MODELING CRYSTALLIZATION OF A BINARY ALLOY

I. G. Getts and A. M. Meirmanov

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A generalized motion model is presented which describes crystallization of a binary alloy from the transitional phase. As a special case this generalized motion model contains the generally accepted model with well-defined phase transition front, convenient for numerical calculations, for example by the indirect count method using implicit configurations.

Within the framework of phenomenological theory the problem of crystallization of a binary alloy is usually formulated in the following manner: in a region Ω one must define a smooth surface $\Gamma(t)$ (the phase transition boundary) which divides the region Ω into two subregions $\Omega^+(t)$ and $\Omega^-(t)$, occupied by liquid and solid phase, respectively. The liquid or solid state of the medium at a given point in space at a given moment in time is defined with the aid of a phase equilibrium diagram (Fig. 1) using the values of the temperature θ and impurity concentration c: if the temperature θ is greater than $\Phi^+(c)$, then the medium is in the liquid state, while if the temperature is less than $\Phi^-(c)$, then it is in the solid state. The curves $L^\pm = \{(\theta, c)|\theta = \varphi^\pm(c), 0 < c < 1\} = \{(\theta, c)|c = f^\pm(\theta), \theta_A{}^* < \theta < \theta_B{}^*\}$ are called the liquidus and solidus. In each of the regions $\Omega^\pm(t)$ the temperature satisfies the thermal conductivity

$$a\partial\theta/\partial t = \operatorname{div}(\varkappa\nabla\theta), \tag{1}$$

while the concentration satisfies the impurity diffusion equation

$$\partial c/\partial t = \operatorname{div}(D\nabla c). \tag{2}$$

Here a, $\varkappa$, and D are the heat capacity, thermal conductivity, and diffusion coefficients, which, as a rule, are assumed constant in each phase but, generally speaking, differ between the phases. For example, $a = a^+ = \text{const}$ in the liquid phase, $a = a^- = \text{const}$ in the solid, while $a^+ \neq a^-$.

On the boundary $\Gamma(t)$ to be determined the energy balance condition (Stefan condition) must be satisfied

$$[U]V_n = -[\varkappa\, \partial\theta/\partial n],\ x \in \Gamma(t) \tag{3}$$

together with the mass-balance condition

$$[c]V_n = -[D\, \partial c/\partial n],\ x \in \Gamma(t), \tag{4}$$

where $[U] = U^+ - U^-$; $U^\pm$ is the limiting value of the enthalpy U on the boundary $\Gamma(t)$ from $\Omega^\pm(t)$; V_n is the displacement rate of the boundary $\Gamma(t)$ in the direction n of the normal to this boundary.

The limiting values of the temperature on $\Gamma(t)$ coincide:

$$[\theta] = 0,\ x \in \Gamma(t), \tag{5}$$

while the limiting concentration values are determinable from the phase equilibrium diagram:

$$\varphi^+(c^+) = \varphi^-(c^-) = \theta^+ = \theta^-,\ x \in \Gamma(t). \tag{6}$$

The mathematical model is completed by two conditions on the boundary of Ω for temperature and concentration together with initial conditions for temperature, concentration, and the phase transition boundary. In the model described, the surface $\Gamma(t)$ is a surface with a strong discontinuity in concentration c and enthalpy U; therefore, it is natural to call this model one of motion with a strong discontinuity (MSD), while in analogy to the Stefan problem [1], its solution is classical.

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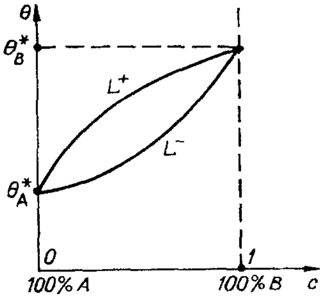

Fig. 1

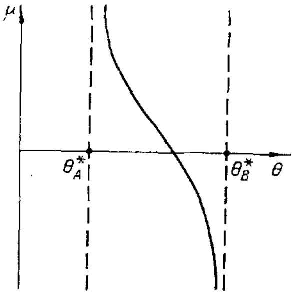

Fig. 2

As an initial-boundary problem the MSD model of Eqs. (1)-(6) is complex, and at present the existence of a classical solution has been proven only for a single spatial variable over a sufficiently short time interval [2]. Moreover, in [3, 4] peculiar solutions were found, in which both behind and ahead of the crystallization front the temperature was less than values determined by the length of the solidus L^- on the phase equilibrium diagram, and it was maintained that these solutions reflected a process of supercooling, although it was obvious that while satisfying conditions (1)-(6), they were not a solution of the MSD model, since the basic requirement for which the boundary $\Gamma(t)$ is meaningful was not satisfied: in $\Omega^-(t)\theta$ the value of $\varphi^-(c)$ is lower, while in $\Omega^+(t)\theta$ the value of $\varphi^+(c)$ is higher.

Thus, it has not been possible to demonstrate the existence of a classical solution over all times, while in some cases such a solution is simply lacking (which in the authors' opinion is the result of [3, 4]). In analogy to the Stefan problem of [1] we will assume that for a binary alloy, crystallization is described by a wider class of generalized solution, containing within itself as a subclass, the classical solutions. Such attempts have been made by a number of authors [5-8], and a quite perfected form of the generalized motion (GM) model for low concentrations was presented in [6].

The goal of the present study is the axiomatic construction of a GM model commencing from the minimum number of generally accepted thermodynamics postulates. As in the case of the Stefan problem of [1], the basic axiom of the model admits the possibility of existence of a transitional phase with the temperature of the medium coinciding with the fusion temperature, while the enthalpy can take on values from the entire interval determined by the limiting values of enthalpy for the liquid and solid phases.

Upon crystallization of a binary alloy the thermodynamic state of the medium is determined by seven parameters: the enthalpy U, temperature θ, entropy S, concentrations c_A and c_B, and chemical potentials μ_A and μ_B corresponding to the materials A and B. In each phase let the indicated parameters satisfy the Gibbs identity $dU = \theta dS + \mu_A dc_A + \mu_B dc_B$ ($c_A + c_B = 1$) while the enthalpy depends solely on temperature:

$$U = \alpha\theta + \beta \ (\alpha, \beta = \text{const}). \tag{7}$$

These assumptions and the Gibbs theorem [9, p. 67] which states that

$$\mu_A \equiv \Psi = U - \theta S - c\mu \tag{8}$$

($c = c_B$, $\mu = \mu_B - \mu_A$) permit the introduction of two independent parameters, for example the temperature θ and the potential μ, which define all the remaining parameters and, consequently, the thermodynamic state of the medium.

The Gibbs identity for the independent parameters θ and μ takes on the form

$$d\Psi = -Sd\theta - cd\mu, \tag{9}$$

whence it follows that $S = -\partial\Psi/\partial\theta$, $c = -\partial\Psi/\partial\mu$. In particular, considering Eq. (8) as a first-order equation for Ψ with the given identity Eq. (7) for the function U, we find that, in each phase,

$$\Psi(\theta, \mu) = \Psi_0(\mu/\theta)\theta - \alpha\theta \ln\theta + \beta \tag{10}$$

[$\Psi_0(\tau)$ is an arbitrary function].

The first axiom A_1 of the GM model states that, in the liquid and solid phases, identity (9) and Eq. (7) are valid, while phase transition from the liquid to the solid state (or the opposite) occurs with local thermodynamic phase equilibrium, i.e., the temperature θ and chemical potentials μ_A and μ_B of the liquid phase are equal to the analogous parameters of the solid phase.

The latter assertion corresponds to the existence within the plane of the variables θ and μ of a curve $\mu = \Phi(\theta)$, which divides the plane into two subregions Π^+ and Π^- such that the values of θ and μ in Π^+ define the liquid phase, while the values of θ and μ in Π^- define the solid phase, while along the indicated curve $\Psi^+(\theta, \mu) = \Psi^-(\theta, \mu)$.

Turning to the concrete form of Ψ in each phase, we have

$$\mu = \Phi(\theta) \equiv \theta\varphi(\theta). \tag{11}$$

The dependence of temperature on potential μ converse to Eq. (11) defines the fusion temperature of the medium $\theta = \theta^*(\mu)$. We will assume that, in each phase, enthalpy is an increasing function of temperature, while upon transition from the solid phase to the liquid this quantity increases, i.e., either $\alpha^+ \geq \alpha^- > 0$, $\theta \geq \theta_0 = -[\beta]/[\alpha]$, or $\alpha^- \geq \alpha^+ > 0$, $\theta \leq \theta_0$.

Following the principles of construction of the GM model, we assume that along the phase equilibrium curve of Eq. (11) there is located a fold, in which the transition state is hidden. . One variant for smoothing this fold is transition to the variables θ and c. To do this, from the equations $c = -\partial\Psi^\pm/\partial\mu$ we find the value $\mu = \theta g^\pm(c)$ and substitute in Eq. (11): $\theta = (\varphi^{-1} \circ g^\pm)(c) \equiv \varphi^\pm(c)$. On the phase equilibrium diagram (see Fig. 1) the region Π^+ of the variables θ and μ corresponds to the region $\{\theta > \varphi^+(c),\ 0 < c < 1\}$ (which we denote by Π^+), while the edge of the fold, Eq. (11), on the liquid-phase side, is the liquidus curve L^+. Analogously, the region Π^- of the variables θ and μ and corresponds to the region $\{\theta < \varphi^-(c),\ 0 < c < 1\}$, while the edge of the fold of Eq. (11) on the solid-phase side is the solidus curve L^-.

Now having the phase-equilibrium diagram in the plane of the variables θ and c, it is simple to reconstruct the phase equilibrium line of Eq. (11). To do this, we differentiate the identity

$$\theta\Psi_0^+(\varphi(\theta)) - \alpha^+\theta\ln\theta + \beta^+ = \theta\Psi_0^-(\varphi(\theta)) - \alpha^-\theta\ln\theta + \beta^-$$

with respect to temperature, and applying Eq. (7), we find

$$\frac{d\varphi}{d\theta} = \frac{1}{\theta^2}\,\frac{U^+ - U^-}{c^+ - c^-} = \frac{1}{\theta^2}\,\frac{[U]}{[c]}.$$

We will assume that the liquidus and solidus lines on the phase equilibrium diagram approach the lines c = 0 and c = 1 at different angles, which are not multiples of $\pi/2$. Then the function φ in Eq. (11) has a logarithmic singularity at the points $\theta_A{}^*$ and $\theta_B{}^*$ and the potential μ along Eq. (11) increases without limit upon approach of the temperature to these values. The approximate form of the phase equilibrium curves in the plane θ and μ is shown in Fig. 2.

The region Π^* in the plane of the variables θ and c, limited by the liquidus and solidus curves, corresponds to the transitional phase, in which no quantities are defined. How do we extend the thermodynamic parameters Ψ, U, S, and μ into the transitional phase? Most natural would be assuming the validity of identity (9) and Eq. (8) for the potential Ψ. Moreover, it is also natural to assume the existence of a process whereby the binary mixture transforms from the liquid state to the solid (or the converse) through a transitional state (in region Π^* of the variables θ and c this process corresponds to a continuous curve joining the liquidus and solidus lines) such that the chemical potentials μ_A and μ_B (or the potentials μ and Ψ) change continuously. In other words, in the region Π of changes in the parameters θ and c the potentials μ and Ψ are defined and continuous.

The requirement of continuity is fundamental, and the potentials μ and Ψ can be reconstructed in the region Π^* in a natural manner. To do this it will be sufficient to consider the segment $I_\theta = \{(\theta, c) \mid \theta = \text{const}\}$ in Π^*, joining the liquidus and solidus lines. In the plane of the variables θ and μ the segment I_θ corresponds to a point on the phase equilibrium curve (11), i.e., along I_θ in Π^* the value of the potential μ is constant. From identity (9) and Eq. (11) it follows that Ψ is also constant along I_θ.

Since $F = \Psi + c\mu$, together with the potentials Ψ and μ in the region Π the free energy F is continuous. Rewriting identity (9) in the form $dF = -Sd\theta + \mu dc$, we can prove that the entropy S is also continuous upon transition through the liquidus and solidus lines. In fact, the latter identity is equivalent to the equalities $\mu = \partial F/\partial c$ and $S = -\partial F/\partial\theta$. Let $F = F^*$, $\mu = \mu^*$ in Π^* and $F = F^+$, $\mu = \mu^+$ in Π^+. Then $F^+(\theta, f^+(\theta)) = f^*(\theta, f^+(\theta))$ and $\mu^*(\theta, f^+(\theta)) = \partial F/\partial c(\theta, f^+(\theta)) = \partial F^+/\partial c(\theta, f^+(\theta)) = \mu^+(\theta, f^+(\theta))$. Differentiating the expression $F^+ = F^*$ along the liquidus, we obtain $\partial F^+/\partial\theta + \mu^+\partial f^+/\partial\theta = \partial F^*/\partial\theta + \mu^*\partial f^+/\partial\theta$, whence follows the continuity of the entropy upon transition through the liquidus. The solidus may be treated analogously.

The continuity of the entropy and the equation $U = F + \theta S$ compel continuity of the enthalpy everywhere in Π. Turning to the easily derived consequence of the Gibbs identity $\partial(\mu/\theta)/\partial\theta + (1/\theta^2)\partial U/\partial c = 0$ and the definition of μ in the transitional phase, we conclude that in the transitional phase the enthalpy depends linearly on concentration:

$$U = \alpha^-\theta + \beta^- + \frac{[\alpha]\theta + [\beta]}{f^+(\theta) - f^-(\theta)}(c - f^-(\theta)) \tag{12}$$

for $f^+(\theta) < c < f^-(\theta)$, $\theta_A^* < \theta < \theta_B^*$.

The second axiom A_2 of the GM model states that all states corresponding to values of the parameters θ and c from the region Π^* are physically realizable, identity (9) and Eq. (7) are valid in Π^*, and the chemical potentials μ_A and μ_B are defined and continuous in Π.

The potential μ increases without limit at the extremal points of the phase equilibrium diagram, so that it is more convenient to consider ν as the unknown function, as defined from the equation $\theta\varphi(\nu) = \mu$. Returning to the concrete form of the potential Ψ and concentration c in the liquid and solid phases we see that there the potential ν depends solely on concentration. By the construction of the model in the transitional phase $\nu = \theta$. This equality is also valid on the boundary Π^* on the liquidus L^+ and solidus L^- lines: $\nu = \theta = f^+(c)$ on L^+ and $\nu = \theta = f^-(c)$ on L^-. Consequently, everywhere in Π^+, $\nu = f^+(c)$, while in Π^-, $\nu = f^-(c)$.

More detailed analysis reveals that the fold along the curve of Eq. (11) in the plane θ and μ, does not smooth completely in the plane of the variables θ and c: at the points $(\theta_A^*, 0)$ and $(\theta_B^*, 1)$ transitional states remain hidden, these corresponding to transitions of the pure substances A and B. In the new variables U and ν the fold smooths completely. In the plane of U and ν the liquid phase corresponds to the region $\Pi^+ = \{U \geq \alpha^+\nu + \beta^+, \theta_A^* \leq \nu \leq \theta_B^*\}$, the solid, to the region $\Pi^- = \{U \leq \alpha^-\nu + \beta^-, \theta_A^* \leq \nu \leq \theta_B^*\}$, and the transitional phase to the region $\Pi^* = \{\beta^- + \alpha^-\nu \leq U \leq \beta^+ + \alpha^+\nu, \theta_A^* \leq \nu \leq \theta_B^*\}$. The transitional state of the pure substances A and B corresponds to the segment $\{\theta_A^* = \nu\}$ and $\{\theta_B^* = \nu\}$ from Π^*.

Dependences of temperature and concentration on enthalpy $U(\nu = \text{const})$ and potential ν $(U = \text{const})$ are shown in Figs. 3 and 4. By construction the functions θ and c are continuous, while their first derivatives have a discontinuity of the first type. The discontinuity points of the derivatives of the function c in Fig. 4 shift along the liquidus and solidus such that the function $c(U, \nu)$ always increases monotonically with increase in ν.

The thermodynamic state of the binary mixture is determined by two independent parameters (θ and c, if $0 < c < 1$, or U and ν). Therefore, for complete description of the behavior of the medium two additional equations are required, these being the laws of conservation of energy and mass. These equations must be defined for all values of the independent thermodynamic parameters everywhere in the region Ω for all values of time. Since the GM model is constructed as an expansion of the MSD model, in those regions occupied by liquid and solid phases the law of conservation of energy should coincide with thermal conductivity equation (1), and the mass conservation law with diffusion equation (2).

In the Stefan problem of [1], which serves as our pilot model, this can be realized in the form of the equation

$$\partial U/\partial t = \operatorname{div}(\varkappa\nabla\theta), \tag{13}$$

in which the dependence of temperature θ on enthalpy U for a given value of ν is shown in Fig. 3. If $\nu = \text{const}$ (fusion temperature of the pure substance constant), then in Eq. (13) the coefficient κ is defined in the liquid and solid phases, while in the transitional phase

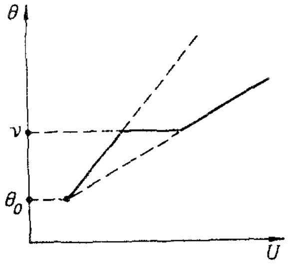

Fig. 3

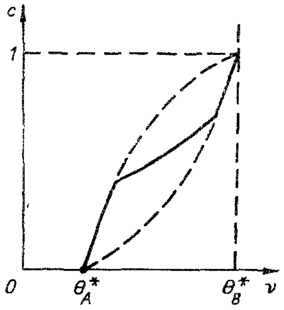

Fig. 4

it is sufficient to consider it finite: there $\kappa\nabla\theta \equiv 0$. But if $\nu = \nu(x, t)$, then in the transitional phase it is necessary to supplementarily define the thermal conductivity coefficient in the transitional phase. There are no further considerations as to how this should be done at present, so that we usually use the simplest possible method of extrapolation: in the transitional phase κ is a linear function of enthalpy, directly joining the values κ^+ and κ^-.

Thus, all quantities in Eq. (13) are defined. Physically the function U, subject to differentiation in Eq. (13), may undergo a discontinuity of the first type. How then are we to understand the equation? Following [10], we must understand it in a generalized sense as an integral identity

$$\int_{\Omega_T}\left\{-U\frac{\partial\zeta}{\partial t}+\varkappa\nabla\theta\cdot\nabla\zeta\right\}dx\,dt=0, \qquad (14)$$

valid for all smooth finites in $\Omega_T = \Omega \times (0, T)$ of the functions ζ. It can easily be shown that if in Ω there exists a smooth surface Γ(t), dividing Ω into subregions $\Omega^{\pm}(t)$ occupied, respectively, by liquid ($U \geq \alpha^+\nu + \beta^+$) and solid ($U \leq \alpha^-\nu + \beta^-$) phases, then in $\Omega^{\pm}(t)$ the temperature θ satisfies Eq. (1), while on the boundary Γ(t) it satisfies the Stefan condition Eq. (3).

In analogy to the Stefan problem we will assume that in the GM model Eq. (13) is satisfied, while the coefficient κ in Π^+ and Π^- coincides with the values of κ^+ and κ^-, respectively, depending linearly on U (if the independent variables are U and ν) or c (if the independent variables are θ and c) in Π^*, and being continuous everywhere in Π. If the independent variables are θ and c, then the temperature dependence of enthalpy in Π^+ and Π^- is given by Eq. (7), and in Π^* by Eq. (12). If the independent variables are U and ν, then $\theta = \theta(U, \nu)$ is given by the diagram in Fig. 3.

We will now consider the law of conservation of mass. If we assume that it is described everywhere by Eq. (2), then by redefining the coefficient D in the transitional phase, as was done in [11], we immediately eliminate classical solutions of the MSD model. As is well known, all solutions of Eq. (2) with $D \geq D_0 = \text{const} > 0$ are continuous [10, p. 238], while in the classical solution the concentration c suffers a discontinuity of the first sort on the phase transition surface Γ(t).

In fact, the impurity diffusion equation has a form other than that of Eq. (2). If we consider that there exists a mass flow vector $\mathbf{j}$ such that $\partial c/\partial t = \operatorname{div}\mathbf{j}$, then using the Gibbs equation $\theta dS = dU + \mu dc$, the principle of nondecrease in entropy for an arbitrary thermally insulated volume ω

$$\frac{d}{dt}\int_{\omega} S\,dx \geqslant 0,\ \mathbf{j}\cdot\mathbf{n}|_{\partial\omega}=0,\ \nabla\theta\cdot\mathbf{n}|_{\partial\omega}=0$$

and the Onsager symmetry principle [9], it is simple to derive the expression $\mathbf{j} = \Lambda\nabla(\mu/\theta) = \lambda\nabla\nu$, which we take as the basis for the impurity diffusion equation

$$\partial c/\partial t = \operatorname{div}(\lambda\nabla\nu). \qquad (15)$$

The latter coincides with Eq. (2) in the liquid and solid phases, if

$$\lambda^{\pm}\frac{d\varphi^{\pm}}{dc}(c) = D^{\pm}.$$

In the transitional phase the coefficient λ may be supplementarily defined as a linear function of enthalpy, continuous for all values of the independent variables. Equation (15), like Eq. (13), is to be understood in a generalized sense as satisfaction of the corresponding identity. If the solutions of Eqs. (13) and (15) are such that θ and ν are continuous in Ω_T, and in the region Ω there exists a smooth surface $\Gamma(t)$ dividing the regions $\Omega^{\pm}(t)$ occupied by liquid and solid phases, then there follows from Eq. (15) the diffusion equation (2) for the concentration in each of the regions $\Omega^{\pm}(t)$ and the mass balance condition (4) on the boundary $\Gamma(t)$.

Conditions (5) and (6) are a consequence of the continuity of θ and ν. Thus, the GM model contains the MSD model as a special case. Axion A_3, which completes the GM model, postulates the validity of Eqs. (13) and (15) everywhere in the region Ω_T and describes the coefficients κ and λ.

The GM binary alloy crystallization model is essentially broader than the MSD model. This can even be seen in the simplest possible case of a steady-state one-dimensional problem where the region Ω is the segment (0, 1). Precise results were formulated in [1], one of which consists of the following: if on one boundary of Ω the liquid state is specified, while the solid state is specified on the other, then for sufficiently small deviations from the equilibrium position in the region Ω there exists a transitional phase occupying the region $\Omega^{*} \subset \Omega$.

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