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A model of binary alloy solidification with convection in the melt

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Abstract—The solidification of a binary alloy is studied on a three-phase model (solid, liquid, mushy zone). The balance equations of the model are formulated globally over the whole region occupied by the alloy and are treated in a distributional sense. Convective phenomena in the melt and the influence of gravitational field are taken into account. The significance of the model for studying solidification processes under different gravity conditions is discussed.

1. INTRODUCTION

SOLIDIFICATION processes are driven by heat and mass transport. The transport itself can be due to the conduction of heat and diffusion of solute and, in addition, convection and radiation may be involved. Hence, phenomenological models of processes of this type should contain the balance equations for mass, momentum and energy, the constitutive relations for generalized fluxes, and the equations of state. In this paper we shall restrict ourselves to the constitutive relations which follow from the axiomatic structure of non-equilibrium thermodynamics [1]. Using the hypothesis of local thermodynamic equilibrium we thus express certain equations of state from the equilibrium phase diagram of the binary alloy under consideration.

We distinguish three phases in the system undergoing solidification, namely a solid phase, a liquid phase and an inter-phase (sometimes called mushy zone or crystallization front), which is a mixture of solid and liquid. There are two main phenomenological approaches to modelling such a system. First, there is a generalization of the classical Stefan problem. Here, the inter-phase is modelled as a discontinuity surface [2] and the model consists of the balance equations in both solid and liquid, while the inter-phase balances take the character of jump conditions across the surface dividing the phases. This approach is analysed in ref. [3]. Another approach formulates the balances globally over the whole region occupied by the alloy. As a consequence, the balances must be treated in a distributional (weak) sense instead of pointwise in each of the phases as with the first approach. A useful example of a model of this type has been presented by Alexiades *et al.* [4]. Our mathematical formulation is, in fact, a generalization of ref. [4], taking the convective phenomena and the influence of gravitational field into account.

2. A MODEL OF BINARY ALLOY SOLIDIFICATION

2.1. *Basic assumptions*

We consider a binary alloy consisting of components A and B and suppose that the alloy is capable of forming solid solutions in all proportions (e.g. Cu–Ni, Au–Pt). The system under consideration is situated in an exterior gravitational field and the mass transfer is due to diffusion (in all the phases) and to convection (in the liquid phase and inter-phase). Heat is transferred by conduction and radiation (in the whole system) and by convection (in the liquid phase and inter-phase). We assume that the liquid phase and the inter-phase are quasi-incompressible Newtonian fluids and thus we can use the Boussinesq approximation and the Navier–Stokes law for the stress tensor in these phases. Since we suppose that no convection takes place in the solid phase the Navier–Stokes law may be applied even there. Further we assume that there are no chemical reactions and that the interactive forces between the components of the alloy are negligible. Finally, we model the alloy as an isotropic material.

The theoretical study of alloys usually employs the model of a mixture [5, 6]. The binary alloy in a solid phase (S), liquid phase (L) and an inter-phase (I) is then, as a whole, described by the respective continua E^k, $k = \mathrm{S, L, I}$, each of which may be viewed as a superposition of one-component continua E^k_α,

NOMENCLATURE

c_p	specific heat under constant pressure
c_V	specific heat under constant volume
C	concentration
D	diffusivity of component B of the alloy
g	specific Gibbs energy (chemical potential)
$\mathbf{g}$	acceleration of gravity
h	specific enthalpy
$\mathbf{j}$	diffusion flux
k	thermal conductivity
L_C	latent heat of crystallization
L_M	latent heat of melting
M	mobility
p	pressure
$\mathbf{q}$	heat flux
T	temperature
$\mathbf{T}$	stress tensor
u	specific internal energy
$\mathbf{v}$	velocity
V	specific volume
$\mathbf{w}$	diffusion velocity.

Greek symbols

α	thermal expansion coefficient
β	Dufour coefficient
γ	solutal expansion coefficient
δ	Soret coefficient
$\boldsymbol{\delta}$	unit tensor
η_v	coefficient of dynamical viscosity
λ	liquid fraction
ρ	density
ϕ	radiation heat source.

Superscripts

k	phase of material, k = I, L, S
I	inter-phase (mushy zone)
L	liquid
S	solid.

Subscripts

A, B	components of the alloy
α	related to particular component, α = A, B.

$\alpha = \mathrm{A}, \mathrm{B}$. Partial quantities X_α^k will be related to the particular components E_α^k, $\alpha = \mathrm{A}, \mathrm{B}$, whereas the total quantities corresponding to the continuum E^k will be denoted by X^k. We thus introduce the densities ρ_α^k, ρ^k, where

$$\rho^k \equiv \sum_{\alpha=\mathrm{A},\mathrm{B}} \rho_\alpha^k, \quad k = \mathrm{S}, \mathrm{L}, \mathrm{I} \tag{1}$$

and define the concentrations C_α^k as

$$C_\alpha^k \equiv \frac{\rho_\alpha^k}{\rho^k}, \quad \sum_\alpha C_\alpha^k = 1. \tag{2}$$

For the velocities $\mathbf{v}_\alpha^k$, $\mathbf{v}^k$ we have

$$\sum_\alpha C_\alpha^k \mathbf{v}_\alpha^k \equiv \mathbf{v}^k, \quad \mathbf{v}^{\mathrm{S}} = 0. \tag{3}$$

Further we introduce the diffusion velocities $\mathbf{w}_\alpha^k$ by

$$\mathbf{w}_\alpha^k \equiv \mathbf{v}_\alpha^k - \mathbf{v}^k \tag{4}$$

and the diffusion fluxes $\mathbf{j}_\alpha^k$, for which

$$\mathbf{j}_\alpha^k = \rho_\alpha^k \mathbf{w}_\alpha^k, \quad \sum_\alpha \mathbf{j}_\alpha^k = 0. \tag{5}$$

We denote by V_α^k, V^k the specific volumes, having

$$V^k \equiv (\rho^k)^{-1}, \quad V^k \equiv \sum_\alpha C_\alpha^k V_\alpha^k, \quad \sum_\alpha \rho_\alpha^k V_\alpha^k = 1. \tag{6}$$

Let $\boldsymbol{\delta}$ be the unit tensor and denote by $\mathbf{T}_\alpha^k$, $\mathbf{T}^k$ the stress tensors and by p_α^k, p^k the pressures. We then have

$$\mathbf{T}^k \equiv -\boldsymbol{\delta} p^k + {}_{\mathrm{D}}\mathbf{T}^k, \quad \mathbf{T}_\alpha^k \equiv -\boldsymbol{\delta} p_\alpha^k + {}_{\mathrm{D}}\mathbf{T}_\alpha^k,$$

$$\sum_\alpha p_\alpha^k \equiv p^k, \quad p_\alpha^k \equiv \rho_\alpha^k V_\alpha^k p^k, \quad \sum_\alpha {}_{\mathrm{D}}\mathbf{T}_\alpha^k \equiv {}_{\mathrm{D}}\mathbf{T}^k \tag{7}$$

where ${}_{\mathrm{D}}\mathbf{T}_\alpha^k$, ${}_{\mathrm{D}}\mathbf{T}^k$ are the dissipative parts of the respective stress tensors. The specific internal energies u_α^k, u^k and the specific enthalpies h_α^k, h^k are given by

$$u^k \equiv \sum_\alpha C_\alpha^k u_\alpha^k, \quad h^k \equiv \sum_\alpha C_\alpha^k h_\alpha^k,$$

$$h_\alpha^k \equiv u_\alpha^k + p^k V_\alpha^k, \quad h^k \equiv u^k + p^k V^k \tag{8}$$

and in addition we put $\eta^k \equiv h_\mathrm{B}^k - h_\mathrm{A}^k$. The heat fluxes $\mathbf{q}_\alpha^k$, $\mathbf{q}^k$ (corresponding to the conductive transport) and the radiation heat sources ϕ_α^k, ϕ^k satisfy

$$\mathbf{q}^k \equiv \sum_\alpha \mathbf{q}_\alpha^k, \quad \phi^k \equiv \sum_\alpha \phi_\alpha^k. \tag{9}$$

For the specific Gibbs energies g_α^k, g^k we have

$$g^k = \sum_\alpha C_\alpha^k g_\alpha^k \tag{10}$$

and put $\mu^k = g_\mathrm{B}^k - g_\mathrm{A}^k$.

Supposing that the temperature field is the same for E_A^k, E_B^k and E^k, we denote the temperature by T^k, the specific heats under constant pressure and constant volume by c_p^k and c_V^k, respectively, the thermal conductivities by k^k, the diffusivities of the component B by D^k, the Soret coefficients by δ^k, the Dufour coefficients by β^k, the thermal and solutal expansion coefficients by α^k and γ^k, respectively, and the coefficients of dynamical viscosity by η_v^k. Finally, we introduce the mobilities as

$$M^k \equiv \frac{\rho^k D^k}{C_\mathrm{A}^k}\left(\frac{\partial \mu^k}{\partial C_\mathrm{B}^k}\right)^{-1}.$$

Some of the quantities introduced are continuous across the inter-phase; the others are piecewise continuous. So, for example, the jump of the enthalpy equals the latent heat of phase transformation. Denoting the latent heat of melting by L_M we thus have

$$L_M = h^L - h^S, \quad L_M = -L_C \tag{11}$$

where L_C is the latent heat of crystallization.

2.2. *Balance equations*

We start by formulating the basic conservation laws for the continua in question, temporarily taking no care about the phase change process. Referring to the assumptions made in Section 2.1 we write the mass balance in the form

$$\operatorname{div} \mathbf{v}^k = 0,$$

$$\rho^k = \bar{\rho}^k - \bar{\rho}^k \alpha^k (T^k - \bar{T}^k) - \bar{\rho}^k \gamma^k (C_B^k - \bar{C}_B^k) \tag{12}$$

$k = $ L, S, I, where the bar denotes a reference value and the expansion coefficients are defined as

$$\alpha^k = \frac{1}{V^k}\left(\frac{\partial V^k}{\partial T^k}\right)_{p^k, C_B^k} = -\frac{1}{\rho^k}\left(\frac{\partial \rho^k}{\partial T^k}\right)_{p^k, C_B^k}$$

$$\gamma^k = \frac{1}{V^k}\left(\frac{\partial V^k}{\partial C_B^k}\right)_{p^k, T^k} = -\frac{1}{\rho^k}\left(\frac{\partial \rho^k}{\partial C_B^k}\right)_{p^k, T^k}. \tag{13}$$

The incompressibility of E^k does not imply the incompressibility of E_α^k, of course. Hence, the mass balance equations for the individual components E_α^k, $\alpha = $ A, B, of the mixture are

$$\rho^k \frac{\mathrm{d}C_\alpha^k}{\mathrm{d}t} + \operatorname{div} \mathbf{j}_\alpha^k = 0 \; (k = \mathrm{L, S, I}) \tag{14}$$

where

$$\frac{\mathrm{d}X_\alpha^k}{\mathrm{d}t} = \frac{\partial X_\alpha^k}{\partial t} + (\mathbf{v}^k \cdot \operatorname{grad} X_\alpha^k)$$

is the material derivative.

Using the 'weak diffusion approximation' by which terms quadratic in $\mathbf{w}_\alpha^k$ and $\mathbf{j}_\alpha^k$ are supposed to be negligible, we obtain the balance of momentum in the liquid phase as

$$\rho^L \frac{\mathrm{d}\mathbf{v}^L}{\mathrm{d}t} = -\operatorname{grad} p^L + \operatorname{div} {}_D\mathbf{T}^L + \rho^L \boldsymbol{g} \tag{15}$$

where $\boldsymbol{g}$ is the gravity and ρ^L is given by (12). If we suppose that the pressure gradient in (15) is due to the weight of the fluid, equation (15) can be split into the relations

$$\operatorname{grad} p^L = \bar{\rho}^L \boldsymbol{g},$$

$$\rho^L \frac{\mathrm{d}\mathbf{v}^L}{\mathrm{d}t} = \operatorname{div} {}_D\mathbf{T}^L - \bar{\rho}^L \boldsymbol{g}[\alpha^L (T^L - \bar{T}^L) + \gamma^L (C_B^L - \bar{C}_B^L)]. \tag{16}$$

Applying the Navier–Stokes law, linearizing and taking (12) into account we finally obtain

$$\rho^L \frac{\partial \mathbf{v}^L}{\partial t} = \operatorname{div} (\eta_v^L \operatorname{grad} \mathbf{v}^L) - \bar{\rho}^L \boldsymbol{g}[\alpha^L (T^L - \bar{T}^L) + \gamma^L (C_B^L - \bar{C}_B^L)]. \tag{17}$$

This equation implies that the viscous forces are compensated by the buoyancy forces in the stationary state.

Assuming formally that the coefficient of dynamic viscosity is a very large number in the solid phase, $\eta_v^S \to \infty$, we may also write (17) in the solid. Then, in accord with the assumption that the inter-phase is a fluid whose properties are determined by the corresponding properties of the solid and liquid phases (cf. the next section), relation (17) also holds in the inter-phase. Consequently, we formally write

$$\rho^k \frac{\partial \mathbf{v}^k}{\partial t} = \operatorname{div} (\eta_v^k \operatorname{grad} \mathbf{v}^k) - \bar{\rho}^k \boldsymbol{g}[\alpha^k (T^k - \bar{T}^k) + \gamma^k (C_B^k - \bar{C}_B^k)] \tag{17'}$$

$k = $ L, S, I. The balances of momentum for the individual components E_α^k, $\alpha = $ A, B are not included in our considerations. The reason is that these balances would be combinations of the balance of momentum for the mixture and a constitutive relation for the diffusion flux which we introduce later in this section.

The balance of internal energy has the form (cf. refs. [5, 7])

$$\frac{\partial \rho^k u^k}{\partial t} + \operatorname{div}\left(\sum_\alpha \rho_\alpha^k u_\alpha^k \mathbf{v}_\alpha^k + \mathbf{q}^k\right) + \sum_\alpha p_\alpha^k \operatorname{div} \mathbf{v}_\alpha^k - \sum_\alpha ({}_D\mathbf{T}_\alpha^k : \operatorname{grad} \mathbf{v}_\alpha^k) - \phi^k = 0 \tag{18}$$

$k = $ L, I, in the liquid phase and inter-phase. Here, $(\mathbf{A} : \mathbf{B})$ denotes the scalar product of the tensors **A** and **B**. The last but one term on the left-hand side of (18) represents viscous dissipation of energy and is usually neglected in heat transfer equations. We thus put

$$\sum_\alpha ({}_D\mathbf{T}_\alpha^k : \operatorname{grad} \mathbf{v}_\alpha^k) \approx 0$$

in our model too. Since we assume $\mathbf{v}^S = 0$, $\mathbf{v}_\alpha^S \approx 0$ we may also write the balance of internal energy for $k = $ S formally in the form (18).

Now, using (1)–(8) and (12), we can modify (18) to obtain

$$\rho^k \frac{\mathrm{d}u^k}{\mathrm{d}t} + \operatorname{div} (\mathbf{q}^k + \eta^k \mathbf{j}_B^k) + (\mathbf{v}^k \cdot \operatorname{grad} p^k) - \sum_\alpha (\mathbf{v}_\alpha^k \cdot \operatorname{grad} \rho_\alpha^k V_\alpha^k p^k) - \phi^k = 0 \quad (k = \mathrm{L, I}). \tag{19}$$

If the alloy is supposed to be diluted we have $C_B^k \ll 1$, say, and thus we may put $\rho_A^k V_A^k \approx 1$, $\rho_B^k V_B^k \approx 0$ and obtain

$$(\mathbf{v}^k \cdot \operatorname{grad} p^k) - \sum_\alpha (\mathbf{v}_\alpha^k \cdot \operatorname{grad} \rho_\alpha^k V_\alpha^k p^k) = (\rho_A^k)^{-1} (\mathbf{j}_B^k \cdot \operatorname{grad} p^k) \tag{20}$$

$k = \mathrm{L, I}$. Taking the first equation of (16) into account and putting $C^k_{\mathrm{A}} \approx \rho^k_{\mathrm{A}}/\bar{\rho}^k$, we finally arrive at the energy balance in the form

$$\rho^k \frac{\mathrm{d}u^k}{\mathrm{d}t} + \mathrm{div}\,(\mathbf{q}^k + \eta^k \mathbf{j}^k_{\mathrm{B}}) + (C^k_{\mathrm{A}})^{-1}(\mathbf{j}^k_{\mathrm{B}} \cdot \boldsymbol{g}) = \phi^k \quad (21)$$

$k = \mathrm{L, I}$. Owing to our assumptions on $\mathbf{v}^{\mathrm{S}}$, $\mathbf{v}^{\mathrm{S}}_{\alpha}$, equation (19) may also be formally written for $k = \mathrm{S}$ and in this case the equivalence of (21) and (19) follows from the fact that $\mathbf{j}^{\mathrm{S}}_{\mathrm{B}} \approx 0$ under our assumptions. Hence, we use the energy balance (21) for $k = \mathrm{L, S, I}$ in what follows.

The phenomenological laws of linear (irreversible) thermodynamics yield the constitutive relations

$$\mathbf{j}^k_{\mathrm{B}} = -\rho^k D^k\, \mathrm{grad}\; C^k_{\mathrm{B}} + M^k \boldsymbol{g} + \rho^k \delta^k\, \mathrm{grad}\; T^k$$

$$\mathbf{q}^k = -k^k\, \mathrm{grad}\; T^k + \beta^k\, \mathrm{grad}\; C^k_{\mathrm{B}} - \frac{\beta^k M^k}{\rho^k D^k}\boldsymbol{g} \quad (22)$$

$k = \mathrm{L, S, I}$, where we suppose that $D^{\mathrm{S}} \approx 0$, $M^{\mathrm{S}} \approx 0$, $\delta^{\mathrm{S}} \approx 0$ to provide consistency with our previous assumption of $\mathbf{j}^{\mathrm{S}}_{\mathrm{B}} \approx 0$. Further, we suppose that $\beta^{\mathrm{S}} M^{\mathrm{S}}/D^{\mathrm{S}} \approx 0$.

Using (14), (17), (21) and (22), we thus finally have the following relations in each of the phases ($k = \mathrm{L, S, I}$):

$$\rho^k = \bar{\rho}^k[1 - \alpha^k(T^k - \bar{T}^k) - \gamma^k(C^k_{\mathrm{B}} - \bar{C}^k_{\mathrm{B}})]$$

$$\mathrm{div}\,\mathbf{v}^k = 0$$

$$\rho^k \frac{\partial \mathbf{v}^k}{\partial t} = \mathrm{div}\,(\eta^k_{\mathrm{v}}\, \mathrm{grad}\; \mathbf{v}^k) - \bar{\rho}^k \boldsymbol{g}[\alpha^k(T^k - \bar{T}^k) + \gamma^k(C^k_{\mathrm{B}} - \bar{C}^k_{\mathrm{B}})]$$

$$\rho^k \frac{\mathrm{d}C^k_{\mathrm{B}}}{\mathrm{d}t} = \mathrm{div}\,(\rho^k D^k\, \mathrm{grad}\; C^k_{\mathrm{B}}) - \mathrm{div}\,(M^k \boldsymbol{g}) - \mathrm{div}\,(\rho^k \delta^k\, \mathrm{grad}\; T^k)$$

$$\begin{aligned}\rho^k \frac{\mathrm{d}u^k}{\mathrm{d}t} = {} & \mathrm{div}\,[(k^k - \eta^k \rho^k \delta^k)\, \mathrm{grad}\; T^k] \\ & + \mathrm{div}\,[(\eta^k \rho^k D^k - \beta^k)\, \mathrm{grad}\; C^k_{\mathrm{B}}] \\ & + \mathrm{div}\left[M^k\left(\frac{\beta^k}{\rho^k D^k} - \eta^k\right)\boldsymbol{g}\right] \\ & - (C^k_{\mathrm{A}})^{-1}[(-\rho^k D^k\, \mathrm{grad}\; C^k_{\mathrm{B}} \\ & + M^k \boldsymbol{g} + \rho^k \delta^k\, \mathrm{grad}\; T^k) \cdot \boldsymbol{g}] + \phi^k. \end{aligned} \quad (23)$$

In addition, the Gibbs relation must hold and equations of state must be specified.

2.3. *The Gibbs relation and equation of state*

Developing the conservation laws and constitutive relations in the previous section we did not pay attention to the phase change process. The particular phases in our model can only be distinguished by introducing the equation of state, which would be subject to the phase diagram and the Gibbs relation.

Modelling the process at a macroscopic level we employ the assumption of local thermodynamic equilibrium, which in turn implies the validity of the equilibrium phase diagram of the alloy locally. Consider an elementary cell P which is small enough to possess nearly uniform properties. The entire cell P thus belongs to one of the three continua, E^{L}, E^{S} or E^{I}. For simplicity, we assume that the liquid and solid curves in the equilibrium phase diagram can be written as $C_{\mathrm{B}} = f^k(T)$, $k = \mathrm{L, S}$, where f^k are continuous functions. Further, we assume that the possible phases for the cell P are

$$\begin{aligned} & P \in E^{\mathrm{L}} \Leftrightarrow C_{\mathrm{B}} \leqslant f^{\mathrm{L}}(T) \\ & P \in E^{\mathrm{S}} \Leftrightarrow C_{\mathrm{B}} \geqslant f^{\mathrm{S}}(T) \\ & P \in E^{\mathrm{I}} \Leftrightarrow f^{\mathrm{L}}(T) < C_{\mathrm{B}} < f^{\mathrm{S}}(T) \end{aligned} \quad (24)$$

for definiteness.

The continuum E^{I} has a special character since it is not a pure phase. It may be viewed not only as a superposition of $E^{\mathrm{I}}_{\mathrm{A}}$ and $E^{\mathrm{I}}_{\mathrm{B}}$ but also as that of E^{L} and E^{S} (i.e. as a mixture of liquid and solid). We apply the 'lever rule' and introduce the liquid fraction λ by

$$\begin{aligned} \lambda & = 1 && \text{for} \quad P \in E^{\mathrm{L}} \\ & = \frac{f^{\mathrm{S}}(T) - C_{\mathrm{B}}}{f^{\mathrm{S}}(T) - f^{\mathrm{L}}(T)} && \text{for} \quad P \in E^{\mathrm{I}} \\ & = 0 && \text{for} \quad P \in E^{\mathrm{S}} \end{aligned} \quad (25)$$

in accordance with ref. [4]. Then, any specific quantity X^{I} defined in the inter-phase E^{I} (namely V^{I}, μ^{I}, h^{I}, η^{I}, g^{I}, u^{I}) can be written as

$$X^{\mathrm{I}} = \lambda X^{\mathrm{L}} + (1 - \lambda) X^{\mathrm{S}}. \quad (26)$$

Equation (26) also holds in E^{L} and E^{S}.

In the liquid or solid the Gibbs relation reads

$$\mathrm{d}u = T\,\mathrm{d}s - \sum_i A_i\, \mathrm{d}a_i \quad (27)$$

where A_i are generalized forces, a_i generalized coordinates and s is the specific entropy. We will make use of the well-known thermodynamic relations

$$A_i + \left(\frac{\partial u}{\partial a_i}\right)_{T, a_k \neq a_i} = T\left(\frac{\partial A_i}{\partial T}\right)_{a_i}.$$

Since we have $i = 1, 2$ and

$$A_1 = p, \quad A_2 = -\mu, \quad a_1 = V, \quad a_2 = C_{\mathrm{B}}$$

it follows that

$$\begin{aligned} p + \left(\frac{\partial u}{\partial V}\right)_{T, C_{\mathrm{B}}} & = T\left(\frac{\partial p}{\partial T}\right)_{V, C_{\mathrm{B}}} \\ -\mu + \left(\frac{\partial u}{\partial C_{\mathrm{B}}}\right)_{T, V} & = -T\left(\frac{\partial \mu}{\partial T}\right)_{V, C_{\mathrm{B}}}. \end{aligned} \quad (28)$$

In fact, up to now we tacitly assumed the concentration C_{B} and temperature T to be the primary independent thermodynamic variables describing the state of the continuum in question. However, the internal energy was considered to be a function of the entropy, volume and concentration in (27). To avoid confusion we emphasize that the specific internal energy will be treated as a function of T, V and C_B in what follows and we thus write the equation of state in the form

$$du = \left(\frac{\partial u}{\partial T}\right)_{V,C_B} dT + \left(\frac{\partial u}{\partial V}\right)_{T,C_B} dV + \left(\frac{\partial u}{\partial C_B}\right)_{T,V} dC_B \quad (29)$$

where we have $(\partial u/\partial T)_{V,C_B} = c_V$. Combining (28) and (29), we obtain

$$du = c_V dT - \left[p - T\left(\frac{\partial p}{\partial T}\right)_{V,C_B}\right] dV + \left[\mu - T\left(\frac{\partial \mu}{\partial T}\right)_{V,C_B}\right] dC_B. \quad (30)$$

We now eliminate the derivative $(\partial \mu/\partial T)_{V,C_B}$ from (30). The chemical potentials g_α can be written as

$$g_\alpha(p, T, C_B) = g_\alpha(p(\rho_\alpha, T), T, C_B)$$

and thus

$$\left(\frac{\partial g_\alpha}{\partial T}\right)_{\rho_\alpha,C_B} = \left(\frac{\partial g_\alpha}{\partial T}\right)_{p,C_B} + \left(\frac{\partial g_\alpha}{\partial p}\right)_{T,C_B}\left(\frac{\partial p}{\partial T}\right)_{\rho_\alpha,C_B}$$

where we have $(\partial g_\alpha/\partial p)_{T,C_B} = V_\alpha$. The definitions (1), (2) and (6) imply that $\rho_\alpha, C_B = \text{const.}$ (α arbitrary) if and only if $V, C_B = \text{const.}$ Hence, taking (10) into account we have

$$\left(\frac{\partial \mu}{\partial T}\right)_{V,C_B} = \left(\frac{\partial \mu}{\partial T}\right)_{p,C_B} + (V_B - V_A)\left(\frac{\partial p}{\partial T}\right)_{V,C_B}. \quad (31)$$

Using the notation $\eta = h_B - h_A$ introduced in (8) and applying the second Gibbs–Helmholtz equation

$$h_\alpha = g_\alpha - T\left(\frac{\partial g_\alpha}{\partial T}\right)_{p,C_B}$$

we combine (30) and (31) to get

$$du = c_V dT - \left[p - T\left(\frac{\partial p}{\partial T}\right)_{V,C_B}\right] dV + \left[\eta - T(V_B - V_A)\left(\frac{\partial p}{\partial T}\right)_{V,C_B}\right] dC_B. \quad (32)$$

Further, equations (6) and (2) imply

$$dV = (V_B - V_A)\, dC_B + \sum_\alpha C_\alpha dV_\alpha.$$

Substituting into (32) we can write

$$du = c_V dT - p\, dV + T\left(\frac{\partial p}{\partial T}\right)_{V,C_B} \sum_\alpha C_\alpha dV_\alpha + \eta\, dC_B \quad (33)$$

where $V_\alpha = V_\alpha(T, p, C_B)$, $\alpha = A, B$, satisfy the generalized Gibbs–Duhem equation

$$\sum_\alpha C_\alpha dV_\alpha = \left(\frac{\partial V}{\partial T}\right)_{p,C_B} dT + \left(\frac{\partial V}{\partial p}\right)_{T,C_B} dp. \quad (34)$$

The equation of state is established from the (T, C_B) phase diagram, which implies the assumption of $dp = 0$ locally.† On this assumption, equations (33) and (34) yield

$$du = c_V dT - p\, dV + T\left(\frac{\partial p}{\partial T}\right)_{V,C_B}\left(\frac{\partial V}{\partial T}\right)_{p,C_B} dT + \eta\, dC_B$$

where

$$T\left(\frac{\partial p}{\partial T}\right)_{V,C_B}\left(\frac{\partial V}{\partial T}\right)_{p,C_B} = c_p - c_V.$$

Hence, the final form of the Gibbs relation for the liquid or the solid is

$$du^k = c_p^k dT - p^k dV^k + \eta^k dC_B \quad (k = L, S). \quad (35)$$

In the inter-phase, applying (26) to the energy u and differentiating we have

$$du^I = \lambda\, du^L + (1 - \lambda)\, du^S + (u^L - u^S)\, d\lambda. \quad (36)$$

Now we substitute into (36) from (35), express the specific properties c_p, V and η in accord with (26) and take equations (8), (11) and the assumption $dp = 0$ into account. We thus arrive at

$$du^I = c_p^I dT - p^I dV^I + \eta^I dC_B + L_M d\lambda \quad (37)$$

where $L_M = (u^L - u^S) + p(V^L - V^S) = h^L - h^S$.

Since $d\lambda = 0$ in the liquid or solid (cf. equation (25)), the Gibbs relation

$$du^k = c_p^k dT - p^k dV^k + \eta^k dC_B + L_M d\lambda^k \quad (38)$$

is valid in each of the phases, $k = L, S, I$. Recalling that the process is isobaric locally we note that $V = V(T, C_B)$, $\lambda = \lambda(T, C_B)$ so that (38) can be given in the form

$$du^k = \left(c_p^k + L_M \frac{\partial \lambda^k}{\partial T} - p^k \alpha^k V^k\right) dT + \left(\eta^k + L_M \frac{\partial \lambda^k}{\partial C_B} - p^k \gamma^k V^k\right) dC_B \quad (39)$$

where $c_p^k = c_p^k(T, C_B)$, $\eta^k = \eta^k(T, C_B)$, $L_M = L_M(T)$, $\alpha^k = \alpha^k(T)$ and $\gamma^k = \gamma^k(C_B)$. The equation of state in the form $u = u(T, C_B)$ can now be obtained by the same integration procedure as in ref. [4].

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† This assumption does not contradict the assumption grad $p = \bar{\rho} g$ of (16). The equation of state is based on the local thermodynamic equilibrium, whereas the above assumption regards the dynamics of the system.

2.4. *The model of solidification*

Combining (23) and (39), we obtain the following equations that the unknown quantities ρ, $\mathbf{v}$, T and C_{B} should satisfy:

$$\rho = \bar{\rho}[1-\alpha(T-\bar{T})-\gamma(C_{\mathrm{B}}-\bar{C}_{\mathrm{B}})]$$

$$\operatorname{div}\mathbf{v} = 0$$

$$\rho\frac{\partial\mathbf{v}}{\partial t} = \operatorname{div}(\eta_{\mathrm{v}}\operatorname{grad}\mathbf{v})-\bar{\rho}\boldsymbol{g}[\alpha(T-\bar{T})+\gamma(C_{\mathrm{B}}-\bar{C}_{\mathrm{B}})]$$

$$\rho\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = \operatorname{div}(\rho D\operatorname{grad}C_{\mathrm{B}})-\operatorname{div}(M\boldsymbol{g}) -\operatorname{div}(\rho\delta\operatorname{grad}T)$$

$$\begin{aligned}\rho\left(c_p+L_{\mathrm{M}}\frac{\partial\lambda}{\partial T}-p\alpha V\right)\frac{\mathrm{d}T}{\mathrm{d}t} &= \operatorname{div}[(k-\eta\rho\delta)\operatorname{grad}T\\ &\quad +(\eta\rho D-\beta)\operatorname{grad}C_{\mathrm{B}}]+\left(\eta+L_{\mathrm{M}}\frac{\partial\lambda}{\partial C_{\mathrm{B}}}-p\gamma V\right)\\ &\quad \times[\operatorname{div}(\rho\delta\operatorname{grad}T)+\operatorname{div}(M\boldsymbol{g})-\operatorname{div}(\rho D\operatorname{grad}C_{\mathrm{B}})]\\ &\quad +\operatorname{div}\left[M\left(\frac{\beta}{\rho D}-\eta\right)\boldsymbol{g}\right]-(C_{\mathrm{A}})^{-1}(-\rho D\operatorname{grad}C_{\mathrm{B}}\\ &\quad +M\boldsymbol{g}+\rho\delta\operatorname{grad}T)\cdot\boldsymbol{g}+\phi. \end{aligned} \tag{40}$$

This system of equations is understood to hold in a distributional sense in the entire domain occupied by the alloy. We suppose that the material properties α, γ, η_{v}, D, k, δ, β, M, L_{M} and the heat sources or sinks are determined experimentally. Furthermore, an equilibrium phase diagram is supposed to be known, giving the possibility to determine $\lambda = \lambda(T, C_{\mathrm{B}})$. The initial and boundary conditions for equations (40) follow from the experimental situation.

3. DISCUSSION

The model of solidification based on the system of equations (40) is still rather complicated. In fact, second-order effects are taken into account in this model. For example, the influence of the forced diffusion due to gravitational forces (represented by the parameter M in our model) can be neglected in many cases [8]. Putting $M \approx 0$ and $\operatorname{grad} M \approx 0$ in (40) and neglecting the radiation term ϕ, the diffusion and heat equations become

$$\rho\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = \operatorname{div}(\rho D\operatorname{grad}C_{\mathrm{B}})-\operatorname{div}(\rho\delta\operatorname{grad}T)$$

$$\begin{aligned}\rho\left(c_p+L_{\mathrm{M}}\frac{\partial\lambda}{\partial T}-p\alpha V\right)\frac{\mathrm{d}T}{\mathrm{d}t} &= \operatorname{div}[(k-\eta\rho\delta)\operatorname{grad}T\\ &\quad +(\eta\rho D-\beta)\operatorname{grad}C_{\mathrm{B}}]+\left(\eta+L_{\mathrm{M}}\frac{\partial\lambda}{\partial C_{\mathrm{B}}}-p\delta V\right)\\ &\quad \times[\operatorname{div}(\rho\delta\operatorname{grad}T)-\operatorname{div}(\rho D\operatorname{grad}C_{\mathrm{B}})]\\ &\quad -(C_{\mathrm{A}})^{-1}(-\rho D\operatorname{grad}C_{\mathrm{B}}+\rho\delta\operatorname{grad}T)\cdot\boldsymbol{g}. \end{aligned} \tag{41}$$

If we simplify further and consider the case of $\rho = \text{const.}$ (i.e. $\alpha = \gamma = 0$) and $\mathbf{v} = \mathbf{0}$, then the diffusion equation will be the same as in (41), whereas the heat equation becomes

$$\begin{aligned}\rho\left(c_p+L_{\mathrm{M}}\frac{\partial\lambda}{\partial T}\right)\frac{\mathrm{d}T}{\mathrm{d}t} &= \operatorname{div}(k\operatorname{grad}T-\beta\operatorname{grad}C_{\mathrm{B}})\\ &\quad +L_{\mathrm{M}}\frac{\partial\lambda}{\partial C_{\mathrm{B}}}[\operatorname{div}(\rho\delta\operatorname{grad}T)-\operatorname{div}(\rho D\operatorname{grad}C_{\mathrm{B}})]\\ &\quad -[\operatorname{grad}\eta+(C_{\mathrm{A}})^{-1}\boldsymbol{g}]\cdot(\rho\delta\operatorname{grad}T-\rho D\operatorname{grad}C_{\mathrm{B}}). \end{aligned} \tag{42}$$

In this case, the only difference between our simplified model and the model of Alexiades *et al.* [9, 10] is the gravity term in the energy equation (42).

We feel, however, that this term itself cannot explain the influence of gravity on solidification phenomena. Roughly speaking, this influence would be significant if we had $|(C_{\mathrm{A}})^{-1}\boldsymbol{g}| \gtrsim |\operatorname{grad}\eta|$ in the simplified model. We think that this is not the case in most experimental situations. For example, the data given in refs. [9, 10] regarding the solidification of CuNi and HgTe–CdTe alloys indicate that $|\operatorname{grad}\eta|$ is two to four orders of magnitude greater than $|(C_{\mathrm{A}})^{-1}\boldsymbol{g}|$ in terrestrial conditions.

Therefore, it is reasonable to assume that the influence of the gravitational field on solidification processes will be manifested through the influence of $\boldsymbol{g}$ on the fluid flow and thus a model taking convection in the melt into account is necessary to study solidification under different gravity conditions. This paper presents an attempt at constructing a relatively simple model of this type.

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UN MODELE DE LA SOLIDIFICATION D'UN ALLIAGE BINAIRE AVEC CONVECTION DANS LE BAIN

Résumé—La solidification d'un alliage binaire est étudiée sur un modèle à trois phases (solide, liquide, boue). Les équations de bilan du modèle sont formulées globalement sur toute la région occupée par l'alliage et sont traitées dans un sens distributionnel. On prend en compte les phénomènes convectifs, dans le bain et l'influence du champ de gravité. On discute la signification du modèle pour étudier les mécanismes de la solidification sous différentes conditions gravitaires.

EIN MODEL FÜR DIE ERSTARRUNG EINER ZWEISTOFFLEGIERUNG MIT KONVEKTION IN DER SCHMELZE

Zusammenfassung—Die Erstarrung einer Zweistofflegierung wird mit Hilfe eines Dreiphasenmodells (Feststoff, Flüssigkeit, Verfestigungszone) untersucht. Die Bilanzgleichungen des Modells sind für das gesamte von der Schmelze eingenommene Gebiet global formuliert und werden als verteilt angesehen. Konvektion in der Schmelze sowie Einflüsse des Schwerefeldes werden berücksichtigt. Die Bedeutung des Modells für die Untersuchung von Verfestigungsvorgängen bei unterschiedlichen Gravitationsbedingungen wird diskutiert.

МОДЕЛЬ ЗАТВЕРДЕВАНИЯ БИНАРНОГО РАСПЛАВА ПРИ НАЛИЧИИ КОНВЕКЦИИ

Аннотация—На терехфазной модели (твердое тело, жидкость, пористая зона) исследуется затвердевание бинарного расплава. Дается глобальная формулировка модельных уравнений баланса для всей области, занятой расплавом, и проводится анализ распределения расплава. Учитываются конвективные явления в расплаве и влияние гравитационного поля. Обсуждается роль модели в изучении процессов затвердевания при различных условиях гравитации.