.

With increasing distance from the front the concentration of the impurity approaches a constant value c_∞. We write the equation of mass balance on the front by means of an equilibrium coefficient for the distribution of the impurity between the phases k, i.e.,

$$(1-k)\sigma\dot{\Sigma} + D\partial\sigma/\partial\xi = 0, \quad \xi = \Sigma(\tau). \tag{3}$$

Also, we assume that the dependence of the crystallization temperature on the composition of the melt at the front is known, i.e.,

$$\theta_s = f(\sigma_s), \quad \sigma_s = \sigma|_{\xi=\Sigma(\tau)}, \tag{4}$$

where θ_s is determined from (2). It should be noted that the function $f(\sigma)$ is nonlinear; this is very important for stabilization of the growing perturbations in the instability region and the establishment of a steady oscillatory regime.

The first equation in (1), with the boundary condition at infinity and conditions (3) and (4) on the front, constitutes a problem the solution of which simultaneously determines the concentration field in the melt and the unknown velocity of the front. For a solidification process independent of time, a constant front velocity is easily obtained from (2) and (4):

$$u_0 = \frac{\alpha(\theta_* - \theta_l)}{\rho[L + C(\theta_\infty - \theta_*)]}, \quad \theta_* = f\left(\frac{c_\infty}{k}\right). \tag{5}$$

If the uniform motion of the front with the velocity u_0 is dynamically unstable and if a periodic, nearly harmonic oscillatory regime of motion is established, then the mean velocity u_s is generally not equal to u_0 from (5). With uniform motion of the front at the velocity u_s, the impurity concentration in the melt is described by the function [10]

$$\sigma_0(\tau, \xi) = c_\infty\left\{1 + \frac{1-k}{k}\exp\left[-\frac{u_s}{D}(\xi - u_s\tau)\right]\right\}. \tag{6}$$

In the general case, assuming that the amplitudes of the oscillations of different quantities is small compared to the moduli of their mean values, we take

$$\sigma(\tau, \xi) = \sigma_0(\tau, \xi) + \sigma_1(\tau, \xi), \quad |\sigma_1| \ll \sigma_0, \tag{7}$$

$$\dot{\Sigma}(\tau) = u_s + \dot{\Sigma}_1(\tau),\ |\dot{\Sigma}_1| \ll u_s,\ |u_s - u_0| \ll u_0.$$

Then the concentration of impurity at the front

$$\sigma_s = \sigma|_{\xi=\Sigma(\tau)} = \sigma_0 + \sigma_1 + \left(\frac{\partial\sigma_0}{\partial\xi} + \frac{\partial\sigma_1}{\partial\xi}\right)\Sigma_1 + \frac{1}{2}\left(\frac{\partial^2\sigma_0}{\partial\xi^2} + \frac{\partial^2\sigma_1}{\partial\xi^2}\right)\Sigma_1^2 + \frac{1}{6}\left(\frac{\partial^3\sigma_0}{\partial\xi^3} + \frac{\partial^3\sigma_1}{\partial\xi^3}\right)\Sigma_1^3 + \ldots, \tag{8}$$

where all of the quantities in the right side are evaluated with $\xi = u_S\tau$ and the function $\sigma_0(\tau, \xi)$ is determined from (6). Without any significant loss of generality we can assume that $f(\sigma)$ is quadratic. Thus, from (4) we obtain

$$\theta_s - \theta_* = \frac{mc_\infty(1-k)}{k}\left[-\frac{k\Delta\sigma}{c_\infty(1-k)} + P\frac{k^2(\Delta\sigma)^2}{c_\infty^2(1-k)^2}\right],$$
$$\Delta\sigma = \sigma_s - \frac{c_\infty}{k}, \tag{9}$$

where we have introduced the parameters

$$m = -\left.\frac{df}{d\sigma}\right|_{\sigma=c_\infty/k},\ P = \frac{c_\infty(1-k)}{2km}\left.\frac{d^2f}{d\sigma^2}\right|_{\sigma=c_\infty/k}. \tag{10}$$

We obtain the following from (2) for the deviation of the temperature at the front θ_S from its value θ_* corresponding to motion with a constant velocity

$$\theta_s - \theta_* = \frac{\rho\alpha[L + (\theta_\infty - \theta_l)C](\dot{\Sigma} - u_0)}{(\alpha + \rho Cu_0)(\alpha + \rho C\dot{\Sigma})} = \frac{\rho\alpha[L + (\theta_\infty - \theta_l)C]}{(\alpha + \rho Cu_0)^2} \times$$
$$\times\left\{u_s - u_0 + \left[1 - \frac{\varepsilon(u_s - u_0)}{u_0 + \varepsilon u_s}\right]\left(1 - \varepsilon\frac{\dot{\Sigma}_1}{u_0} + \varepsilon^2\frac{\dot{\Sigma}_1^2}{u_0^2} - \ldots\right)\dot{\Sigma}_1\right\},\ \varepsilon = \frac{\rho Cu_0}{\alpha + \rho Cu_0}. \tag{11}$$

Characteristic values of the quantities entering into the determination of ε are [11]: $\alpha \sim 10^{3,5}\text{-}10^5$ J/m²·sec·°C, $u_0 \sim 10^{-6}\text{-}10^{-5}$ m/sec, $\rho C \sim 10^{5,5}\text{-}10^6$ J/m³·°C. Thus, one usually takes $\varepsilon \sim 10^{-2}\text{-}10^{-3}$. Ignoring terms on the order of ε and higher in (11), we obtain

$$\theta_s - \theta_* = \rho\alpha^{-1}[L + (\theta_\infty - \theta_l)C](u_s - u_0 + \dot{\Sigma}_1). \tag{12}$$

It follows from (1) that the perturbation of concentration σ_1 introduced in (7) should satisfy the diffusion equation with a zero condition at an infinite distance from the front. The boundary condition on the front and the necessary equation for Σ_1 in (7) are obtained by inserting (8) and (12) into (3) and (9). For convenience, we introduce the dimensionless variables:

$$t = \frac{u_0^2}{D}\tau,\ x = \frac{u_0}{D}\xi,\ c_1 = \frac{k}{1-k}\frac{\sigma_1}{c_\infty},\ X_1 = \frac{u_0}{D}\Sigma_1,\ \dot{X}_1 = \frac{\dot{\Sigma}_1}{u_0} \tag{13}$$

and use them in writing and analyzing the above two relations.

Since we are proposing to examine perturbations of relatively small (but finite) amplitude, to obtain the main informative results it will suffice to consider terms no higher than the third order of magnitude with respect to relative amplitudes in these relations [12]. With this degree of accuracy we write the relations in dimensionless variables (13) as follows:

$$-R\dot{X}_1 + \frac{u_s}{u_0}X_1 - c_1 - R\left(\frac{u_s}{u_0} - 1\right) - \frac{1}{2}X_1^2 -$$
$$-\frac{\partial c_1}{\partial x}X_1 + P(c_1 - X_1)^2 + \frac{1}{6}X_1^3 - \frac{1}{2}\frac{\partial^2 c_1}{\partial x^2}X_1^2 + P\left(-X_1^3 + c_1X_1^2 +\right.$$
$$\left. + 2c_1\frac{\partial c_1}{\partial x}X_1 - 2\frac{\partial c_1}{\partial x}X_1^2\right) = 0,\ x = \frac{u_s}{u_0}t, \tag{14}$$

$$\dot{X}_1 + (1-k)\frac{u_s}{u_0}c_1 + \frac{\partial c_1}{\partial x} + k\left(\frac{2u_s}{u_0} - 1\right)X_1 +$$

$$+(1-k)\frac{\partial c_1}{\partial x}X_1-\frac{1}{2}kX_1^2-(1-k)X_1\dot{X}_1+(1-k)c_1\dot{X}_1+$$
$$+\frac{\partial^2 c_1}{\partial x^2}X_1+\frac{k}{6}X_1^3+\frac{1}{2}(1-k)X_1^2\dot{X}_1+(1-k)\frac{\partial c_1}{\partial x}X_1\dot{X}_1+ \tag{15}$$
$$+\frac{1}{2}(1-k)\frac{\partial^2 c_1}{\partial x^2}X_1^2+\frac{1}{2}\frac{\partial^3 c_1}{\partial x^3}X_1^2=0,\ x=\frac{u_s}{u_0}t.$$

The quantity c_1 and its derivatives with respect to x entering into these equations are calculated at $x = (u_s/u_0)t$, i.e., boundary conditions (3) and (9), leading to (14) and (15), are usually "taken down" on a front moving at a constant velocity u_s. In writing (14) and (15) we considered that the quantity $u_3/u_0 - 1$ is of the second order of magnitude, and we introduced the dimensionless parameter

$$R=\frac{\rho\,[L+(\theta_\infty-\theta_l)\,C]\,ku_0}{\alpha\,(1-k)\,mc_\infty}=\frac{(\theta_\infty-\theta_l)\,k}{(1-k)\,mc_\infty}. \tag{16}$$

We represent dimensionless perturbations of the velocity and coordinates of the crystallization front in the form of Fourier expansions:

$$\dot{X}_1=\lambda\sum_{\substack{n=-\infty\\ n\neq 0}}^{\infty} nB_n e^{n\lambda t},\quad X_1=\sum_{\substack{n=-\infty\\ n\neq 0}}^{\infty} B_n e^{n\lambda t},\quad B_{-n}=B_n, \tag{17}$$

in which λ is a certain complex constant. Since Eqs. (17) determine a steady oscillatory regime, then $\mathrm{Re}\,\lambda = 0$. We emphasize that as the unperturbed front we formally examine the motion of a front with the velocity u_s rather than u_0. Thus, for example, the total perturbation of the dimensionless velocity of the front occurring as a result of instability of the solidification process is the sum of the variable part of $\dot{X}_1$ from (17) and the additional "zero" harmonic $u_s/u_0 - 1$ already considered in writing (14) and (15).

Representing $c_1(t, x)$ in the form of a two-layer potential and using the method described in [10], we obtain

$$c_1(t,x)=\sum_{n=-\infty}^{\infty} A_n\left(x-\frac{u_s}{u_0}t\right)e^{n\lambda t},\quad A_{-n}=A_n,$$
$$A_n(y)=A_n\exp\left[-\frac{y}{2}\left(1+\sqrt{1+4n\lambda}\right)\right]. \tag{18}$$

Insertion of expansions (17) and (18) into Eqs. (14) and (15) leads to an infinite system of algebraic equations for the amplitudes A_n and B_n which can, in principle, be solved with an arbitrarily prescribed accuracy. However, Eqs. (14) and (15) themselves are written to within third-order terms for the amplitudes of the first (fundamental) harmonics, which corresponds to analysis of slightly nonlinear, nearly harmonic oscillations established by "mild" disturbance of a steady solidification process occurring with a constant velocity u_0 of the crystallization front. In this case, as can be shown [12], the amplitudes A_n and B_n are proportional to the quantity $q^{n/2}$, where $q = B_1B_{-1}$ is the square of the amplitude of the fundamental harmonic associated with dimensionless perturbation of the front velocity, and $u_s/u_0 - 1 \sim q$. Thus, the above-mentioned system of algebraic equations can be analyzed within the accuracy limits established only by allowing for the terms of order no greater than $q^{3/2}$. The latter requires the retention of only the first two terms with positive and negative n in expansions (17) and (18). As a result, from (14), (15), (17), and (18) we obtain a system of only six algebraic equations to determine A_n and B_n with n = 1, 2 and A_0 and $u_s/u_0 - 1$. We omit the system here due to its awkwardness. We note that the slightly nonlinear, nearly harmonic oscillatory regimes of solidification of the type examined here are very common in experimental and commercial practice (see [1, 13-15], for example).

In a linear approximation, the above-noted system of six equations reduces to two linear homogeneous algebraic equations for A_1 and B_1. The condition of the existence of a nontrivial solution for these equations determines the curve of neutral stability R = 0 obtained earlier in [10] (the region of instability corresponds to R > 0). Also, from here we obtain the linear relation

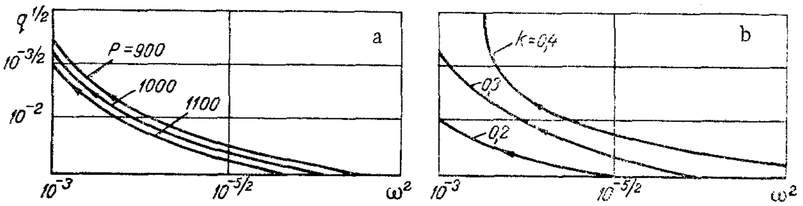

Fig. 1. Dependence of the amplitude of oscillations of crystallization-front velocity on frequency: a) k = 0.3; b) P = 1000. The arrow indicates the direction of the increase in the parameter R.

$$A_1 = (1+\varphi)B_1,\quad \varphi(\lambda,\,k) = \frac{2\lambda+1-\sqrt{1+4\lambda}}{2k-1+\sqrt{1+4\lambda}}, \tag{19}$$

which, with the same accuracy as noted above, can be used in modifying several of the nonlinear terms in the system of six equations mentioned previously. Here, we have the following relations from four of the equations of this system corresponding to the zeroth and second harmonics:

$$\begin{gathered} A_0 = \left\{-1+2\,\mathrm{Re}\left[(1+\varphi)\left(\frac{\gamma^2}{k}-\frac{1-k}{k}\lambda-\frac{1-k}{k}\gamma\right)\right]\right\}q, \\ B_0 = \frac{u_s}{u_0}-1 = \frac{1}{R}\{-A_0-(1-2P|\varphi|^2)\,q+ \\ +2\,\mathrm{Re}\,[(1+\varphi)\,\gamma q]\},\quad \gamma(\lambda) = (1/2)\,(1+\sqrt{1+4\lambda}), \end{gathered} \tag{20}$$

as well as

$$\begin{gathered} A_2 = \frac{1}{\Delta}\left\{(1-2R\lambda)\left[\frac{k}{2}-(1-k)\,\lambda\varphi+(1+\varphi)\,(1-k-\gamma)\,\gamma\right]-(k+2\lambda)\,[1/2-(1+\varphi)\,\gamma-P\varphi^2]\right\}q, \\ B_2 = \frac{1}{\Delta}\{(1-k-\gamma')\,[1/2-(1+\varphi)\,\gamma-P\varphi^2]+k/2-(1-k)\,\lambda\varphi+(1+\varphi)\,(1-k-\gamma)\,\gamma\}\,q,\quad \gamma' = \gamma(2\lambda), \\ \Delta = 2\lambda+1+2\,(1+k)\,R\lambda-(1+2R\lambda)\,\gamma'. \end{gathered} \tag{21}$$

Inserting (20) and (21) into the remaining two equations of the system (for the amplitudes of the first harmonic), we again obtain a system of two homogeneous equations for A_1 and B_1. This system is linear if we regard the value of q, on which depends the coefficients of the equations, as fixed. In this case, we take the condition of existence of a nontrivial solution in the form

$$\begin{gathered} R\gamma\lambda+kR\lambda-R\lambda+1+\lambda-\gamma+B_0\,(2-R\lambda-\gamma)+A_0[(1-k)\,\lambda+1-\gamma]+ \\ +B_2\,[\gamma-1-\gamma\gamma^*\,(\varphi^*+1)+2\,(1-k)\,\lambda\varphi^*+(1-k)\,\lambda+(\gamma^2)^*\,(\varphi^*+1)]+ \\ +A_2\,[\gamma'^2-\gamma\gamma'-(1-k)\,\lambda]+q\left[\frac{(\gamma^2)^*\gamma}{2}\,(\varphi^*+1)+\right. \\ \left.+\frac{1-\gamma+(1-k)\,\lambda}{2}-(1-k)\,\lambda\gamma^*\,(\varphi^*+1)-\frac{(\gamma^3)^*}{2}\,(\varphi^*+1)\right]+ \\ +2P\,(1-k-\gamma)\left[A_0\varphi+A_2\varphi^*-B_2\varphi+2q\,(\varphi+1)\,\gamma+q\,(\varphi^*+1)\,\gamma^*+\right. \\ \left.+\frac{q}{2}\,(\varphi+\varphi^*/2)-q\,(\varphi+1)\,(\varphi^*+1)\,(\gamma+\gamma^*)-q\gamma\,(\varphi+1)^2\right]=0, \end{gathered} \tag{22}$$

where the quantities A_0, B_0, A_2, and B_2 are determined in (20) and (21), respectively, and the asterisk above a quantity denotes complex conjugation.

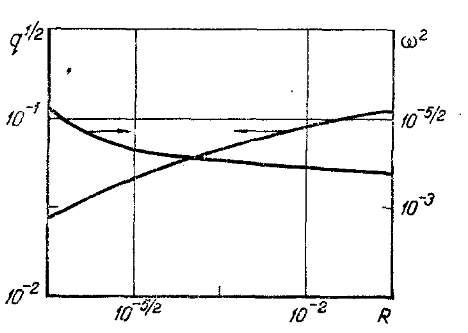

Fig. 2

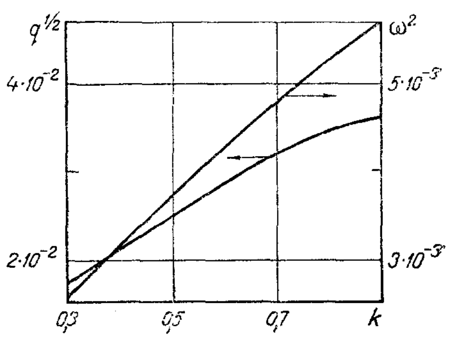

Fig. 3

Fig. 2. Dependence of the amplitude of oscillations of crystallization-front velocity and the square of the frequency on the parameter R ($P = 10^3$, $k = 0.5$).

Fig. 3. Dependence of the amplitude of oscillations of crystallization-front velocity and frequency on the parameter k ($P = 5\cdot10^2$, $R = 10^{-2}$).

Complex equation (22) is equivalent to two real equations and completely determines the possible regimes of slightly nonlinear oscillation – their amplitude characteristic q and frequency $\omega = \text{Im}\,\lambda$.

Satisfaction of the conditions $q > 0$ and $q \ll 1$ is connected with the existence of a "mild" type of instability and so-called aperiodic bifurcation of the steady solidification regime. The amplitude of the oscillations increases with increasing depth into the region of instability $R > 0$ [10]. At $q < 0$, stability is disturbed in a "severe" manner, and no nearly harmonic crystallization regime is formed.

Usually in actual systems $\omega \sim 10^{-2}$-10^2 [16, 17]. For simplicity, below we look at the example of a low-frequency oscillation ($\omega \ll 1$, $\omega \ll k$). In this case, we have the following from (20) and (21) for the coefficients with the harmonics with numbers n = 0.2

$$A_0 \approx q,\ B_0 \approx 2PR^{-1}\omega^4k^{-2}q,\ A_2 = \frac{q}{2} - P\frac{\omega^2}{4k}q,$$
$$B_2 = -P\frac{\omega^2}{4k}q,\ A_2 - B_2 \approx q\left(\frac{1}{2} + i\omega\right). \tag{23}$$

In Eqs. (23) we considered terms of the order q in the real part and of the order $q\omega$ in the imaginary part. The indicated accuracy is determined by Eq. (22). Terms of the order $q\omega$ are omitted from the expressions for A_2 and B_2, since the quantities A_2 and B_2 enter only into expressions of the types $A_2\omega$ and $B_2\omega$ after picking out the difference $A_2 - B_2$ in Eq. (22).

Expanding the radicals in (22) into series in small ω and separating the real and imaginary parts, we obtain

$$2P\omega^2q = Rk^2,\quad Rk + \omega^2 - Pq\omega^2k^{-2}(2k+1)(P\omega^2 - 2k) = 0. \tag{24}$$

For the squares of the amplitude and frequency from (24) we obtain

$$\omega^2 = \frac{4kR(1+k)}{PR(2k+1)-2},\quad q = \frac{[PR(2k+1)-2]\,k}{8P(1+k)}. \tag{25}$$

The conditions for realization of oscillations take the form

$$0 < R \ll 1,\ PR > 2(2k+1)^{-1}. \tag{26}$$

As follows from (10), the second condition in (26) means that the liquidus should be concave and that its curvature should be fairly great. The dependence of the amplitude and frequency on the parameters R, P, and k is shown in Figs. 1-3. Figure 1 shows the decrease in the amplitude of oscillations of crystallization-front velocity with an increase in frequency, which was noted in [18]. It is apparent (Fig. 2) that an increase in R is accompanied by an increase in the amplitude of the oscillations. The parameter R is directly proportional to the crystallization rate u_0 (see Eq. (16)), so that an increase in u_0 leads to an increase in the amplitude of front velocity oscillations and the impurity content of the liquid and solid phases. This fact was also noted in several experimental studies [15, 19, 20]. An increase in the rate of heat removal from the front (which means an increase in the effective heat-transfer coefficient α) with a constant velocity u_0 entails an increase in the temperature gradient in the liquid phase, which leads to a decrease in supercooling and oscillation amplitude. This follows from Fig. 3 and from the fact that the parameter is inversely proportional to R.

After calculations, we have the following for the velocity of the crystallization front and the impurity distribution along a single crystal

$$\begin{gathered} u = u_0\left[1 + \omega^2 - 2\omega q^{1/2}\sin\omega t + P\omega^3 q k^{-1}\sin 2\omega t\right], \\ \sigma_* = c_\infty(1-k)\left[\frac{1}{1-k} + 2q\cos\left(\frac{2u_0^2\omega l}{u_s D}\right)\right], \end{gathered} \tag{27}$$

where ℓ is the distance along the single crystal reckoned from an arbitrary coordinate, where $\sigma_* = c_\infty$. It should be noted that at $\omega \ll 1$ the coefficient with the first harmonic in the expression for σ_* is small, and the corresponding term can therefore be ignored.

The parameter $P > 0$, so that $u_s > u_0$, i.e., when an oscillatory crystallization regime develops, the mean rate of crystallization increases for an arbitrary small value of dimensionless frequency ω.

Regular periodic oscillations of impurity concentration in the case of crystallization with a planar front have been noted in numerous studies [1, 13-15, 18-25]. However, most of them contain inadequate or no information on the temperature conditions of the experiments, the coefficients of impurity distribution k, or other physicochemical parameters. Also, the final results presented above are valid only for $\omega \ll 1$, while obtaining similar results for arbitrary ω would require very cumbersome numerical calculations. Such calculations may be the subject of a special study. None of this permits a more detailed comparison to be made with the results of specific experiments. However, it is clear that allowing for the nonlinearity of Eq. (4) gives essentially new information on the process in question.

NOTATION

a, diffusivity in the melt; A_n, B_n, amplitudes of n-th harmonic asociated with perturbation of impurity concentration and coordinate of crystallization front; c_1, dimensionless perturbation of concentration; C, specific heat of melt; D, diffusion coefficient of melt; k, equilibrium coefficient of impurity distribution; m, parameter introduced in (10); L, heat of phase transformation; P, R, parameters introduced in (10) and (16), respectively; q, square of amplitude of fundamental harmonic B_1; t, dimensionless time; u, velocity of crystallization front; u_s, mean velocity of front; x, dimensionless coordinate; X_1, dimensionless perturbation of coordinate of front; α, heat-transfer coefficient; γ, Φ, functions introduced in (20) and (19), respectively; ε, parameter introduced in (11); θ, temperature; θ_ℓ, θ_*, temperature of external thermostat and temperature on a crystallization front moving at a velocity u_0; λ, parameter introduced in (17); ξ, coordinate; ρ, density of melt; σ, σ_1, concentration and perturbation of concentration in melt; σ_*, concentration of impurity in crystal; Σ, Σ_1, coordinate of crystallization front and its perturbation; τ, time; ω, frequency. Indices: 0 pertains to characteristics of a steady-state regime of solidification with the velocity u_0; ∞ pertains to characteristics away from the crystallization front; s pertains to quantities determined on the phase boundary; a superimposed dot denotes differentiation with respect to dimensionless time; an asterisk above a quantity denotes the operation of complex conjugation.

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