CONDITION FOR THE STABILITY OF A PLANE INTERFACE BETWEEN SOLID AND LIQUID PHASES DURING CRYSTALLIZATION OF A BINARY ALLOY

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Abstract

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CONDITION FOR THE STABILITY OF A PLANE INTERFACE BETWEEN SOLID AND LIQUID PHASES DURING CRYSTALLIZATION OF A BINARY ALLOY

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If a small protrusion appears on a plane crystallization front, and the crystallization conditions are such that the growth rate at the tip of the protrusion is greater than on the plane front far from it, then the protrusion will elongate. Consequently, the plane front is unstable under these conditions. Loss of stability leads to the formation of cellular and dendritic structures (^{1}). Since the growth rate is proportional to the total heat flux into the solid and liquid phases, in order to determine the condition of stability it is necessary to compare the heat removal from the tip of the protrusion with the heat removal from the plane front. The front is stable if the inequality

$$q_1 + q_2 \leqslant q_{1,0} + q_{2,0}, \tag{1}$$

is satisfied, where $q_{1,0}, q_{2,0}$ are the heat fluxes, respectively, into the solid and liquid phases from the plane crystallization front far from the protrusion; q_1, q_2 are the heat fluxes from the tip of the protrusion. We shall call the criterion (boundary) of stability of a plane crystallization front the set of crystallization conditions ensuring, under a steady thermal regime, the advance with the same velocity of the plane front and of the tip of the protrusion, or, in other words, ensuring that equality holds in expression (1).

Consider a binary alloy for which the distribution coefficient $k = C_1/C_2$ does not depend on concentration (C_1 and C_2 are the concentrations of the second component (impurity) in the solid and liquid phases that are in equilibrium), and the liquidus line is described by the equation $T_k = T_{k,0} - AC_2$ ($T_{k,0}$ is the melting temperature of the pure solvent). An alloy with initial concentration C_0 crystallizes from an infinite stationary melt in such a way that a plane front with a protrusion on it moves at constant velocity v. The temperature of the melt at infinity is T_0. In view of the smallness of the diffusion coefficient of the impurity in the solid phase D_1, we shall take $D_1 = 0$.

Without dwelling on the possible causes and mechanism of formation of the protrusion, we shall regard it as hemispherical with radius ρ (Fig. 1). To determine the heat fluxes q_1 and q_2 of interest to us, it is necessary to solve the problem of the stationary distribution of temperatures $T_i(x,y,z)$ ($i = 1, 2$; index 1 refers to the solid, and 2 to the liquid phase) and concentrations $C_2(x,y,z)$. The formulation of this problem in the moving coordinate system indicated in Fig. 1 can be written as:

$$\Delta T_i + \frac{v}{a_i}\frac{\partial T_i}{\partial z} = 0, \qquad \Delta C_2 - \frac{v}{D_2}\frac{\partial C_2}{\partial z} = 0; \tag{2}$$

$$T_i(x,y,z)\big|_{z=0} = T_{k,0} - AC_2(x,y,z)\big|_{z=0} \quad (\text{for } x^2+y^2 \geqslant \rho^2); \tag{3}$$

$$T_i(x,y,z)\big|_{z=\sqrt{\rho^2-x^2-y^2}} = g\left[T_{k,0} - AC_2(x,y,z)\big|_{z=\sqrt{\rho^2-x^2-y^2}}\right] \quad (\text{for } x^2+y^2 \leqslant \rho^2); \tag{4}$$

$$T_i(x,y,z)\big|_{(x^2+y^2+z^2)\to\infty} = T_{i,0}(z), \qquad C_2(x,y,z)\big|_{(x^2+y^2+z^2)\to\infty} = C_{2,0}(z). \tag{5}$$

In addition, at the crystallization front the conditions of heat balance must be satisfied,

$$\gamma_1 Q v_n = \lambda_1 \frac{\partial T_1}{\partial n} - \lambda_2 \frac{\partial T_2}{\partial n}. \tag{6}$$

and of solute balance,

$$(k-1)C_2 v_n = D_2 \frac{\partial C_2}{\partial n}. \tag{7}$$

Here $a_i = \lambda_i / c_i \gamma_i$ is the thermal diffusivity; λ_i is the coefficient of thermal conductivity; c_i is the heat capacity; γ_i is the density; Q is the heat of crystallization; D_2 is the diffusion coefficient of the solute in the melt; the factor $g = [1 - 2\sigma/\gamma_1 Q \rho]$ takes into account the lowering of the equilibrium temperature at the crystal-melt boundary caused by boundary curvature and the surface tension σ; $\partial/\partial n$ and v_n are the derivative along the normal and the velocity of motion normal to the crystallization front. $T_{i,0}(z)$ and $C_{2,0}(z)$ are the stationary fields of temperatures and concentrations in the absence of, or far from, a protrusion, which are the solution of equations (3) under the conditions (4) and (6)–(7) at $z = 0$:

Fig. 1

$$T_{1,0}(z) = T'_k + \left[(Q/c_1) - (T'_k - T_0)c_2\gamma_2/c_1\gamma_1\right]\left(1 - e^{-vz/a_1}\right),$$

Fig. 1

Figure 1: Fig. 1

$$T_{2,0}(z) = T_0 + (T_k' - T_0)e^{-vz/a_2}, \qquad C_{2,0}(z) = C_0 + C_0\frac{(1-k)}{k}e^{-vz/D_2}, \tag{8}$$

where $T_k' = T_{k,0} - AC_0/k$ is the temperature at the crystallization front.

Since the shape of the crystallization front is prescribed, problem (3)–(7) is overdetermined and has a solution for certain values of the parameters entering into (3)–(7). In order to obtain an approximate solution, we shall prescribe the concentration of the solute at the crystallization front in the form

$$C_2 = (C_0/k) - Bz/\rho, \tag{9}$$

where the constant B is as yet arbitrary. The solution of equations (3)–(5), with allowance for (9), can easily be obtained in spherical coordinates for the liquid phase and in toroidal coordinates (for $v\rho/2a_1 \ll 1$) for the solid.

Without dwelling on the solution, we write the expressions obtained for the heat fluxes from the tip of the protrusion:

$$q_1 = \lambda_1 \left.\frac{\partial T_1}{\partial z}\right|_{\substack{z=\rho\\x=y=0}} = 0.098(1-\varepsilon_1)q_{1,0} - (0.158 - 0.256\varepsilon_1)(1-g)T_k'\left(\frac{\lambda_1}{\rho}\right) +$$

$$+(0.902 - 0.519\varepsilon_1)gAB\frac{\lambda_1}{\rho}; \tag{10}$$

$$q_2 = -\lambda_2 \left.\frac{\partial T_2}{\partial z}\right|_{\substack{z=\rho\\x=y=0}} = 3(1-\varepsilon_2)q_{2,0} - (1.42 + 2.58\varepsilon_2)(1-g)T_k'\left(\frac{\lambda_2}{\rho}\right) +$$

$$+(2 + 1.438\varepsilon_2)gAB\frac{\lambda_2}{\rho} \tag{11}$$

and the solute flux into the melt,

$$q_{\mathrm{m}} = -D_2 \left.\frac{\partial C_2}{\partial z}\right|_{\substack{z=\rho\\x=y=0}} = \frac{2(1-k)\mu D_2}{k\rho}C_0\Psi_1(\mu) - \frac{D_2}{\rho}B\Psi_2(\mu). \tag{12}$$

Here

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

$$\varepsilon_i = \frac{vp}{2a_i}, \quad \mu = \frac{vp}{2D_2}, \quad q_{1,0} = \lambda_1 \left.\frac{dT_{1,0}}{dz}\right|_{z=0} = \frac{2\varepsilon_1\lambda_1}{p}\left[\frac{Q}{c_1} - (T_k' - T_0)\frac{c_2\gamma_2}{c_1\gamma_1}\right],$$

$$q_{2,0} = -\lambda_2 \left.\frac{dT_{2,0}}{dz}\right|_{z=0} = \frac{2\varepsilon_2\lambda_2}{p}(T_k' - T_0).$$

The functions $\Psi_1(\mu)$ and $\Psi_2(\mu)$ up to $\mu = 2$ are presented in Fig. 2. Since the solution was obtained for the case $\varepsilon_i \ll 1$, in expressions (10) and (11) the terms ε_i to the first power have been retained. From expressions (10) and (11) it is seen that heat removal from the tip of the protrusion changes in comparison with the planar front for the following reasons: a) because of the geometry of the protrusion surface (the first terms on the right-hand side of equations (10) and (11)); b) because of the decrease in the equilibrium temperature caused by the curvature of the interface (the second terms); c) because of the increase in the surface temperature of the protrusion associated with a decrease (for $k < 1$) in the impurity concentration (the third terms).

Fig. 2

Fig. 3. 1 $-v \to 0$; 2 $-v = 0.003$ cm/sec;
3–0.007 cm/sec; 4–0.013 cm/sec

The balance conditions (6) and (7) still remain unsatisfied. Since in the solution the approximate expression (9) was used, these conditions cannot be satisfied over the entire surface of the crystallization front. Far from the protrusion, $T_i(x, y, z)$ and $C_2(x, y, z)$ pass into $T_{i,0}(z)$ and $C_{2,0}(z)$, and conditions (6)–(7) are satisfied. Since expression (9) contains one arbitrary constant, we require that (6)–(7) also be satisfied at one more point—at the tip of the protrusion. Then, taking (9)–(12) into account, we have

$$\gamma_1 Q v = q_1 + q_2; \tag{13}$$

$$(1 - k)[(C_0/k) - B]v = q_m. \tag{14}$$

Eliminating B from (13) and (14), we obtain, according to the definition, the equation of the stability boundary. If $\varepsilon_1, \varepsilon_2$ and $(2\sigma/\gamma_1 Q p)$ are neglected in comparison with 1, this equation may be written as

$$C_0 = \frac{k}{(1-k)A}\frac{Q\gamma_1 D_2}{c_2\gamma_2 a_2} f(\mu)\times$$

$$\times\frac{[0.902 + 2.902(\lambda_2 G/\gamma_1 Qv) + 2(1.42 + 0.158\lambda_1/\lambda_2)\lambda_2\sigma T_k'/(\gamma_1 Qp)^2 v]}{2 + 0.902\lambda_{12}\lambda_2} \qquad (15)$$

(here $f(\mu) = [\Psi_2(\mu) - 2\mu(1-k)]/[\Psi_1(\mu) - 1]$, $G = (dT_{2,0}/dz)_{z=0} = -q_{2,0}/\lambda_2$).

For the ratio of parameters determined by equation (15), problem (3)–(7) has a solution and the tip of the hemispherical protrusion moves-

moves with the same velocity v as the planar crystallization front. For C_0 less than the value given by equation (15), the velocity of motion of the tip is less than v, and the planar front is stable; for larger C_0, the velocity at the tip is greater than v, and the front is unstable.

For $C_0 = 0$, from (15) we obtain the expression for the stability boundary in the case of crystallization of a pure substance*

$$\frac{G}{v} = -0.311\,\frac{\gamma_1 Q}{\lambda_2} - \frac{2(1.42 + 0.158\lambda_1/\lambda_2)\,\sigma T_{k,0}'}{2.902\gamma_1 Q\rho^2 v}. \qquad (16)$$

The position of the stability boundary depends on the radius of the protrusion ρ. For a certain $\rho = \rho_0$ satisfying the equation:

$$\mu_0^3 F(\mu_0) = \frac{v}{2D_2^2}\,\frac{(1.42 + 0.158\lambda_1/\lambda_2)}{(0.902 + 2.902\lambda_2 G/\gamma_1 Qv)}\,\frac{\lambda_2\sigma T_k'}{(\gamma_1 Q)^2}, \qquad (17)$$

where $\mu_0 = v\rho_0/2D_2$ and $F(\mu) = f'(\mu)/[2f(\mu) - \mu f'(\mu)]$, the concentration C_0 is minimal. Equations (15) and (17) jointly describe such an optimal position of the stability boundary that, for given G and v, the planar crystallization front is always stable if the alloy concentration is less than C_0, regardless of the magnitude of the protrusion that appears on it.

In Fig. 3, the results of the experimental determination of the stability boundary for a Pb–Sn alloy (Sn impurity) (1) are shown as points, and the results of calculations by equations (15) and (17) for various v are also given. The thermophysical parameters were taken as for pure Pb:

$$T_k' \simeq T_{k,0} = 600^\circ\text{K}, \quad \lambda_1 = 0.070\ \text{cal/cm}\cdot\text{s}\cdot{}^\circ\text{C}, \quad \lambda_2 = 0.059\ \text{cal/cm}\cdot\text{s}\cdot{}^\circ\text{C},$$

$$\gamma_1 = 11.0\ \text{g/cm}^3, \quad \gamma_2 = 10.7\ \text{g/cm}^3, \quad Q = 5.5\ \text{cal/g}, \quad c_1 = 0.036\ \text{cal/g}\cdot{}^\circ\text{C},$$

$$c_2 = 0.034 \text{ cal/g} \cdot {}^\circ\text{C}, \quad k = 0.57, \quad \sigma = 7.9 \cdot 10^{-7} \text{ cal/cm}^2, \quad A = 2.7^\circ\text{C/wt. \%},$$

$$D_2 = 5 \cdot 10^{-5} \text{ cm}^2/\text{s}.$$

Usually the loss of stability is associated with the presence, in the melt ahead of the crystallization front, of a zone of "constitutional supercooling" (3). Therefore the condition for the appearance of this supercooling

$$C_0 = \frac{kD_2G}{(1-k)Av} \tag{18}$$

is regarded as coinciding with the equation of the stability boundary, which seems to us physically unjustified. It is not difficult to show that, for large G/v, equation (15) coincides with (18) to within a factor of order 1. However, for small G/v, there is an essential difference between (15) and (18), connected with the fact that, according to (18), $C_0 = 0$ when $G/v = 0$, whereas according to (15) and (17) $C_0 = 0$ when $G/v = -0.311\,\gamma_1 Q/\lambda_2$. Therefore, to verify the considerations expressed in the present article, additional experimental investigations of stability during crystallization of a pure substance and of an alloy with very small impurity contents are needed.

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REFERENCES

1. W. A. Tiller, J. W. Rutter, *Canad. J. Phys.*, **34**, No. 1, 96 (1956).
2. D. E. Temkin, *Collected Works of TsNIICHERMET*, No. 4 (1960).
3. W. A. Tiller, K. A. Jackson, J. W. Rutter, B. Chalmers, *Acta Metall.*, **1**, No. 4, 428 (1953).

* This relation, but without taking into account the effect of surface tension ($\sigma = 0$), was obtained in work (2).

Note: Figure translations are in progress. See original paper for figures.

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