

Alloy solidification problems

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The classical statement of the alloy solidification problem, and a weak formulation of this problem which is the basis of both analytical and numerical work are described. Some numerical methods are outlined and results in both one and two space dimensions are shown. From these results arises a discussion of some open questions relating to so-called 'mushy regions', cellular and dendritic solidification, and the modelling of surface tension effects.

1. Introduction

The problem of modelling the solidification of a binary alloy involves coupled heat conduction and mass diffusion of the solute. Unlike the classical Stefan problem of freezing a pure substance, where the solidification temperature is constant in the alloy problem the phase change temperature is determined by the local concentration of the solute. In certain situations the phase change temperature may also depend on other parameters, such as the velocity or curvature of the interface. At the phase change surface the latent heat is released as the material solidifies, and the concentration of the solute is also discontinuous. Thus the process of alloy solidification is described by a pair of coupled parabolic equations with an unknown moving boundary (the phase change surface), the position of which is to be determined by requiring that certain conditions must be satisfied there. This problem has attracted considerable interest in recent years, following the advances made in the mathematical treatment of the classical Stefan problem. The possible effects of fluid convection in the melt will not be considered in this paper.

The description of the solidification history of an alloy and the consequent redistribution of the solute is a problem of importance in many physical situations. In metallurgical processes solute redistribution during solidification may have a detrimental effect on the strength of the alloy produced.

Problems of this type also arise in the fabrication of semi-conductor devices, where pure substrate material is doped with an impurity by ion bombardment, and the crystalline damage is repaired using a high temperature annealing process.

In this paper a weak formulation of such problems will be outlined. This conservation form is the starting point of most mathematical analyses and numerical techniques which have been developed. In the following section some numerical methods which have proved suitable for both one and two dimensional calculations will be described, and some typical solutions shown. There arise, in subsequent sections, some interesting questions as to the occurrence of regions where solid and liquid phases coexist (i.e. mushy regions), and whether these are related to the cellular and dendritic growth regimes seen experimentally when a planar interface becomes unstable due to constitutional supercooling.

We commence now with a description of the classical statement of the alloy solidification problem as given by Rubinstein [1]. In this model it is assumed that heat transport is due solely to molecular heat conduction; both the energy flux associated with the mass flux at constant temperature and the cross-diffusion terms are neglected. Likewise the solute propagates by mass diffusion alone. For simplicity the thermal conductivity k , specific heat σ , and the diffusion coefficient D , are taken as piecewise constant in each phase and the density is normalised to unity. The governing equations are then:

Heat conduction

$$\sigma \frac{\partial u}{\partial t} = k_i \nabla^2 u, \quad i = s, L \quad (1)$$

Solute diffusion

$$\frac{\partial c}{\partial t} = D_i \nabla^2 c, \quad i = s, L \quad (2)$$

where u denotes temperature, c solute concentration, and t time. The subscripts s, L denote quantities pertaining to the solid, liquid phases respectively. On the phase change surface $S(x, t) = 0$ energy conservation gives

$$L \frac{\partial S}{\partial t} = [k_i \nabla u \cdot \nabla S]_s^L \quad (3)$$

and mass conservation

$$[c]_s^L \frac{\partial S}{\partial t} = [D_i \nabla c \cdot \nabla S]_s^L \quad (4)$$

where $[f]$ denotes the jump in the quantity f on crossing $S(x, t) = 0$. Here L denotes the latent heat of the pure solvent.

The state of the material with given values of u and c is determined from the equilibrium diagram, which for a dilute binary alloy is typically as shown in Fig. 1. Here the solidification temperature of the pure solvent has been chosen as the origin of the temperature scale for convenience. If the local values of u and c are such that $u - m_L c > 0$ then the material is in the stable liquid phase, while if $u - m_s c < 0$ then the material is in the stable solid phase. If $m_s c < u < m_L c$ then the material is not in chemical equilibrium. For some solvent and solutes the effect of the solute is to raise the solidification temperature, corresponding to an equilibrium diagram where liquidus and solidus lines have positive slope.

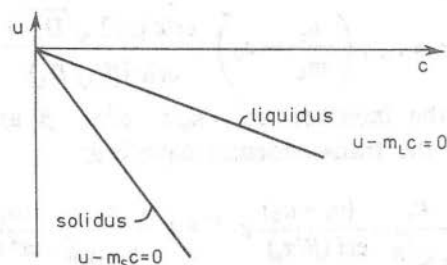


Fig. 1.

Assuming that the material at the phase change surface is in chemical equilibrium and that the temperature is continuous there, the conditions there may be written as

$$u = m_s c_s = m_L c_L, \quad (5)$$

and there exists a concentration discontinuity at the surface with

$$c_s = \frac{m_L}{m_s} c_L. \quad (6)$$

The ratio m_L/m_s is known as the distribution coefficient. The equations (1) and (2), together with conditions (3)–(6) at the phase change surface and appropriate conditions on the fixed boundaries and initially, complete the classical statement of the alloy problem.

As is the case for the classical Stefan problem, there is an analytical solution for a one-dimensional quenching problem in terms of error functions, which is given in [1]. On a semi-infinite region the alloy problem as given by (1)–(6) with initial conditions

$$u(x, 0) = u_0 > 0, \quad c(x, 0) = c_0, \quad (7)$$

and boundary conditions

$$u(0, t) = u_1 < 0, \quad \frac{\partial c}{\partial x}(0, t) = 0, \quad (8)$$

$$u(x, t) \rightarrow u_0, c(x, t) \rightarrow c_0 \text{ as } x \rightarrow \infty$$

has the solution

$$\begin{aligned} S(t) &= 2\beta t^{\frac{1}{2}} \\ u &= u_1 + (u_s - u_1) \frac{\operatorname{erf}(x/2\alpha_s \sqrt{t})}{\operatorname{erf}(\beta/\alpha_s)} \quad 0 < x < s(t) \\ c &= u_s/m_s \\ u &= u_0 + (u_s - u_0) \frac{\operatorname{erfc}(x/2\alpha_L \sqrt{t})}{\operatorname{erfc}(\beta/\alpha_L)} \quad x > s(t) \\ c &= c_0 + \left(\frac{u_s}{m_L} - c_0 \right) \frac{\operatorname{erfc}(x/2\sqrt{D_L t})}{\operatorname{erfc}(\beta/\sqrt{D_L})} \end{aligned} \quad (9)$$

where $x = s(t)$ is the interface, $\alpha_s^2 = k_s/\sigma$, α_L^2/σ , β and u_s are determined as the solutions of the transcendental equations

$$L\beta = \frac{k_s}{\alpha_s \sqrt{\pi}} \frac{(u_s - u_1)}{\operatorname{erf}(\beta/\alpha_s)} e^{-\beta^2/\alpha_s^2} + \frac{k_L}{\alpha_L \sqrt{\pi}} \frac{(u_s - u_0)}{\operatorname{erf}(\beta/\alpha_L)} e^{-\beta^2/\alpha_L^2} \quad (10)$$

and

$$\beta \left(\frac{u_s}{m_L} - \frac{u_s}{m_s} \right) = \frac{\sqrt{D_L}}{\sqrt{\pi}} \frac{(u_s/m_L - c_0)}{\operatorname{erfc}(\beta/\sqrt{D_L})} e^{-\beta^2/D_L},$$

which are obtained by substituting from the above expressions for temperature and concentration into (3) and (4). It is shown in [1] that a solution of these exists. This analytical solution may be used to test the accuracy of numerical methods for the solution of (1)–(6).

2. Weak formulation

We next consider the weak formulation of the problem stated above, employing a similar approach to that used in the enthalpy formulation of the classical Stefan problem [2]. This approach has been successfully extended to the treatment of other moving boundary problems governed by a single parabolic or elliptic partial differential equation [3, 4]. Here the enthalpy variable is defined by

$$H = \begin{cases} \sigma u & \text{if } u - m_s c < 0, \\ \sigma u + L & \text{if } u - m_L c > 0. \end{cases} \quad (11)$$

For the solute diffusion problem, the concentration, being discontinuous at the phase change surface, is an enthalpy-like variable. The condition $m_s c_s = m_L c_L$ at the interface is simply a statement of the continuity of the

chemical potential, or equivalently the chemical activity, at the interface. For dilute solutions, where the temperature range is not too great, the chemical activity may be taken as proportional to the solute concentration (see Guggenheim [5]). Thus we introduce the chemical activity normalised so that

$$v = -m_i c_i \quad (12)$$

in each phase. The mass diffusion equation (2) then becomes

$$\frac{\partial c}{\partial t} = \nabla \cdot (D'_i \nabla v) \text{ where } D'_i = -D_i/m_i$$

Thus, as for the classical Stefan problem, we have

$$\frac{\partial H}{\partial t} = \nabla \cdot (k_i \nabla u), \quad \frac{\partial c}{\partial t} = \nabla \cdot (D'_i \nabla v) \quad (13)$$

with the constitutive relations

$$H = \begin{cases} \sigma u \\ \varepsilon [\sigma u, \sigma u + L] \\ \sigma u + L \end{cases}, \quad C = \begin{cases} -v_s/m_s & \text{if } u+v < 0 \\ \varepsilon [-v_s/m_s, -v_L/m_L] & \text{if } u+v = 0 \\ -v_L/m_L & \text{if } u+v > 0 \end{cases} \quad (14)$$

Across any surface of discontinuity the jump conditions for (13a,b) are precisely the conditions (3,4) of energy and solute conservation. These equations may therefore be regarded as holding throughout the region occupied by the material provided the derivatives are understood in a weak or distributional sense. Hence (13) and (14) are known as the conservation form of the alloy solidification problem. Denoting (H, c) by \underline{H} and (u, v) by \underline{u} the equations may be written as

$$\frac{\partial \underline{H}}{\partial t} = \nabla \cdot (\kappa_i \nabla \underline{u}),$$

where

$$\kappa_i = \begin{pmatrix} k_i & 0 \\ 0 & D'_i \end{pmatrix}.$$

A weak solution $\{H, u\}$ of (15), (14) is defined as a pair of bounded measurable vector functions related by (14), such that $\nabla \underline{u}$ is integrable, the boundary conditions are satisfied on $\partial\Omega$, and

$$\int_0^T \int_{\Omega} \left(\underline{H} \cdot \frac{\partial \underline{\Phi}}{\partial t} - \kappa \nabla \underline{u} \cdot \nabla \underline{\Phi} \right) dX dt = - \int_{\Omega} \underline{H}(\underline{x}, 0) \cdot \underline{\Phi}(\underline{x}, 0) dX \quad (16)$$

is satisfied for all vector test functions $\underline{\Phi} = (\Phi_1, \Phi_2)$, such that Φ_1, Φ_2 have continuous first order partial derivatives and $\Phi(x, T) = 0, \Phi|_{\partial\Omega} = 0$. (16) may

be derived from (15) by taking the dot product of (15) with Φ and integrating by parts, using the jump conditions (3) and (4) at the phase change surface.

It should be noted that this definition of the weak solution is different from that commonly used for the classical Stefan problem (see for example the treatment in [6] in that only integration has been performed on the term $\Phi \nabla \kappa \cdot \nabla u$). For a pure substance, where the phase change temperature is constant, it is usual to use the Kirchhoff transformation

$$\tilde{u} = \int_0^u k(r) dr$$

to transform $\nabla \cdot (k \nabla u)$ to $\nabla^2 \tilde{u}$. The weak solution to a problem with boundary data $u|_{\partial\Omega} = g$, is then defined as a pair of bounded measurable functions (H, u) , related by (14a), such that

$$\begin{aligned} \int_0^T \int_{\Omega} \left(H \frac{\partial \Phi}{\partial t} + u \nabla^2 \Phi \right) dx dt &= \\ &= - \int_{\Omega} H(x, 0) \Phi(x, 0) dx + \int_0^T \int_{\partial\Omega} g \frac{\partial \Phi}{\partial n} dx dt \end{aligned} \quad (17)$$

is satisfied for all test functions Φ such that Φ , $\frac{\partial \Phi}{\partial t}$, $\frac{\partial^2 \Phi}{\partial x_i \partial x_j}$ exist and are continuous, $\Phi(x, T) = 0$, and $\Phi|_{\partial\Omega} = 0$. For the alloy problem the phase boundary, at which the thermal conductivity and diffusion coefficient may be discontinuous, is defined by $u+v=0$. Thus the thermal conductivity (diffusion coefficient) is not determined as a function of temperature (chemical activity) alone but depends also on the phase, so a transformation of Kirchhoff type is not available.

In the derivation of the conservation form (13) and the weak solution (16) it has been assumed that a sharp interface between the solid and liquid phases exists. This is not necessarily so. For pure substances it has been shown that in problems of melting by volume heat sources a mushy region, where $u=0$ and $0 < H < L$, is formed [7]. This may be interpreted as a region where solid and liquid phases coexist on a microscopic scale, with the temperature equal to the melting temperature to leading order (see Lacey & Tayler [8] for a discussion of the modelling of mushy regions in a pure material). Thus in modelling the alloy problem the possibility of mushy regions, now defined as regions where $m_s c < H < m_L c + L$ and $u+v \equiv 0$, must be considered. Following Chalmers [9] we assume that in such a region the material may be regarded as a fraction f solid and $(1-f)$ liquid, with concentrations in each part corresponding to the solidus and liquidus

concentrations at that temperature. Then

$$\begin{aligned} H &= \sigma u + (1-f)L, \\ c &= fc_s + (1-f)c_L, \end{aligned}$$

where $u = m_L c_L = m_s c_s$. The diffusion coefficient and thermal conductivity in such a region may be defined as weighted averages of their solid and liquid values, and the governing equations (13) still hold. This treatment is essentially that used in both [10] and [11, 12]. We shall return to mushy regions and their physical interpretation in a later section of this paper.

3. Numerical solution

Two distinct approaches to the numerical solution of the alloy solidification problem as described above have been employed. Both of these use the conservation form of the equations (13) and the constitutive relation (14). One approach is to use a straightforward explicit finite difference scheme [10], while the other uses a time discretisation leading to a system of quasi-variational inequalities [11, 12]. In this section both schemes are outlined, using one space dimension for simplicity.

Writing $H_n^i = H(n\delta x, i\delta t)$ where $\delta x, \delta t$ are the step lengths in the x and t directions respectively, an explicit finite difference scheme for (13) is

$$\begin{aligned} H_n^{i+1} &= H_n^i + \frac{\delta t}{\delta x^2} k_n^i (u_{n+1}^i - 2u_n^i + u_{n-1}^i) \\ C_n^{i+1} &= C_n^i + \frac{\delta t}{\delta x^2} D_n^i (v_{n+1}^i - 2v_n^i + v_{n-1}^i). \end{aligned} \quad (19)$$

Having determined values of H_n^{i+1} , c_n^{i+1} , u_n^{i+1} and v_n^{i+1} are calculated from the inverse of (14). In order to invert (14), suitable values of u, v corresponding to values of H, c in the region $m_s c < H < m_L c + L$ between the solidus and liquidus in the equilibrium diagram must be found. This is achieved by regarding this region as a mushy region where solid and liquid coexist, as discussed above. Eliminating f, c_s and c_L from (18), and taking the root of the resulting quadratic which corresponds to $u = H/\sigma$ on the solidus, $(H-L)/\sigma$ on the liquidus yields

$$\begin{aligned} u &= u^* = \\ &= \frac{-(Lm_L + H(m_s - m_L)) - \{(Lm_L + H(m_s - m_L))^2 + 4Lm_s m_L(m_L - m_s)C\}^{\frac{1}{2}}}{2(m_L - m_s)\sigma}. \end{aligned} \quad (20)$$

The complete inversion of (14) is then

$$u = \begin{cases} H/\sigma \\ u^* \\ (H-L)/\sigma \end{cases}, \quad v = \begin{cases} -m_s c & \text{if } H - m_s c < 0 \\ -u^* & \text{if } m_s c < H < m_L c + L \\ -m_L c & \text{if } H - m_L c > L. \end{cases} \quad (21)$$

This numerical scheme extends readily to two-dimensional calculations, where (19a) is replaced by

$$H_n^{i+1} = H_n^i + \frac{\delta t}{\delta x^2} k_n^i (u_{n+1}^i - 2u_n^i + u_{n-1}^i) + \frac{\delta t}{\delta y^2} k_n^i (u_{n+1}^i - 2u_n^i + u_{n-1}^i), \quad (22)$$

and (19b) is modified similarly. The advantage of the finite difference scheme is that it is straightforward to program.

In problems where there is a sharp interface between liquid and solid phases, it has been observed that a slight oscillation occurs near the interface in the temperature and concentration histories at a point. This is analogous to the oscillation seen when the usual finite difference scheme for the enthalpy method is applied to a classical Stefan problem. This oscillation may be removed by using an improved discretisation near the interface, following the approach used by Tacke [13] for the classical Stefan problem. The modified discretisation for the alloy problem is described in [14]. Figs. 2 and 3 show the temperature and concentration histories at $x = 0.1$, as computed using both discretisations, for the quenching problem described, above. Here the parameters used were $u_0 = 1$, $c_0 = 0.1$, $u_1 = -1$, $L = 1$, $D'_s = D'_L = 1$, $k_s = k_L = 1$, $m_s = -1$ and $m_L = -0.5$. With the improved discretisation the oscillations are removed; the computed results for the temperature history are indistinguishable from the analytical solution.

The alternative approach developed by Bermudez and Saguez [11, 12] is as follows. The governing equations (13) are supplemented by (14) written as

$$H \in H_v(u), \quad c \in G_u(v).$$

Introducing $V = H^1(\Omega)$ and V' the dual space, and the operators

$$(A(u, v), z)_{V', V} = \int_{\Omega} k \nabla u \cdot \nabla z \, d\Omega$$

$$(B(u, v), z)_{V', V} = \int_{\Omega} D' \nabla v \cdot \nabla z \, d\Omega$$

and $h(t)$ defined by

$$(h(t), z)_{V', V} = \int_{\partial\Omega} q(\tau) z \, d\tau,$$

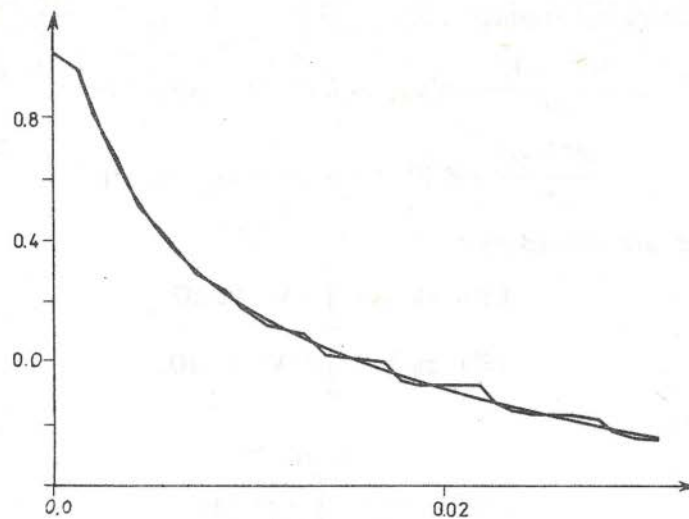


Fig. 2.

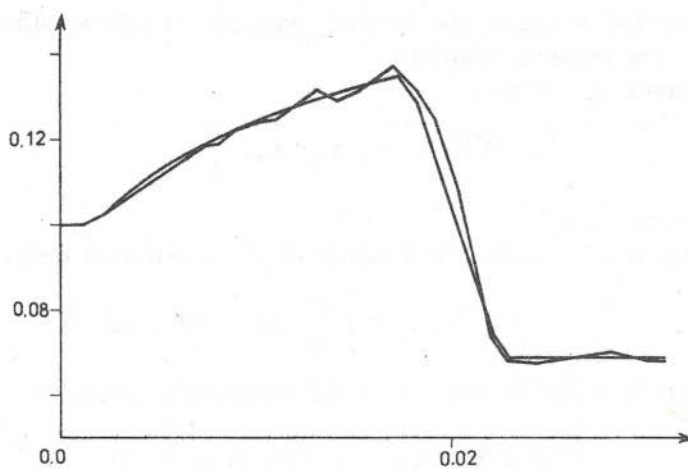


Fig. 3.

the global formulation

$$\frac{\partial H}{\partial t} + A(u, v) = h, \quad H \in H_v(u),$$

$$\frac{\partial c}{\partial t} + B(u, v) = 0, \quad c \in G_u(v),$$

with appropriate initial conditions is obtained. Here $q(t)$ denotes the prescribed heat flux across the boundary. Discretisation in time then yields the system

of quasi-variational inequalities:

$$\frac{H^{i+1} - H^i}{\delta t} + A^i u^{i+1} = h^{i+1}, H^{i+1} \in H_{V^{i+1}}(u^{i+1}),$$

$$\frac{c^{i+1} - c^i}{\delta t} + B^i v^{i+1} = 0, c^{i+1} \in G_{u^{i+1}}(v^{i+1}).$$

Here A^i, B^i are defined by

$$(A^i u, z)_{V', V} = \int_{\Omega} k^i \nabla u \cdot \nabla z \, d\Omega$$

$$(B^i v, z)_{V', V} = \int_{\Omega} D^i \nabla v \cdot \nabla z \, d\Omega,$$

and h^{i+1} by

$$h^{i+1} = \frac{1}{\delta t} \int_{i\delta t}^{(i+1)\delta t} h(\tau) \, d\tau.$$

It may be shown that for fixed H^i, c^i, u^i, v^i there exists a unique solution $H^{i+1}, c^{i+1}, u^{i+1}, v^{i+1}$, of the discretised problem.

For numerical solution, the method proceeds as follows (the algorithm given is for the minimal solution)

i) Compute v^{i+1} from

$$\frac{-m_s v^{i+1}}{\delta t} + B^i v^{i+1} = \frac{v^i}{\delta t}$$

ii) $j = 0, v_0^{i+1} = v^{i+1}$

iii) Compute H_k^{i+1} from the solution of the variational inequality

$$\frac{H_k^{i+1}}{\delta t} + A^i u_k^{i+1} = h^{i+1} + \frac{u^i}{\delta t}, H_k^{i+1} \in H_{v_k^{i+1}}(u_k^{i+1}).$$

iv) Compute c_{k+1}^{i+1} the solution of the variational inequality

$$\frac{c_{k+1}^{i+1}}{\delta t} + B^i v_{k+1}^{i+1} = \frac{c^i}{\delta t}, c_{k+1}^{i+1} \in G_{u_k^{i+1}}(v_{k+1}^{i+1}).$$

Iterations are then continued on iii) and iv) until convergence to the required accuracy is achieved. Results for the one-dimensional problem from the two numerical methods are virtually identical (private communication).

4. Extensions of the basic model

We have thus far considered the simplest model for alloy solidification, with constant thermal and mass diffusion coefficients, constant specific heat and straight liquidus and solidus lines in the equilibrium diagram. This

approach is used for clarity in the explanation of the basic problem and numerical methods. We now consider the removal of such restrictions to obtain more realistic models.

It is straightforward to allow the thermal conductivity and mass diffusion coefficients to be functions of temperature and activity. The governing equations (1), (2), then become

$$\sigma \frac{\partial u}{\partial t} = \nabla \cdot (k_i \nabla u), \quad \frac{\partial c}{\partial t} = \nabla \cdot (D_i \nabla c),$$

with corresponding modifications to the finite difference scheme (19).

If the specific heat σ is a function of temperature the alterations are slightly more complex. Firstly, if σ is different in the two phases the boundary condition at the phase change surface (3) becomes

$$[H]_s^L \frac{\partial S}{\partial t} = (L + (\sigma_L - \sigma_s) u) \frac{\partial S}{\partial t} = [k_i \nabla u \cdot \nabla S]_s^L$$

because the heat content or enthalpy is given by

$$H = \begin{cases} \sigma_s u, & u+v < 0, \\ \varepsilon [\sigma_s u, \sigma_L u + L], & u+v = 0, \\ \sigma_L u, & u+v > 0. \end{cases}$$

If the boundary condition were not modified in this way the heat content would be dependent on the precise conditions at which the material changed phase, that is, on the past history of the material. This boundary condition fits immediately into the weak formulation of the problem. When σ_s, σ_L are functions of temperature, the enthalpy is given by

$$H = \begin{cases} \int_0^u \sigma_s(\tilde{u}) d\tilde{u}, & u+v < 0 \\ \varepsilon \left[\int_0^u \sigma_s(\tilde{u}) d\tilde{u}, \int_0^u \sigma_L(u) du + L \right], & u+v = 0 \\ \int_0^u \sigma_L(\tilde{u}) d\tilde{u} + L, & u+v > 0. \end{cases}$$

In each case the inversion of (14) to express (u, v) in terms of (H, c) for the finite difference numerical solution becomes more complex, but the equivalent of (21) may be obtained.

The equilibrium diagram shown in Fig. 1 is of the form, with straight liquidus and solidus lines, usually employed in the analysis of dilute binary alloy solidification problems, that is ones in which the solute concentration is small. In more general cases, when a range of concentrations from pure substance A to pure substance B may be obtained the equilibrium diagram may be of forms shown below.

In the first case, suppose the liquidus is given by $u = f_L(c)$, the solidus

by $u = f_s(c)$. Then $u - f_L(c) > 0$ is the stable liquid region of the equilibrium diagram, $u - f_s(c) < 0$ is the stable solid region. The activity v is defined by $v = f_L(c)$ in the liquid phase, and by $v = f_s(c)$ in the solid. The mass diffusion equation in the liquid may then be written

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) = \nabla \cdot \left(\frac{D}{f'_L(f_L^{-1}(v))} \nabla v \right)$$

together with a similar equation in the solid phase. This is discussed briefly in [11].

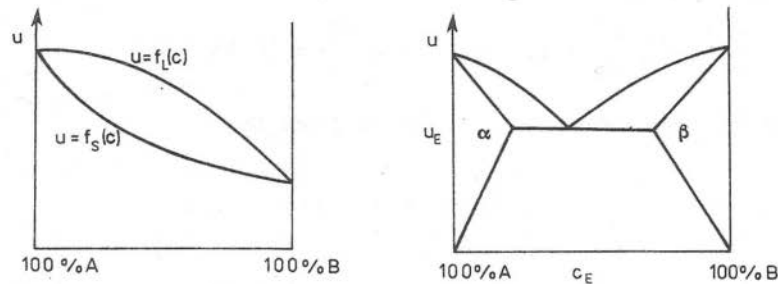


Fig. 4.

If the phase diagram is of the second type, then the point (c_E, u_E) is known as the eutectic point. To the left of this point solidification occurs in which substance B is rejected into the melt and vice versa to the right of (c_E, u_E) . If material solidifies at the eutectic point, then no segregation occurs on a macroscopic scale, but microscopic lamellae of solids α and β are formed parallel to the direction of solidification. (The interpretation of equilibrium diagrams and eutectic solidification are discussed at length in Flemings [15]). On each side of the eutectic point the activity may be defined as above.

Another approach to the modelling of alloy solidification problems has been employed by Donnelly [16] and Luckhaus and Visintin [17]. This is based on the ideas of non-equilibrium thermodynamics, and yields a specific form of the equations

$$\frac{\partial w}{\partial t} = -\nabla \cdot J$$

where $w = (H, c)$ and J is a generalised flux defined by a constitutive relation of the form

$$J = F(w, \nabla U)$$

$$U = \frac{\partial s(w)}{\partial w}, \quad -s \text{ a given convex function,}$$

U being given by $(1/u, -\mu/u)$. Here $\mu (= Ru \ln v$ in our earlier notation) is the chemical potential of the solute, and F is coercive in its second argument. In [16] the existence of a unique weak solution is proved for the particular case

$$J = L \nabla U, \quad L \text{ a real symmetric matrix,}$$

when the problem can be transformed into a variational inequality. In [17] the existence of a weak solution is proved for more general F , but without uniqueness. This form of the equations includes cross-diffusion terms (that is a heat flux due to mass transport in the thermal equation and vice versa) in the governing equations. These terms are usually considered as negligibly small, allowing the system to be simplified to one of the form (15) with variable coefficients. The disadvantage of this approach is that the coefficients in the governing equations have a specific dependence on temperature and activity so that flexibility is lost. While this approach has proved useful for mathematical results concerning existence and uniqueness it has not yet, to the author's knowledge, been used to obtain numerical solutions.

5. Mushy regions and allied open questions

It has been implicitly assumed thus far that a sharp interface between solid and liquid phases exists, although the possibility of a two-phase region was mentioned in section 2. In this section we discuss briefly the stability of a planar interface to small perturbations, and the link with dendritic growth. Also mentioned is the evidence of numerical solutions, indicating the need for more detailed modelling of such phenomena. The use of asymptotic methods in this role is discussed elsewhere in this volume [18].

To metallurgists it is well known that if a binary alloy is cooled unidirectionally in such a way that the liquid in front of the solidification interface has concentration and temperature values for which $u - m_L c < 0$, then the interface becomes unstable and cellular growth (shown schematically in Fig. 5) occurs. If $u - m_L c < 0$, the liquid has entered the metastable region between the liquidus and solidus on the equilibrium diagram, and is said to be constitutionally supercooled (so called as this usually occurs from a drop in local solute concentration causing a rise in the phase-change

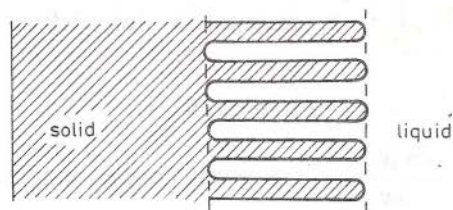


Fig. 5.

temperature). In cellular growth there are essentially three distinct regions in the solidifying material, as shown in Fig. 5. Typically the aspect ratio of the 'fingers' is in the region of 100:1 to 500:1. If sidearms form on the fingers, the growth is said to be dendritic. This occurs as the degree of constitutional supercooling is increased.

A perturbation analysis of the stability of a phase-change surface moving at constant velocity [19] yields the criterion that when

$$-\frac{1}{2} \left(\frac{k_s}{k_s + k_L} \frac{\partial u}{\partial x} \Big|_s + \frac{k_L}{k_s + k_L} \frac{\partial u}{\partial x} \Big|_L \right) + m_L \frac{\partial c}{\partial x} \Big|_L < 0$$

the interface is stable. Here it is assumed that the solute diffusion coefficient in the solid phase may be taken as zero, and that surface tension effects are negligible. This criterion is similar to the constitutional supercooling criterion, except that the thermal gradient in the liquid is replaced by a weighted average of the gradients on the solid and liquid sides of the interface. The analysis shows the shortest wavelength perturbations grow fastest. Adding surface tension effects to the model modifies the liquidus condition (5) to

$$u - m_L c = -\gamma K, \quad (23)$$

where γ is related to the solid/liquid interfacial energy, and K is the curvature of the interface (positive when convex towards the liquid). This change stabilises very short wavelength perturbations, and determines a preferred wavenumber at which perturbations grow fastest.

For a quenching problem of the type described in section 1, it is found that constitutional supercooling occurs in the analytical solution if $(D_L \sigma / k_L) \ll 1$. A mushy region then appears in the numerical solution with either of the methods based on the weak formulation described in section 3. Thus the weak formulation yields a solution with a two-phase region when the sharp interface becomes unstable.

As cells/dendrites are so thin in comparison with their length, for a one dimensional model the cellular/dendritic region may be regarded as the coexistence of liquid and solid phases. That is, the mushy region seen

numerically is in some sense a crude representation of a zone of cellular/dendritic growth. For a more realistic representation, improved models of the structure of the solute and temperature fields in the region of the dendrite tips are required. Information from these could then be incorporated in the weak formulation through changes to the relationship of (u, v) to (H, c) for $m_s c < H < m_L c + L$. Towards this end local models near the dendrite tips, using asymptotic methods on the length scale of the cell spacing, are currently being studied [18].

Another work which considers the use of weak solutions and the existence of two-phase regions is that by Avdonin [20]. Here averaged equations for heat and mass transport within the two-phase region are derived to yield a system of equations which is parabolic in the sense of Petrovskii. The crystallisation regime envisaged, volume crystallisation or equiaxed growth, is slightly different from that described in this paper. Equiaxed growth occurs when detached solid crystals nucleate in the supercooled melt ahead of the fully solid region, and is most commonly seen when the melt is initially constitutionally supercooled.

An interesting open problem is that of finding a suitable weak formulation for computational work when surface tension effects are included so that the liquidus condition is (23). With such a formulation it might be possible to follow the evolution of a planar interface towards a cellular growth regime as constitutional supercooling develops. Some discussion of weak formulations with surface tension effects is given by Rogers [21]. Solutions of the problem have been obtained numerically in the two-dimensional case using front-tracking methods, but these methods are somewhat cumbersome and lack the elegance of weak solution techniques.

In certain situations of extremely rapid solidification, such as occur in the laser annealing of semi-conductor devices with implanted dopant, another effect is found. At solidification rates of m/sec, rather than the more usual cm/hr, the phase change temperature is depressed below its equilibrium value by an amount dependent on the front velocity. This phenomenon, known as kinetic undercooling, occurs when the time for an atom to be incorporated into the crystalline structure becomes significant, and is an example of non-equilibrium solidification. In the laser annealing case the kinetic undercooling dominates the freezing point depression due to the solute concentration. The boundary condition on the phase-change surface $x = s(t)$ (with liquid on the left) becomes

$$u + v = \frac{\beta ds}{dt}$$

where β is zero if the liquid phase is advancing, $\beta > 0$ if the solid phase is growing. Numerical solutions can be obtained for this problem using

the method described in [14], which is basically a weak solution approach although the front position is explicitly calculated.

Postscript

It is hoped that this paper gives the reader some of the flavour of alloy solidification problems, and will serve as a useful introduction to the recent mathematical work in this area. The study of moving boundary problems such as this is applicable to a variety of physical processes, the modelling of some of the phenomena is far from complete, and there are as yet few mathematical results for such systems. It is a challenging field in which to work.

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Problemy zastygania stopów

Praca dotyczy problemów zastygania stopów. Badane są sformułowania klasyczne i uogólnione (słabe) problemów, będące podstawą rozważań zarówno analitycznych jak i numerycznych. Przedstawione zostają pewne metody numeryczne łącznie z wynikami obliczeń w przypadku jedno- i dwuwymiarowym. Wyniki te stanowią podstawę dyskusji wielu otwartych problemów związanych z tzw. obszarami mieszanymi, zastyganiem komórkowym i dendrytycznym, jak również z modelowaniem efektów naprężenia powierzchniowego.

Проблемы затвердевания сплавов

В работе обсуждается классическую и обобщенную (слабую) формулировку проблемы затвердевания сплавов, лежащие в основе так аналитических как и численных рассуждений. Представляются численные методы решения этих задач, включены тоже результаты численных экспериментов в одно- и двухмерных случаях. Эти результаты приняты основой дискуссии ряда открытых вопросов касающихся так называемых „mushy regions”, клеточного и дендритного затвердевания, кроме того моделирования эффектов поверхностного напряжения.

