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MODEL OF A NONEQUILIBRIUM TWO-PHASE ZONE TAKING INTO ACCOUNT CONVECTION OF A BINARY MELT

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A mathematical model of a two-phase dendrite zone was constructed in [1, 2] for nonequilibrium crystallization of a binary melt. In this case, the change in the density of the melt in the phase transformation process was neglected and the melt was assumed to be stationary. It is evident that when a crystal grows, as a result of settling phenomena, a flow of the liquid phase, oriented toward the crystal, must exist in the melt. This effect was examined in [3, 4] for crystallization of pure metals. It is shown therein that the flows of the melt arising affect the temperature and pressure field in the liquid phase. In the process of nonequilibrium crystallization of a binary melt, these flows will also affect the distribution of the admixture in the liquid phase and, therefore, the structure of diffusion overcooling as well. Since the kinetics of the growth and morphology of dendrites in the two-phase zone are determined by overcooling of the melt, this effect will affect the development of the two-phase zone as a whole, as well as the nature of the chemical inhomogeneity and formation of porosity in the ingot.

In what follows, based on phenomenological assumptions, we formulate a mathematical model of heat and mass transfer processes in the two-phase zone of a solidifying binary alloy taking into account the kinetics of growth of dendrites and the density discontinuity along the phase separation surface.

Let us examine directed crystallization of a binary melt in the presence of a two-phase zone. The scheme of the physical model is illustrated in Fig. 1. We assume that the two-phase zone consists of homogeneous dendrites with a column ($\nu = 1$) or plate ($\nu = 0$) form, while their growth velocity along the normal to the surface of the crystal is an exponential function of the local overcooling ΔT:

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$$v_n = K(\Delta T)^m. \tag{1}$$

Based on this relation, equations are obtained in [2] for the kinetics of the three-dimensional growth of dendrites, which, taking into account the effect of the change in local values of the pressure p and the dynamic head $p_v = \rho\varepsilon^2 v_n^2/2$ on the temperature of the liquidus, take the form [for y = R(x, t)]

$$R'_t = K\sqrt{1 + R'^2_x}\,[T_l(C)(1 + p_\Sigma/\varkappa_0\rho_s) - T]^m, \quad p_\Sigma = 2^\nu\sigma k_r + \varepsilon\Delta p - p_v; \tag{2}$$

$$\xi'_{ft} = K_0\,[T_l(C)(1 + p_\Sigma/\varkappa_0\rho_s) - T]^{m_0}_{x=\xi_f}, \quad 2^\nu k_r = R''_{xx}/\omega^3 - \nu/R\omega,$$
$$\omega = \sqrt{1 + R'^2_x}, \tag{3}$$

where 2R is the transverse size of the dendrite; σ is the surface tension; k_r is the average local curvature of the dendrite surface; $\varkappa_0$ is the latent heat of fusion; ρ_s and ρ are the densities of the solid and liquid phases, respectively; C is the concentration of the dissolved mixture; $T_l(C)$ is the equilibrium temperature of the liquidus with $p_\Sigma \equiv 0$; $\xi_f(t)$ is the coordinate of the front of the two-phase zone; K and K_0 are kinetic constants; $\varepsilon = (\rho_s - \rho)/\rho$; the prime indicates a derivative with respect to the lower index.

Equations (2) and (3) depend on the local values of temperature, concentration, and pressure, which are determined by the equations of convective heat and mass transfer in the liquid phase

$$c\rho(\partial T/\partial t + \mathbf{v}\nabla T) = \mathrm{div}(\lambda\nabla T); \tag{4}$$
$$\partial C/\partial t + \mathbf{v}\nabla C = \mathrm{div}(D\nabla C); \tag{5}$$

by the equations of thermal conductivity and diffusion in the solid phase

$$c\rho\partial T/\partial t = \mathrm{div}(\lambda\nabla T); \tag{6}$$
$$\partial C/\partial t = \mathrm{div}(D\nabla C); \tag{7}$$

and by the Navier–Stokes and continuity equations for an incompressible fluid

$$\rho[\partial\mathbf{v}/\partial t + (\mathbf{v}\nabla)\mathbf{v}] = -\nabla p + \mathrm{div}\,\tau + \rho\mathbf{g}, \quad \tau = \mu[\nabla\mathbf{v} + (\nabla\mathbf{v})^T]; \tag{8}$$
$$\mathrm{div}\,\mathbf{v} = 0, \tag{9}$$

where $\mathbf{v} = \{u, w\}$ is the velocity vector of the melt; τ is the viscous stress tensor; $(\nabla\mathbf{v})^T$ is the transposed dyad; **g** is the acceleration of gravity vector; λ, c, D, and μ are the coefficients of thermal conductivity, heat capacity, diffusion, and viscosity, respectively, assumed to be independent of temperature. Since the two-phase zone is assumed to consist of uniform dendritic cells, it is sufficient to find the solution in the region $\Omega \in [0 \leqslant x < \infty,\ 0 \leqslant y \leqslant d/2]$ with appropriate initial and boundary conditions, as well as the balance relations along the phase separation boundary y = R(x, t):

$$\lambda\frac{\partial T}{\partial n}\bigg|_{y=R-0} - \lambda\frac{\partial T}{\partial n}\bigg|_{y=R+0} = \varkappa_0(1 + \varepsilon)\rho v_n; \tag{10}$$
$$D\frac{\partial C}{\partial n}\bigg|_{y=R-0} - D\frac{\partial C}{\partial n}\bigg|_{y=R+0} = (1 - k + \varepsilon)v_n C|_{y=R+0}; \tag{11}$$
$$u\sin\alpha + w\cos\alpha = -\varepsilon v_n, \tag{12}$$

where d is the distance between the initial axes of the dendrites; $\partial/\partial n$ is the derivative along the normal **n**; α is the angle between the normal **n** and the y axis (see Fig. 1).

In order to close the system of equations presented above, it is necessary to determine the quantity d. Experimental and theoretical studies [5, 6] indicate that the interdendritic distance d depends on the product of the temperature gradient G along the crystallization front in the melt and the crystallization velocity v. This dependence has the form

$$d = b(Gv)^{-s}, \tag{13}$$

where $0 \leq s \leq 0.5$; b is some constant, characteristic for the melt being studied. For this reason, in what follows, we will assume for d a dependence of the form (13), taking G and v to mean the temperature gradient in the melt along the front of the two-phase zone and the velocity of the front, respectively, at the time $t = t_0$ taken as the initial time, for which the condition of stability of the two-dimensional front [5] is no longer satisfied. In this case, the change in the density of dendrites $n_0 = 2^{2\nu}/\pi^\nu d^{1+\nu}$ due to the appearance of new dendrites or suppression of existing dendrites is not taken into account.

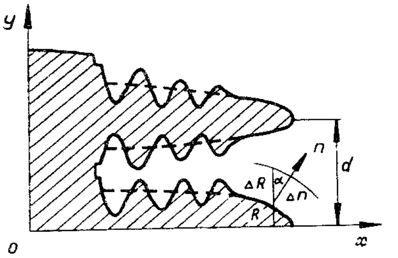

Fig. 1

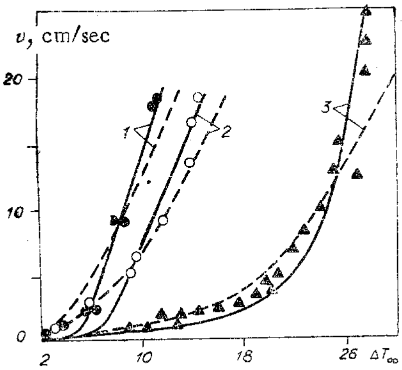

Fig. 2

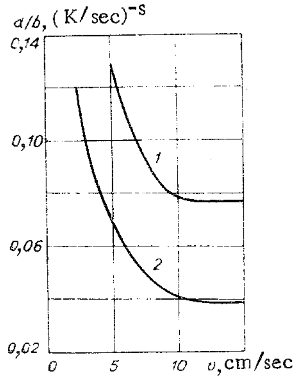

Fig. 3

The model constructed describes dynamic phenomena in the two-phase zone: kinetic growth of dendrites, microsegregation of impurities, change in temperature, diffusion overcooling, and pressure fields in the dendritic cell, which permits studying theoretically the formation of the initial structure and chemical and physical inhomogeneities with crystallization of binary melts. The equations obtained represent a system of two-dimensional nonlinear partial differential equations with complicated boundary conditions whose solution involves well-known mathematical difficulties. For most real processes of crystallization of ingots, an extended dendritic two-phase zone is characteristic. The distance between the axes of the dendrites is usually 10-100 μm. For this reason, for a macroscopic investigation, it is useful to average Eqs. (4)-(9) over the cross section of a dendritic cell, taking into account conditions (10)-(12) and the symmetry conditions for y = 0 and y = d/2. In carrying out the averaging, we will assume that the extent of the zone L greatly exceeds the size of a cell (L ≫ d), while the average magnitudes of the concentration in the solid C_1 and liquid C_2 phases are related to each other just as the distributed quantities on the phase separation boundary ($C_1 = kC_2$). Due to the continuity of temperature on transition through the phase boundary, its average value in the solid and liquid phases must be equal ($T_1 = T_2$). Carrying out the necessary computational steps, we write the equations obtained in the form

$$c_V \frac{\partial T}{\partial t} + c_{V_2} S u \frac{\partial T}{\partial x} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T}{\partial x}\right) + \varkappa_0 (1+\varepsilon) \rho \frac{\partial \Psi}{\partial t}; \tag{14}$$

$$\frac{\partial}{\partial t}[(k\Psi + S) C] + \frac{\partial}{\partial x}(SuC) = \frac{\partial}{\partial x}\left(D \frac{\partial C}{\partial x}\right); \tag{15}$$

$$\rho\left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x}\right) = -\frac{\partial p}{\partial x} - \frac{\mu}{K_p(S)} u + 2 \frac{\partial}{\partial x}\left(\mu \frac{\partial u}{\partial x}\right); \tag{16}$$

$$\varepsilon \frac{\partial S}{\partial t} = \frac{\partial}{\partial x}(uS), \tag{17}$$

where $\Psi = (2R/d)^{1+\nu}$, $S = 1 - \Psi$ are the cross section of the solid and liquid phases, respectively; $c_V = c_1\rho_1\Psi + c_2\rho_2 S$; $c_{V_2} = c_2\rho_2$; $\lambda = \lambda_1\Psi + \lambda_2 S$; $D = kD_1\Psi + D_2 S$. In deriving Eq. (16) from (8), we assumed that the viscous friction force is proportional to the averaged velocity of the melt in the dendritic cell, which corresponds to the assumption that Reynolds number Re is small. It is possible to make such an assumption, since the flow velocity of the melt in the zone is not high ($|u| \sim \varepsilon v$ and for $v = 10^{-3}$ m/sec, $\varepsilon \sim 0.1$, $d \sim 10^{-4}$ m, $\nu \sim 10^{-6}$ m^2/sec, Reynold's number is $Re = |u| d/\nu \sim 10^{-2}$). It can also be shown that the terms on the left and the third term on the right of the equal sign in (16) can be neglected compared to the second term and Eq. (16) can be written in the form of Darcy's law $u = -[K_p(S)/\mu](\partial p/\partial x)$, used in studying transport phenomena in capillary-porous media, where $K_p(S)$ is the permeability of the two-phase zone, which depends on its structure [7, 8]. Equations (14)-(17) together with (2), (3), and (13) describe the macroscopic transport phenomenona and the growth kinetics of dendrites with directed crystallization of the melt. For a macroscopic analysis of processes occurring in the two-phase zone, in the first approximation it is possible to neglect the effect of pressure and curvature on the temperature of the liquidus, while Eqs. (2) and (3) can be represented in the form

$$S'_t = -K\left[\frac{4(1+\nu)^2}{d^2}(1-S)^{2\nu/(1+\nu)} + (S'_x)^2\right]^{1/2} [T_l(C) - T]^m,$$
$$x \in [\xi_s, \xi_f]; \tag{18}$$

$$\xi'_{ft} = K_0 [T_l(C) - T]^{m_0}_{x=\xi_f}. \tag{19}$$

In the general case of three-dimensional crystallization, we will examine the two-phase zone as a dispersed medium, consisting of a heterogeneous mixture of crystals with a plate-like ($\nu = 0$) or cylindrical ($\nu = 1$) form, growing in an overcooled melt. In order to obtain the macroscopic equations, in this case, it is necessary to average the three-dimensional transport equations in a small volume of the two-phase zone, whose linear size is much greater than the characteristic size of the crystal cell, but much less than the extent of the two-phase zone. The balance relations (10)-(12) must be taken into account, as above, along the phase separation surface. As a result of such averaging, we obtain the macroscopic equations of convective heat and mass transfer with nonequilibrium crystallization of a binary melt:

$$c_V \frac{\partial T}{\partial t} + c_{V_2} S (\mathbf{v}\nabla) T = \operatorname{div}(\lambda \nabla T) - \varkappa_0 (1+\varepsilon) \rho \frac{\partial S}{\partial t}; \tag{20}$$

$$\frac{\partial}{\partial t}\{[k + (1-k) S] C\} = \operatorname{div}(D\nabla C - S\mathbf{v}C); \tag{21}$$

$$\begin{gathered} \rho\left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}\nabla)\mathbf{v}\right] = -\nabla p - \frac{\mu}{K_p(S)}\mathbf{v} + \operatorname{div}\tau, \\ K_p(S) = \infty \quad \text{for} \quad S = 1; \end{gathered} \tag{22}$$

$$\varepsilon \frac{\partial S}{\partial t} = \operatorname{div}(S\mathbf{v}), \quad S \equiv 1 \quad \text{for} \quad x \geqslant \xi_f, \quad S \equiv 0 \quad \text{for} \quad x < \xi_s. \tag{23}$$

Using Kozeni's theory [9], we find that $K_p = a_k^{-2\nu}(d/2\varphi)^2 S^3/(1-S)^{\alpha}$, where $\alpha = \nu(2-\nu)$, φ is the ratio of the surface area of a real dendrite to the surface area of the crystal being examined, and a_k is Kozeni's constant.

Equation (22) is a superposition of Darcy's law and the equation for viscous flow of an incompressible fluid and can be used over a wide range of variation of the coefficient of permeability of the zone. The system (20)-(23) is closed by Eq. (18), while relation (19) now takes the form $\xi'_{ft}/\sqrt{1 + \xi'^2_{fy} + \xi'^2_{fz}} = K_0(\Delta T)^{m_0}|_{x=\xi_f(t,y,z)}$. The well-known equations for a quasiequilibrium two-phase zone, taking into account hydrodynamic processes, follow from the system of equations obtained in [8], if the diffusion in the solid phase ($D_1 \equiv 0$) and overcooling in the zone ($\Delta T \equiv 0$) are neglected, while Eq. (22) is written in the form of Darcy's law. An exception is Eq. (21), which differs from the corresponding equation in [8] by the presence of the term $k(1-S)\partial C/\partial t$ and for $\mathbf{v} \equiv 0$ coincides with the equation of mass transfer obtained in [10].

In order to compare the theoretical results following from the model proposed with well-known experimental data, we examine the problem of directed crystallization of an overcooled binary melt for the case of constant velocity of the zone. Under certain simplifying assumptions [2], the solution of the problem can be represented in analytic form, establishing a dependence between the crystallization velocity v and the overcooling of the melt Θ_∞, as well as between the size of the dendritic cell d and the velocity v. In terms of dimensionless quantities, these dependences have the form

$$\begin{gathered} B(\Theta_\infty - v)^s v^{2s} + v(2\Theta_\infty - v) - \sqrt{[B(\Theta_\infty - v)^s v^{2s} - v^2]^2 + 4B\gamma(\Theta_\infty - v)^s v^{2(1+s)}} = 0, \\ d = [b_1(\Theta_\infty - v)^s v^{2s}]^{-1}, \end{gathered} \tag{24}$$

where $B = A\beta(1-k)b_1$; $v \to v/K_0 T_{l0}$; $\Theta_\infty = (T_{l0} - T_\infty)/T_{l0}$; $b_1 = (aT_{l0})^s/b(K_0 T_{l0}/a)^{1-2s}$; $\beta = (T_A - T_{l0})/T_{l0}$; $\varkappa = \varkappa_0/cT_{l0}$; $\gamma = 1 + \varkappa_0/\beta(1-k)$; and $A = K/K_0$.

A comparison of theory with experimental data obtained for binary alloys Sn + 2% Bi (by weight), Sn + 0.5% Bi (by weight) [11] (curves 1, 2, respectively), and Ga + 2% In (by weight) [12] (curve 3) is presented in Fig. 2. The physical parameters were set according to [13, 14]. The value of the kinetic coefficient K_0 was assumed equal to 2, 1.6, and 5 for the first, second, and third alloys, respectively. The parameter B was determined from one of the points corresponding to the experimental curve.

In the region with high overcooling ($\Delta T_\infty > \Delta T^*_\infty$, where $\Delta T_\infty = T_{l_0} - T_\infty$), the theoretical curves calculated for s = 0 (solid lines) agree well with experiment. For low overcooling ($\Delta T_\infty < \Delta T^*_\infty$), curves corresponding to the value s = 1/3 (dashed lines) agree better with experiment. From here, it may be concluded that for low overcooling of the melt (low crystallization velocities), the cell size d depends both on the state of the melt and on the rate of cooling according to Eq. (13). For high overcooling [$\Delta T_\infty > \Delta T^*_\infty$, $v > v^*(\Delta T^*_\infty)$], the quantity d is mainly determined by the state of the melt. The dependence v on ΔT_∞ for $\Delta T_\infty \to \infty$ approaches a linear dependence and is determined by the equation $v = K_0 \Delta T_\infty$.

In studying the dependence of the interdendritic distance on the crystallization velocity defined by Eqs. (24), it is convenient to represent this expression in the form d/b_1, which does not contain the empirical constant b_1, depending on the state of the melt. Figure 3 illustrates this dependence (in dimensional quantities) for the alloys Sn + Bi (curve 1) and Ga + In (curve 2). In accordance with the preceding conclusion, the index s was chosen as s = 1/3 for $v \leq 10$ and s = 0 for $v > 10$, where v is in cm/sec. As is evident from the graphs, the quantity d rapidly decreases in the interval $0 \leq v < 10$ and then assumes some finite value, corresponding to the rapid (kinetic) stage in the growth of dendrites. The decrease in d with an increase in v agrees qualitatively with experimental data [5, 15] on the reduction of the structure of the solidified alloy with increasing crystallization velocity.

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