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Self-similar regime of thermally controlled solidification of binary melts

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Abstract—When heat supply to a binary melt at its outer boundary is absent, macrokinetics of solidification are governed by progressive cooling of the melt rather than by withdrawal of an admixture. Because the former process is much faster than the latter one, a metastable region of concentrational supercooling arises and has time to expand before the ingot surface noticeably changes its position. This leads to bulk crystallization within such a region prior to solidification at the surface. If crystalline grains are forming and growing rapidly enough, the two-phase region is practically at the state of thermodynamic equilibrium. This case is considered under the assumptions that the melt phase diagram consists of straight liquidus and solidus lines with one eutectic point and that the physical parameters are constant. A simple self-similar solution of relevant equations is obtained which approximately describes unidirectional processes.

1. INTRODUCTION AND BACKGROUND

THE RATE of solidification of binary melts and solutions is usually supposed to be determined by that of mass transport of an admixture either to or from the crystallization front [1, 2]. Accordingly, the time scale of solidification then happens to be of the same order of magnitude as the relaxation time of the concentration field. The latter quantity, $t_D \sim l^2/D$ (l is the characteristic length and D is the diffusivity of the admixture in the liquid), is several orders of magnitude higher than the thermal relaxation time $t_a \sim l^2/a$, a being the thermal diffusivity. That is why the temperature fields in both the melt and the alloy can be regarded as quasi-stationary during such a solidification process.

This is encountered in practice if the heat released at the interface is removed through an ingot and there is a heat influx to a melt so that the actual temperature remains higher throughout the melt than the phase transition temperature, depending upon the admixture concentration. When the front velocity increases, there may appear an adjoining layer of concentrational supercooling where the relation between the temperatures mentioned is reversed [3]. This results in the initiation of a two-phase mushy region containing solid phase elements formed by either a system of growing dendrites or newly born crystals. As a consequence, the front ceases to be sharp and exhibits a complicated dendritic interface. The establishment of a steady regime is possible when the front velocity (u) and the mushy zone thickness ($\sim D/u$) are constant or quasi-stationary, depending on externally imposed conditions. Macrokinetics of solidification are governed, as before, by the rate of mass transfer. Considerable theoretical and experimental attempts have been and are being made in order to elucidate characteristics of dendritic interface growth and of the mushy zone structure (see, for example, refs. [4–9]).

If there is no two-phase zone adjoining the front, the processes of directional solidification are studied theoretically in a standard manner with the help of the known Stefan problem. Otherwise, the necessity arises to deal with the temperature and admixture concentration fields within the zone, which requires tedious and rather cumbersome numerical calculation, with the results obtained being hardly of much help to ensure better understanding of the physics of the problem [8, 9]. However, when the zone thickness is much smaller than the pertinent linear scales of the process under consideration, the zone itself may be successfully regarded as an interface of zero thickness. Then a new formulation of the corresponding mathematical problem with an unknown boundary is conceivable, which modifies the Stefan problem by means of replacing the mass balance condition at a smooth interface with a new one stemming from the analysis of the zone structure. The latter condition has been formulated so far for the cases when the zone can be thought of as being approximately in the state of thermodynamic equilibrium [10]. This enables one to apply the well-developed mathematical technique to processes with a mushy zone and to derive physically transparent conclusions.

The situation changes radically when there is no heat supply to the melt from an environment, as is the case, for example, in all solidification processes in closed cavities externally cooled at their boundaries. A thermal wave propagates into the melt much faster than the crystallization front moves and, thus, the metastable supercooled region, which allows new crystals to form, rapidly becomes very wide. It has to cover, in fact, all the liquid region in question before the front appreciably changes its position, if the con-

NOMENCLATURE

a	thermal diffusivity
A, A'	coordinates of the outer and inner boundaries of the two-phase region (functions of time)
B, B'	dimensionless forms of A, A', defined by equations (15)
c	dimensionless concentration
C	specific thermal capacity
D	diffusivity of the admixture in the liquid
H	length of experimental cell
k	equilibrium solute distribution coefficient
l	characteristic length
L	latent heat of freezing
m	liquidus slope
n, R	dimensionless parameters, equations (5) and (6)
t	time
T	dimensionless temperature
u	characteristic velocity scale
x	coordinate
z	dimensionless variable, equation (11).

Greek symbols

α	parameter
ε	dimensionless parameter, equation (9)
θ	temperature
λ	thermal conductivity
π	$\pi = 3.14\ldots$
ρ	density
σ	concentration
φ	concentration of the solid phase in the two-phase region.

Subscripts

a	thermal
D	diffusional
e	eutectic
L	liquid
s	solid
$*$	referred to phase transition of pure solvent
∞	initial and at infinity
0	cold boundary.

cept of temperature quasi-stationarity is presumed. New crystals, are able, then, to grow on either spontaneously arising critical nuclei or impurities everywhere in the melt. The onset of a steady regime of the solidification process is impossible under these conditions. This shows that the idea of the process being governed by slow diffusional transport is incorrect under the present circumstances, and one needs to treat the mushy zone evolution by taking account of much lower time scales specific to heat conduction. On the other hand, just for that reason one is free to neglect diffusion and, consequently, the front motion while studying both the zone expansion and the growth of crystals inside the zone.

Strangely enough, and as far as the authors are aware of, the existence and significance of such thermally controlled processes of directional solidification have not been clearly indicated, with the exception of the freezing of natural water solutions in porous media and some other geophysical phenomena [11, 12]. Nevertheless, there are many experiments witnessing the formation of discrete crystals far ahead of the crystallization front at casting [13, 14] and a few attempts to attack the problem theoretically have been made [15]. It seems that the most simple and entirely convincing experimental confirmation of the above reasoning is provided, perhaps, by a bottle of beer or mineral water taken out of a freezing chamber.

If the temperature of an external cooler is above that of the eutectic point, the final state of the melt presents a suspension of microscopically inhomogeneous crystalline grains in an ambient liquid medium in which the admixture concentration coincides with the eutectic one.

The inequality $t_a \ll t_D$ follows from $D \ll a$, which always holds and ensures that the above reasoning is sound when only the molecular diffusion is present. Another situation takes place where there is a convective flow near the front due to either the crystal–melt density difference or the natural convection caused by the melt density dependence upon temperature and concentration variations in the gravity field and stimulating double-diffusive phenomena [16–18]. In this case the convection dominates the mass transfer and an additional time scale appears, $t_u \sim l/u$, u being the characteristic velocity scale. It is easy to see that the main conclusion concerning feasibility of thermally controlled solidification of binary melts remains true when $t_a \ll t_u$, that is, when $l \gg a/u$. The latter inequality imposes a restriction from above onto the size l of the system under study. The restriction may well be fulfilled in many practicable applications.

The structure of the metastable mushy region depends, first of all, upon the relation between the kinetics of both the origin and growth of solid grains and the rate of the region broadening. When the latter is much slower than the former, the region is clearly near the thermodynamic equilibrium. Its temperature then coincides with that of the phase transition at any point. This property permits the heat and mass transfer problem to be stated in the mushy region without going into particulars of the solid phase formation. It is worth noting that a reduction in the degree of metastability, attained through bringing down the supercooling, leads to the heat release inside the region and so somewhat hinders the melt cooling and diminishes the velocity of the outer region boundary.

2. STATEMENT OF THE PROBLEM

Let us consider a semi-space $x > 0$ filled with a binary melt whose initial temperature θ_∞ and concentration σ_∞ are uniform. For the sake of simplicity, the relevant portion of the melt phase diagram is assumed to consist of two straight liquidus and solidus lines with one eutectic point, as shown in Fig. 1. The incline parameter m of the liquidus and the equilibrium solute distribution coefficient k are both constant. Let the temperature at the plane $x = 0$ be reduced at an initial moment $t = 0$ to a value $\theta_0 < \theta'_* = \theta_* - m\sigma_\infty$, where θ_* designates the phase transition temperature of a pure solvent. Then a metastable region forms near the plane and begins to broaden into the melt. The coordinate $A(t)$ of its outer boundary, which can be conveniently defined as that corresponding to $\theta(t, A) = \theta'_*$, is a monotonously increasing function of time, $A(0) = 0$. If θ_0 happens to be smaller than even the eutectic temperature θ_e, a front of complete solidification also appears at $x = A'(t)$, $A'(0) = 0$, and follows the thermal wave of cooling so that the regions $0 < x < A'(t)$, $A'(t) < x < A(t)$ and $A(t) < x < \infty$ are occupied with the solid alloy, two-phase mixture and with the liquid melt, respectively.

Below we neglect, in accordance with the above discussion, a slow process of either purely diffusive or convective solute mass transfer in all the regions indicated and assume the condition of thermodynamic equilibrium to be approximately valid inside the two-phase region. In order to leave the main ideas unencumbered with superfluous details, we also suppose that the pertinent physical parameters are independent of temperature and solute concentration. This leads to the following set of equations governing the transfer in the alloy:

$$\rho_s C_s \frac{\partial \theta_s}{\partial t} = \lambda_s \frac{\partial^2 \theta_s}{\partial x^2}, \quad 0 < x < A'(t) \tag{1}$$

in the nearly equilibrium two-phase region

$$\rho C \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial \theta}{\partial x}\right) + \rho_s L \frac{\partial \varphi}{\partial t}, \quad \theta = \theta_* - m\sigma$$

$$\frac{\partial}{\partial t}[(1-\varphi)\sigma] + k\sigma \frac{\partial \varphi}{\partial t} = 0, \quad A'(t) < x < A(t) \tag{2}$$

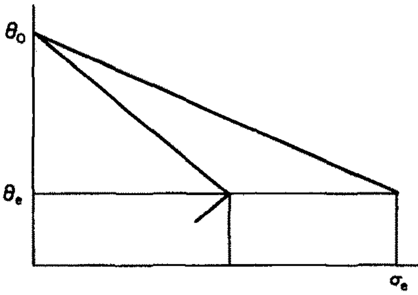

FIG. 1. A sketch of the phase diagram used in the analysis.

and in the melt

$$\rho_L C_L \frac{\partial \theta_L}{\partial t} = \lambda_L \frac{\partial^2 \theta_L}{\partial x^2}, \quad \sigma_L = \sigma_\infty, \quad A(t) < x < \infty. \tag{3}$$

Here φ denotes the concentration of the solid phase in the two-phase mixture by volume, ρ, C, λ and L are the density, the specific thermal capacity, the heat conductivity and the latent solidification heat, respectively, and the subscripts s and L mark quantities pertaining to the solid and liquid phases. The heat capacity per unit volume of the mixture is defined as follows:

$$\rho C = \varphi \rho_s C_s + (1-\varphi)\rho_L C_L.$$

In accordance with the mixture rule, an expression of this kind should be used for the effective thermal conductivity. This rule, however, is applicable merely to heterogeneous systems whose phases or ingredients possess identical topological properties. This is evidently not the case for disperse mixtures when there is no continuous infinite cluster formed by particles of the dispersed phase, and

$$\lambda = \lambda_L F(\varphi, \lambda_s/\lambda_L)$$

where F is a certain function of its arguments depending on the type of particle packing and on the form of the particles. There are many empirical and theoretical formulae for F cited, some in ref. [19]. However, to simplify the matter further we assume the density and the thermophysical properties of the phases to be roughly the same, that is, $\rho = \rho_s = \rho_L$, $C = C_s = C_L$ and $\lambda = \lambda_s = \lambda_L$.

However far fetched it sometimes is, the concept of the state of the two-phase mixture, being close to that of thermodynamic equilibrium, simplifies the problem to a great extent by means of enabling one to omit a kinetic equation governing the evolution of the distribution of crystals over their size.

The solution of equations (1)–(3) is subject to the following initial and boundary conditions:

$$t = 0: \quad A'(0) = A(0) = 0, \quad \theta_L(0, x) = \theta_\infty$$

$$x = 0: \quad \theta_s(t, 0) = \theta_0 < \theta_L$$

$$x = A'(t): \quad \theta_s(t, A') = \theta(t, A') = \theta_e$$

$$\lambda\left(\frac{\partial \theta_s}{\partial x} - \frac{\partial \theta}{\partial x}\right) = \rho L (1-\varphi) \frac{dA'}{dt}$$

$$x = A(t): \quad \theta(t, A) = \theta_L(t, A) = \theta'_* = \theta_* - m\sigma_\infty$$

$$\frac{\partial \theta}{\partial x} = \frac{\partial \theta_L}{\partial x}, \quad \varphi(t, A) = 0$$

$$x \to \infty: \quad \theta(t, x) \to \theta_\infty. \tag{4}$$

It is easy to see that there are two excessive conditions at the two-phase region boundaries as compared with the set of boundary conditions needed for a correct formulation of the mathematical problem. These serve to find the functions $A'(t)$ and $A(t)$. There is no condition on φ at the solid surface $x = A'(t)$ since the requirement for φ to be equal to unity, which is sometimes used, is obviously wrong. On the contrary, the condition of this quantity being equal to zero at $x = A(t)$ results from the binodal line equation.

The third equation in (2) can be integrated without difficulty. By taking into account the conditions at $x = A(t)$ from equation (4) one gets a familiar relationship [9, 10]

$$\varphi = 1 - \frac{1}{c^n}, \quad c = \frac{\sigma}{\sigma_\infty}, \quad n = \frac{1}{1-k}. \tag{5}$$

The second equation also yields

$$T = T_* - Rc, \quad \{T, T_*\} = \frac{\{\theta, \theta_*\}}{\theta_\infty}, \quad R = \frac{m\sigma_\infty}{\theta_\infty}. \tag{6}$$

Allowance for equations (5) and (6) in equations (1)–(4) leads to a boundary problem containing the equations

$$\frac{\partial T_s}{\partial t} = \frac{\lambda}{\rho C}\frac{\partial^2 T_s}{\partial x^2}, \quad 0 < x < A'(t)$$

$$\left(\frac{1}{c^{1+n}} + \varepsilon\right)\frac{\partial c}{\partial t} = \frac{m\sigma_\infty \lambda}{n\rho L}\frac{\partial^2 c}{\partial x^2}, \quad A'(t) < x < A(t)$$

$$\frac{\partial T_L}{\partial t} = \frac{\lambda}{\rho C}\frac{\partial^2 T_L}{\partial x^2}, \quad A(t) < x < \infty \tag{7}$$

and initial and boundary conditions

$$t = 0: \quad A'(0) = A(0) = 0, \quad T_L(0, x) = 1$$

$$x = 0: \quad T_s(t, 0) = T_0, \quad x \to \infty: \quad T_L(t, x) \to 1$$

$$x = A'(t): \quad T_s(t, A') = T_* - Rc_e, \quad c(t, A') = c_e$$

$$\frac{\partial T_s}{\partial x} + R\frac{\partial c}{\partial x} = \frac{\rho L}{\theta_\infty \lambda c_e^n}\frac{dA'}{dt}$$

$$x = A(t): \quad T_L(t, A) = T_* - R, \quad c(t, A) = 1,$$

$$\frac{\partial T_L}{\partial x} + R\frac{\partial c}{\partial x} = 0. \tag{8}$$

Here c_e is the eutectic concentration divided by σ_∞, $T_0 = \theta_0/\theta_\infty$ and a dimensionless parameter

$$\varepsilon = m\sigma_\infty C/nL \tag{9}$$

is introduced in addition to the quantities defined in equations (5) and (6).

The problem (7), (8) can be readily extended to cases when the boundary temperature θ_0 is larger than θ_e. To do so, one has to make allowance for only two regions occupied by the liquid and the two-phase mixture. In this case there is no region which would be entirely solid. The second and third equations in (7) hold good again but the former one is now defined within the range $0 < x < A(t)$. The conditions (8) are also retained, except that those at $x = 0$ and $x = A(t)$ have to be replaced with

$$x = 0: \quad T(t, 0) = T_0,$$

$$c(t, 0) = c_0 = R^{-1}(T_* - T_0) > c_e. \tag{10}$$

In both cases generalization to solidification within a finite region is performed in quite a straightforward way. This amounts merely to substitution of a boundary condition imposed at the external boundary $x = X$ for that at $x \to \infty$ in equation (8). Likewise, it is simple to extend the formulation of equations (7) and (8) to non-unidirectional solidification processes by means of replacing $\partial^2/\partial x^2$ by the Laplace operator and $\partial/\partial x$ in equation (8) by the operations of differentiation over respective coordinates normal to interfaces separating distinct regions which now replace the planes $x = A'(t)$ and $x = A(t)$. Thus, the statement of the problem suggested above is suitable, in fact, for a rather wide range of applications.

Let us emphasize once more that there is a principal difference between diffusionally and thermally controlled processes of directional solidification. In the first case the temperature fields have time to adjust themselves to the solute concentration field in a melt and become, in this manner, quasi-stationary, whereas in the second case the latter field has practically no time to change noticeably and so has to be regarded as a steady one.

3. SELF-SIMILAR PROCESSES

In order to make the basic physical features of the thermally controlled solidification clearer it is expedient, as usual, to consider relatively simple examples allowing an analytical treatment. Self-similar regimes, if they exist, offer a good opportunity to do so. Let us bring into play a new dimensionless variable

$$z = \left(\frac{n\rho L}{2m\sigma_\infty \lambda t}\right)^{1/2} x, \tag{11}$$

and assume all the unknown variables to be dependent solely on z. We then get from equation (7) the equations

$$\frac{\partial^2 T_s}{\partial z^2} + \varepsilon z\frac{\partial T_s}{\partial z} = 0, \quad 0 < z < B'$$

$$\frac{d^2 c}{dz^2} + z\left(\frac{1}{c^{1+n}} + \varepsilon\right)\frac{\partial c}{\partial z} = 0, \quad B' < z < B$$

$$\frac{d^2 T_L}{\partial z^2} + \varepsilon z\frac{\partial T_L}{\partial z} = 0, \quad B < z < \infty \tag{12}$$

and from equation (8) the conditions

$$z = 0: \quad T_s(0) = T_0, \quad z \to \infty: \quad T_L(z) \to 1$$

$$z = B': \quad T_s(B') = T_* - Rc_e, \quad c(B') = c_e$$

$$z = B: \quad T_L(B) = T_* - R, \quad c(B) = 1 \tag{13}$$

and also

$$z = B: \quad \frac{dT_L}{dz} + R\frac{dc}{dz} = 0$$

$$z = B': \quad B' = \frac{nc_e^n}{R}\left(\frac{dT_s}{dz} + R\frac{dc}{dz}\right). \tag{14}$$

The parameters n, R and ε are defined in equations

(5), (6) and (9). The dimensional coordinates of the boundary planes are found from

$$\{A', A\} = \{B', B\}\left(\frac{2m\sigma_\infty \lambda}{n\rho L}\right)^{1/2} t^{1/2}. \tag{15}$$

A beneficial property of the problem (12), (13) consists in that it splits into three separate problems for each of the unknown variables which may be treated quite independently. A link between the latter problems is due only to conditions (14). Without going into particulars, we point out that the same property is also inherent in more complicated problems listed at the end of the preceding section. It helps to a considerable degree to simplify the analysis. Solving these separate problems enables one to calculate the derivative in equation (14) and to determine both B' and B and, subsequently, A' and A.

Another possible approach is justified by the notion that the parameter ε is usually small as compared with unity. Simple evaluation shows that $\varepsilon < 0.05$–0.06, $\varepsilon < 3\times10^{-3}$ and $\varepsilon < 5\times10^{-5}$ for water solutions of various salts and Fe–Ni and Al–Cu melts, respectively. Actually this parameter is proportional to the ratio of the inner melt overheat corresponding to the temperature difference $m\sigma_\infty$ to the latent solidification heat. This permits the use of the classical perturbation method by means of introducing expansions of quantities of interest in powers of ε:

$$\{T_s, T_L, c, B', B\} = \sum_{j=0}^{\infty} \varepsilon^j\{T_s, T_L, c, B', B\}. \tag{16}$$

In a general case this procedure can be shown to be a singular one requiring special means of regularization. If we restrict ourselves only to the first approximation, then the equations in both the ingot and the melt take the simplest form, $d^2T/dz^2 = 0$. The boundary condition imposed on the first one can be easily fulfilled. It is not so, however, for the equation in the infinite region which is due to a singularity caused by the infiniteness of the region. Really, however small the parameter ε may be, the requirement of the second term in this equation in set (12) being much smaller than the first one is inevitably violated far away from the plane $z = B$. Bearing in mind that managing such singularities can be readily effected by means of the well-developed procedure of matching of asymptotic expansions and presents no principal difficulty in the problem under consideration, we restrict ourselves in what follows to a simple case when $T_* - R = 1$. It is worthwhile noting that results are also approximately valid if $1-(T_*-R) \ll 1-T_e$, which is quite common in practice. In this case

$$T_s = T_0 + (T_e - T_0)z/B', \quad T_L = 1 \tag{17}$$

and the problem for c from equations (12)–(14) becomes

$$\frac{d^2c}{dz^2} + \frac{z}{c^{1+n}}\frac{dc}{dz} = 0, \quad c(B') = c_e,$$

$$c(B) = 1, \quad \left.\frac{dc}{dz}\right|_{z=B} = 0. \tag{18}$$

The last condition results from the first one in equation (14) and serves to determine B.

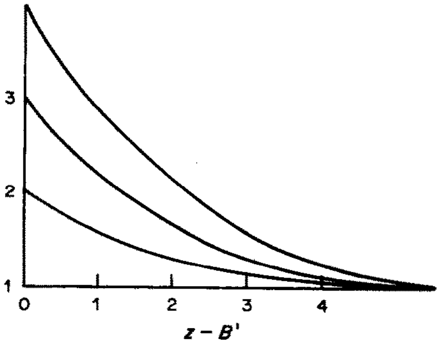

FIG. 2. Dimensionless distributions of the solute concentration of the liquid phase within the two-phase region; $k = 0.1$.

Dependences of c upon z at different c_e are plotted in Fig. 2. They describe the distribution of concentration inside the mushy region expanding without bound. If a solidification process is developing in a finite range, the curves in Fig. 2 also characterize the process until plane $x = A(t)$ reaches the external boundary. After that, the process loses its self-similar nature. The same curves also determine the quantity B depending on c_e as on a parameter. The dependence of $B - B'$ upon c_e is shown in Fig. 3.

Taking account of equation (17), one gets from the second condition in equation (14)

$$(B')^2 + nc_e^n\left|\frac{dc}{dz}\right|_{z=B'}\cdot B' - \frac{nc_e^n}{R}(T_e - T_0) = 0$$

whence

$$B' = \frac{nc_e^n}{2}\left\{\left[\left(\frac{dc}{dz}\right)^2_{z=B'} + \frac{4(T_e-T_0)}{Rnc_e^n}\right]^{1/2} - \left.\frac{dc}{dz}\right|_{z=B'}\right\}. \tag{19}$$

This determines the solid surface motion if the con-

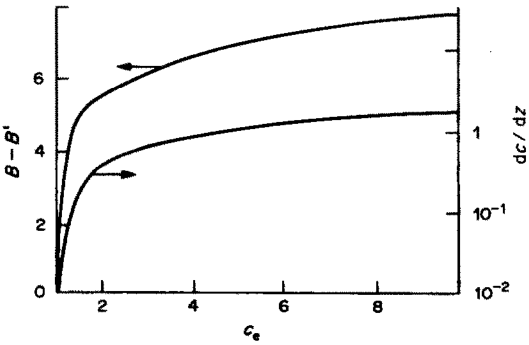

FIG. 3. Dependences of B–B' and dc/dz at $z = B'$ on c_e; $k = 0.1$.

centration derivative is known. The latter can be found from the solution of equation (18) and is illustrated in Fig. 3.

The temperature and the volume concentration of the dispersed phase within the mushy region are now calculated from equations (5) and (6). The form of the temperature distribution repeats that of the profile of concentration $c(z)$, whereas $\varphi(z)$ depends essentially on n. Typical dependences of φ on z at different n are presented in Fig. 4.

To give an idea of the effect of the initial overheat of the melt, we consider, without going into particulars, results following from the solution of the above equations in the region $z > B$ at $T_* - R < 1$. The rigorous solution leads to

$$T_{\mathrm{L}}(z) = 1-(1-(T_*-R))\,\mathrm{erfc}\,(\sqrt{(\varepsilon/2)}z)\times[\mathrm{erfc}\,(\sqrt{(\varepsilon/2)}B)]^{-1}$$

$$\left.\frac{\mathrm{d}c}{\mathrm{d}z}\right|_{z=B} = -\frac{1-(T_*-R)}{R}\left(\frac{2\pi}{\varepsilon}\right)^{1/2}\frac{\exp(-\varepsilon z^2/2)}{\mathrm{erfc}\,(\sqrt{(\varepsilon/2)}B)},$$

whereas the utilization of the matching technique for inner and outer asymptotic expansions yields

$$T_{\mathrm{L}}(z) = 1-(1-(T_*-R))\,\mathrm{erfc}\,(\sqrt{(\varepsilon/2)}z)$$

$$\left.\frac{\mathrm{d}c}{\mathrm{d}z}\right|_{z=B} = -\frac{1-(T_*-R)}{R}\left(\frac{2\pi}{\varepsilon}\right)^{1/2}\exp\left(-\frac{\varepsilon z^2}{2}\right)$$

instead of the corresponding relations included in equations (17) and (18). These expressions aid in obtaining small corrections to the values of B and B' derived at $T_* - R = 1$ and $\varepsilon = 0$.

A more detailed discussion of the influence of physical and regime parameters upon both the velocities of the boundary planes and the solute and dispersed phase concentrations within the mushy region is unlikely to be of much use since its nature is rather evident from the formulae presented and from the curves in Figs. 2–4.

In contrast to the usual diffusionally controlled processes, in the case under study the solute concentration in the solid is non-uniform on the linear scale of separate crystalline grains, which are inhomogeneous on the microscopic level. The solid alloy contains the grains and the material of the eutectic composition within the interstices. If $\theta_0 > \theta_e$, the asymptotic state of the two-phase mixture attained at $t \to \infty$ corresponds to a suspension of the grains in a liquid whose composition is determined by c_0 from equation (10). The mushy region structure and the rate of its broadening are again described by the derived formulae and the curves at B' equalling zero and c_e being substituted by c_0.

Figure 5 demonstrates rather close agreement between experimental data obtained in ref. [20] for solidification of n-octadecane–n-hexadecane mixtures and the self-similar interpretation of these experiments according to the present paper. The theory leads to the equation $A/H = \alpha\sqrt{t}$, where H is the length of the experimental cell used in ref. [20]. Theoretical curves obtained by the authors of ref. [20] by means of numerical calculation based on unwarrantable usage of the lever rule are also shown.

4. CONCLUDING REMARKS

The majority of assumptions put forward above to simplify the mathematical part of the analysis are not of principal nature and can be successfully avoided without much difficulty at the cost of complicating the calculation. This statement is also true for extending the theory to problems, the conditioning and geometry of which are more complex than those of the problem actually studied. There are, however, certain points that should be especially stressed.

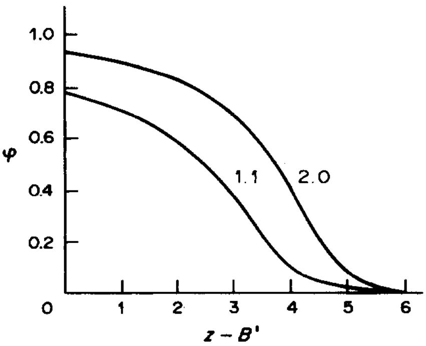

FIG. 4. Distributions of the volume concentration of the solid phase inside the two-phase region at $c_e = 4$ and different n (numerical values on the curves).

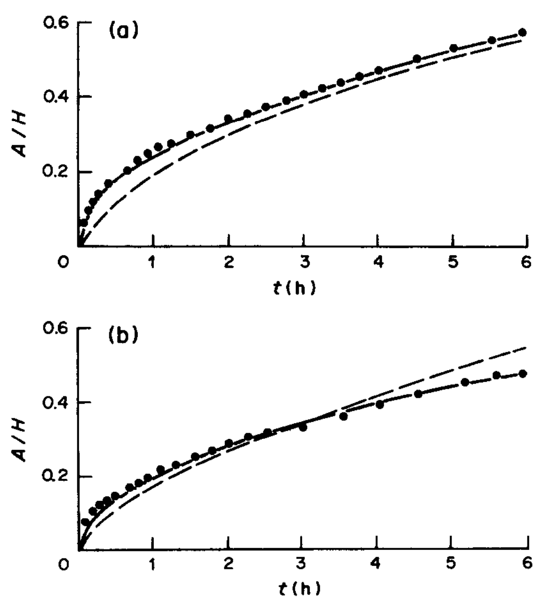

FIG. 5. Propagation of the outer boundary of the metastable region in cooled n-octadecane–n-hexadecane mixtures. Points and dashed lines, experiments and calculation of ref. [20]; solid lines, the self-similar theory of this paper. (a) $\sigma_\infty = 40\%$ (n-hexadecane), $\theta'_* = 18.3$°C, $\alpha = 0.234\ \mathrm{h}^{-1/2}$. (b) $\sigma_\infty = 60\%$, $\theta'_* = 16.2$°C, $\alpha = 0.200\ \mathrm{h}^{-1/2}$.

The first point concerns the neglect of convection irrespective of its origin. Taking into account the convective motion and convective transfer alters the situation rather drastically, even with reference to thermally controlled solidification processes. Really, the form of both the heat and mass conservation equations in the liquid and the two-phase regions undergoes a radical change so that the solution of these equations requires the use of more elaborate methods.

The second point has relevance to solidification inside closed volumes with rigid boundaries and is connected with the alloy–melt density change. Even if the convective transfer due to this reason is negligible, the effect must be accounted for because it results in either an increase or a drop of the pressure depending on the sign of this density change. Variations of the pressure eventually become quite substantial and cause appreciable shifts in the phase equilibrium conditions. This has to be taken into account, beyond doubt, on the final stage of solidification in any closed volume.

Finally, the third point pertains to the necessity of the allowance for deviations of an actual state of the two-phase region from that of thermodynamic equilibrium. This brings into play, along with the transfer equations, a kinetic equation governing the evolution of the crystal size distribution as well as relations describing the rate of crystal origin and growth. Apart from the fact that the deviations affect the thermal wave propagation velocity by decreasing the intensity of inner heat release, they also influence the size and properties of the crystalline grains being incorporated afterwards in the final ingot and, thus, have a bearing on the ingot microstructure. It can be easily imagined that one is able, in principle, to choose the external conditions of solidification in such a way as to try to get a desired structure. A constructive analysis of non-equilibrium effects within the expanding two-phase region can be performed, in principle, on the basis of the consideration and method developed in ref. [21].

In conclusion, it is worthwhile pointing out that thermally and diffusionally controlled processes present extreme models of directional solidification. The mere fact that real processes can differ greatly from such idealization suggests the necessity to obtain corrections for the solute transfer in the first case and for the non-stationarity of temperature in the second case.

All these questions are of primary interest and have to be looked upon, therefore, as certain indications concerning possible expedient directions of further work.

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SOLUTION AFFINE DE LA SOLIDIFICATION THERMIQUEMENT CONTROLEE DE BAINS BINAIRES FONDUS

Résumé—Quand on n'apporte pas de chaleur à travers le contour d'un bain binaire, la macrocinétique de solidification est gouvernée par le refroidissement progressif du bain plutôt que par le retrait d'un composant. Le dernier mécanisme étant plus rapide que l'autre, une région métastable de surrefroidissement concentrationnaire apparaît et elle s'étend avant que la surface du lingot change notablement de position. Ceci conduit à une cristallisation en masse dans une telle région, avant la solidification à la surface. Si les grains de cristaux se forment et croissent suffisamment rapidement, la région biphasique est pratiquement à l'état d'équilibre thermodynamique. On considère ce cas en supposant que le diagramme de phase du bain consiste en des lignes droites de liquidus et solidus avec un point entectique et que les paramètres physiques sont constants. On obtient une simple solution affine des équations qui décrit de façon approchée les mécanismes unidirectionnels.

DAS GEBIET DER SELBSTÄHNLICHKEIT BEI DER THERMISCH GESTEUERTEN VERFESTIGUNG BINÄRER SCHMELZEN

Zusammenfassung—Wird an der äußeren Grenzfläche einer binären Schmelze keine Wärme zugeführt, so wird die Makrokinetik der Verfestigung wesentlich stärker von der fortschreitenden Abkühlung der Schmelze als von den Entmischungsvorgängen bestimmt. Da der Abkühlungsvorgang wesentlich schneller als der Entmischungsvorgang vor sich geht, entsteht ein metastabiles Gebiet mit konzentrationsbedingter Unterkühlung, welches sich so lange ausdehnt bis eine herannahende Oberfläche seine Position wesentlich beeinflußt. Dies führt zu Blockkristallisation innerhalb einer solchen Region noch bevor die Verfestigung an der Grenzfläche auftritt. Wenn sich die Kristallkörner schnell genug bilden und schnell genug wachsen, ist das Zweiphasengebiet praktisch im thermodynamischen Gleichgewicht. Dieser Fall wird unter der Annahme betrachtet, daß die physikalischen Parameter konstant sind, daß im Phasendiagramm die Liquidus- und Soliduslinien Geraden sind, und daß es nur einen Eutektischen Punkt gibt. So wird eine einfache Selbstähnlichkeitslösung der relevanten Gleichungen erhalten, welche die ungerichteten Vorgänge näherungsweise beschreiben kann.

АВТОМОДЕЛЬНЫЙ РЕЖИМ ТЕРМИЧЕСКИ КОНТРОЛИРУЕМОГО ЗАТВЕРДЕВАНИЯ БИНАРНЫХ РАСПЛАВОВ

Аннотация—Если подвод тепла к внешней границе расплва отсутствует, то процесс направленной кристаллизации утрачивает обычный фронтальный характер. Образование твердой фазы одновременно происходит в протяженной нестабильной области, примыкающей к поверхности слитка. Кинетика расширения этой области определяется скоростью распространения тепловой волны охлаждения в глубь расплава, которая на несколько порядков выше скорости диффузионной волны вытеснения движущимся фронтом. Если зарождение и рост кристаллов в метастабильной области происходит достаточно интенсивно, то двухфазная зона является, по-существу, равновесной. Именно эта ситуация рассмотрена в статье в предположении, что фазовую диаграмму сплава образуют прямые линии ликвидуса и солидуса с единственной точкой эвтектики и физические параметры постоянны. Получено простое автомодельное решение для таких термически контролируемых процессов затвердевания.