ANALYSIS OF HEAT AND MASS TRANSFER PROCESSES IN GROWING CRYSTALS BY THE ZONE-MELTING METHOD

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One of the disadvantages of papers devoted to the investigation of heat and mass transfer processes during crystal growth by numerical methods (see [1, 2], e.g.) is that the melting point is assumed independent of the phase composition. Therefore, the model of crystallization of a single-component melt was used in studying the solidification of binary alloys. At the same time, the construction of models for growing technologically important crystalline materials requires taking account of all fundamental heat and mass transfer processes governing the influence of inhomogeneity of the composition distribution in the liquid phase on the curvature of the phase interfacial boundary (see [3], say).

The aim of this paper is to construct a method for solving the thermodiffusion problem of solidification of a two-component melt under conditions when no two-phase zone is formed. The method is expounded in application to the axisymmetric problem of zone melting of PbTe, which has a stationary solution permitting utilization of the built-up method to obtain it.

The influence of natural convection on the zone shape and the component temperature and concentration distribution in the melt for different values of the acceleration of gravity is studied in the example of this problem.

The heat conduction equation for the temperature normalized by the maximal temperature on the ampul side surface $T_m = 1073°K$ is solved in the liquid and solid phases while the Navier–Stokes equation in stream function ψ–vortex function ω variables and the diffusion equation for the tellurium concentration are examined just in the liquid phase (the solid phase has the stoichiometric composition PbTe). The ratio between the heat conduction coefficients of the solid and liquid phases is given as $\lambda_s/\lambda_l = 0.203$, of the specific heat as $c_s/c_l = 0.357$, and of the densities as $\rho_s/\rho_l = 1$.

1. In a reference system connected with the heater moving at a velocity $V = 0.55 \cdot 10^{-7}$ m/sec along the z axis in a cylindrical (r, z) coordinate system ($r \in [0, 1]$, $z \in [-L, L]$), and with axial symmetry taken into account, the equations have the form

$$\rho_k c_k \frac{\partial T}{\partial t} + \rho_k c_k (\mathbf{v}\nabla) T = \frac{1}{\mathrm{Pr}} \operatorname{div} (\lambda_k \operatorname{grad} T) \quad k = s, l; \tag{1.1}$$

$$\frac{\partial c}{\partial t} + \operatorname{div} (c\mathbf{v}) = \frac{1}{\mathrm{Sc}} \operatorname{div} \operatorname{grad} c; \tag{1.2}$$

$$\frac{\partial \omega}{\partial t} + \frac{\partial (u\omega)}{\partial r} + \frac{\partial (v - V)\omega}{\partial z} = \Delta\omega + \mathrm{Gr}\,(\mathbf{g} \times \operatorname{grad} T); \tag{1.3}$$

$$\Delta\psi = -\omega; \tag{1.4}$$

$$u = -\frac{\partial \psi}{\partial z}; \tag{1.5}$$

$$v = \frac{1}{r} \frac{\partial (r\psi)}{\partial r}. \tag{1.6}$$

In the solid phase the vector $\mathbf{v} = (0, -V)$, in the liquid $\mathbf{v} = (u, v - V)$, u, v are projections of the melt flow velocity vector on the r and z axes, respectively, the operator Δ is the Laplacian of the vector function, $\mathbf{g}$ is a unit vector parallel to the free-fall acceleration vector.

The characteristic Prandtl, Schmidt, and Grashof numbers are selected equal to $\mathrm{Pr} = \nu\rho_l c_l/\lambda_l = 0.025$, $\mathrm{Sc} = \nu/D = 13$, $\mathrm{Gr} = \beta g R^3 T_m \nu^{-2}$, $0 \leqslant \mathrm{Gr} \leqslant 1.86 \cdot 10^6$.

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The problem (1.1)-(1.6) is solved with the following boundary conditions:

1) On the axis of symmetry Γ_1 (Fig. 1)

$$\partial T/\partial r = 0,\ \partial c/\partial r = 0,\ \psi = 0,\ \omega = 0;$$

2) On the ampul side surface Γ_2

$$\partial c/\partial r = 0,\ \psi = 0,\ \partial\psi/\partial r = 0,\ T = 1 - \gamma|z|,$$
$$\text{where } \gamma = \begin{cases} RG/T_m, & z < 0, \\ -RG/T_m, & z > 0, \end{cases} \quad G = 80\ ^\circ\text{K/cm};$$

3) On the interphasal surfaces Γ_3 and Γ_4 given by the equations $z_1 = z_1(r)$ and $z_2 = z_2(r)$, component mass and energy conservation conditions are realized

$$\partial c/\partial n = -(1 - m)\,\mathrm{Sc}\,(V + v_i)_n c,\ v_{in} = k(c - c_{li}) - V_n, \tag{1.7}$$
$$\lambda_s \partial T/\partial n - \partial T/\partial n = \mathrm{St}\,(V + v_i)_n,\ i = 1, 2,\ 0 \leqslant r \leqslant 1,\ z = z_i(r),$$
$$\psi = 0,\ \partial\psi/\partial n = 0,$$

where the dimensionless parameter is $\mathrm{St} = \rho_l \varkappa v / T_m \lambda_l$; $\varkappa$ is the specific heat of crystallization, m is the distribution coefficient, v_i is the velocity of phase interface motion in a reference system connected to the heater, c_{li} is the equilibrium concentration determined by the equilibrium phase diagram $c = \varphi(T)$. Quantities with the subscript n denote the projections of their corresponding vectors on the interior normal to Γ_3, Γ_4;

4) On Γ_5 conditions are posed only for (1.1) and have the form

$$\partial T/\partial z = \gamma \text{ for } r \in [0, 1],\ z = -L \text{ and}$$
$$\partial T/\partial z = -\gamma \text{ for } r \in [0, 1],\ z = L.$$

Therefore, the basic distinction of the proposed formulation of the problem is the utilization of the kinetic condition (1.7) in place of giving the equilibrium phase diagram on the crystallization front $c_i = c_{li} = \varphi(T)$, $r \in [0, 1]$, $z_i = z_i(r)$, $i = 1, 2$. By applying an iteration build-up method, this permits modeling the motion of the phase interfaces.

Condition (1.7) affords the possibility of investigating nonstationary and kinetic growth regimes by using kinetic phase diagrams in (1.7) to obtain m. The solution of problems close to equilibrium is obtained as the limit of solutions of nonequilibrium problems for low growth rates ($k \to \infty$ and $c \to c_l$ on the interphasal boundary).

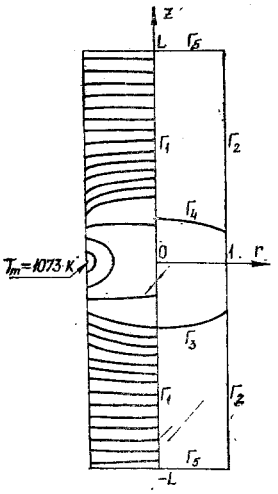

Fig. 1

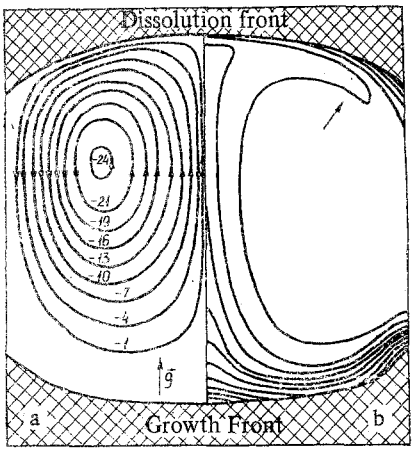

Fig. 2

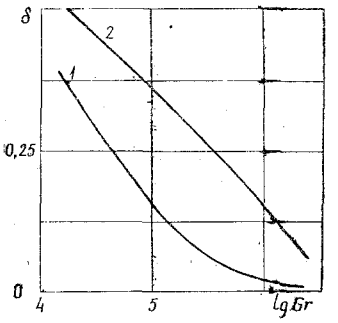

Fig. 3

The initial conditions for the problem (1.1)-(1.6) were given as follows: $T(r, z) = 1 - \gamma|z|$, $\psi = 0$, $\omega = 0$, $c = \text{const}$, $z_1 = z_1^0$, $z_2 = z_2^0$.

2. METHOD OF SOLUTION

The solution of (1.2)-(1.6) is complicated by the fact that the domain occupied by the liquid phase changes shape. Hence, it is expedient to solve the equation determined in the melted zone on different meshes rearranged in the shape of the melted zone.

This affords the possibility of using relatively coarse meshes for (1.1) in both phases and fine meshes for (1.2)-(1.6) in the liquid phase by compressing them in domains with large gradients or singularities. Equation (1.1) is solved by the method in [4] with the insertion of a domain of latent heat of crystallization liberation that is 4-6 difference-mesh nodes wide. The difference schemes for (1.2)-(1.6) are obtained by using the difference operators div, grad, and Δ defined in [5]. They result in a conservative difference scheme on a 9-point pattern. Implicit schemes were used and the passage to the n + 1 time layer is realized iteratively.

The sequence of solving the system of equations is proposed as follows: a) T^{n+1} is found from the T^n, v^n, z_1^n, z_2^n known on the n-th layer; b) z_1^{n+1}, z_2^{n+1} are determined by using z_1^n, z_2^n $v_{1n} = k(c^n - c_{l1}^n) - V_n$, $v_{2n} = k(c^n - c_{l2}^n) - V_n$; c) the difference mesh is rearranged around z_1^{n+1}, z_2^{n+1}; d) c^{n+1}, ω^{n+1}, ψ^{n+1}, v^{n+1} are computed; e) by using the temperature $T_i^{n+1}(r)$ (i = 1, 2) is computed from the quantities z_1^{n+1}, z_2^{n+1}, T^{n+1} on the phase interface $z_i^{n+1} = z_i^{n+1}(r)$; f) the equilibrium concentrations $c_{li}^{n+1}(r)$ and $m_{li}^{n+1}(r)$ are calculated by using $T_i^{n+1}(r)$. When using rough initial approximations and in kinetic growth regimes, a kinetic phase diagram should be used and iterations should be made in the stages a-f.

The value of the coefficient k was selected between 10 and 50. Computations showed that the change in k between these limits affects the solution of this problem slightly, and therefore, it is not expedient to give k > 50 in analyzing diffusion growth regimes since it will result in the need to iterate steps a-f and in a substantial increase in the machine time.

3. INFLUENCE OF NATURAL CONVECTION

A solution of the axisymmetric thermodiffusion problem of zone melting of PbTe was obtained by the method proposed.

In the absence of natural convection, mass transfer in the bulk of the melt is assured by diffusion, and the concentration distribution is such that its gradient is practically constant in the bulk of the melt. The liquid zone is shifted opposite to heater motion. For r = 0 the front coordinates z_1 and z_2 are 0.92 and 0.55, respectively, while the curvatures are $\Delta z_1 = z_1(0) - z_1(1) = -0.27$, $\Delta z_2 = z_2(0) - z_2(1) = 0.18$. The phase interfaces are convex towards the solid phase. The isotherms for this case are presented in Fig. 1 with a 10.7°K spacing. The front deviation from the isotherm is slight and only noticeable near the ampul walls.

For $Gr = 1.86 \cdot 10^4 - 1.86 \cdot 10^6$ ($Gr = 1.86 \cdot 10^6$ corresponds to conditions on earth) the temperature distribution differs slightly from that represented in Fig. 1 since the number $Pr \ll 1$ and a single-vortex convective flow, whose streamlines are presented in Fig. 2a for $Gr = 1.86 \cdot 10^6$, is realized in the melt. The maximal value of the velocity in the melt is here $0.35 \cdot 10^{-2}$ m/sec.

Convection stirs up the melt intensively by resulting in the Te concentration distribution for $Gr = 1.86 \cdot 10^6$, which is represented by the constant concentration lines with the 10^{-4} spacing in Fig. 2b. A mixing domain that occupies practically the whole volume of the melt is formed at the center of the melted zone, while thin diffusion boundary layers are formed near the interphasal boundaries.

Since the vortex is shifted to the dissolution front, the flow velocities near the dissolution front are higher than at the growth front. The results in the entrainment of melt with a somewhat smaller Te content from the zone axis to the ampul wall (shown by the arrow in Fig. 2b). Curvature of the growth front becomes equal to -0.26 for $Gr = 1.86 \cdot 10^5$ and of the dissolution front $+0.26$. The dependence of the diffusion boundary layer thickness δ on log Gr is represented in Fig. 3 for $0 \leq Gr \leq 1.86 \cdot 10^6$ (the diffusion boundary layer thickness is defined as the distance from the interphasal boundary to a point at which the concentration gradient equals the mean gradient over the zone length to this point). Curve 1 is the dependence $\delta(\log Gr)$ near the dissolution front, while 2 is at the growth front for $r = 0.5$.

An increase in the velocity of heater motion in the absence of convection will result in displacement of the zone relative to the temperature maximum until collapse of the process. Results of the computations confirm the deductions obtained from an analysis of the one-dimensional problem in [6], and they show that natural convection diminishes zone displacement by increasing the effective coefficient of diffusion, and therefore makes the process more stable, which permits raising the velocity of heater motion.

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