

Oscillatory crystallization of a stratifying alloy

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(Submitted 7 July 1982)

Pis'ma Zh. Eksp. Teor. Fiz. 36, No. 7, 238–241 (5 October 1982)

It is shown that in a certain range of parameters, an oscillatory process leading to the formation of a layered structure arises. The position of the kinetic transition line from this regime to the stationary regime, which leads to the formation of a solid phase with homogeneous composition, is indicated.

PACS numbers: 81.30.Fb

A first-order phase transition, occurring with finite rate and with finite deviations from equilibrium, leads to the formation of a phase with nonuniform properties. A kinetic transition from the growth of an ordered crystal to growth of a disordered crystal with crystallization of an ordering alloy was investigated in Ref. 1. An analogous transition can be expected with crystallization of a stratifying alloy, namely, a transition from growth of a stratified crystal to growth of a crystal with uniform composition.

The kinetics of isothermal crystallization of an alloy is limited by diffusion processes. We shall examine the crystallization of a binary substitutional alloy from components A and B . The concentration distribution in the liquid phase is described by the diffusion equation, which we shall write in a system of coordinates moving with velocity V together with the planar interface

$$\frac{\partial C_L}{\partial t} = D_L \frac{\partial^2 C_L}{\partial z^2} + V \frac{\partial C_L}{\partial z}, \quad C_L(z, 0) = C_L(\infty, t) = C_0. \quad (1)$$

Here C_L is the concentration of component B (the indices L and S refer to the liquid and solid phases); D_L is the coefficient of mutual diffusion; C_0 is the starting composition of the liquid phase. On the interface, at $z = 0$, the condition for continuity of flow must be satisfied

$$D_L \frac{\partial C_L}{\partial z} + VC_L = VC_S \quad \text{at } z = 0 \quad (2)$$

and the kinetic conditions,² which have the following form for a substitutional alloy, must also be satisfied:

$$V = J_A + J_B, \quad VC_S = J_B, \quad V(1 - C_S) = J_A \quad \text{at } z = 0, \quad (3)$$

where J_A and J_B are the fluxes of components from the liquid to the solid phase on their mutual boundary. Within the scope of the linear irreversible thermodynamics

$$J_i = W_{ij}(\mu_{Lj} - \mu_{Sj}). \quad (4)$$

Here $i, j = A, B$; μ_{Li} and μ_{Si} are the chemical potentials of the components; and W_{ij} are the kinetic coefficients. We ignore diffusion in the solid phase, which is admissible

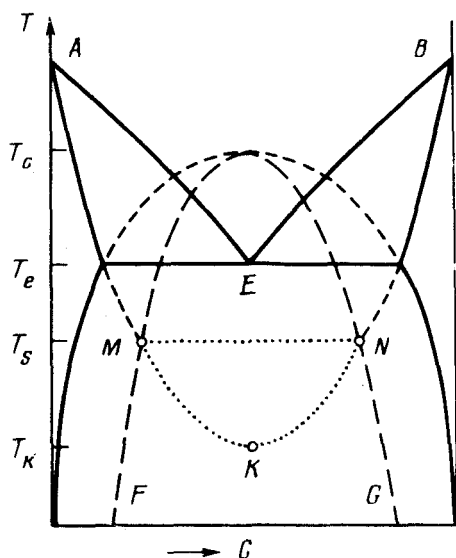


FIG. 1.

for $VL/D_S \gg 1$, where L is the characteristic scale of the structure, which appears as a result of crystallization or decomposition after crystallization.

Below the critical stratification temperature, T_c , the solid phase must decompose into two isomorphous phases with different compositions. In this case, the equilibrium diagram of the solid and liquid phases can have a eutectic point (Fig. 1).³ For simplicity, we shall examine an alloy consisting of equivalent components such that $C_{S,c}$ at the critical point and $C_{L,e}$ at the eutectic point are equal to $1/2$ and, in addition to the Onsager relation $W_{AB} = W_{BA}$, the condition $W_{AA} = W_{BB}$, is satisfied. If the eutectic temperature T_e is close to the critical temperature T_c ($T_c - T_e \ll T_e$), then in vicinity of T_e , it is possible to use a power-law expansion for the thermodynamic potentials of the phases

$$f(T, C) = f_0(T) + a(T)(C - 1/2)^2 + b(C - 1/2)^4. \quad (5)$$

In the solid phase $a_S(T) \sim -\tau < 0$, where $\tau = (T_c - T)/T_c \ll 1$ while the liquid phase $a_L > 0$, so that for it the fourth order terms in (4) can be ignored. From Eqs. (3)–(5) we find the relation between V , C_L , and C_S on the boundary:

$$V = 2(W_{AA} + W_{AB}) \left[\Delta(T) - \frac{a_S^2}{3b} + 3b(\eta^2 - \eta_0^2)^2 \right], \quad (6)$$

$$C_L - \frac{1}{2} = -a_L^{-1} \left(|a_S| - \frac{V}{W_{AA} - W_{AB}} \right) \eta + \frac{2b}{a_L} \eta^3. \quad (7)$$

Here $\eta = C_S - 1/2$; and $\eta_0 = \pm \sqrt{-a_S/6b}$ are the spinodal concentrations determined from the condition $\partial^2 f_S / \partial C_S^2 = 0$, $\Delta(T) = f_{0L}(T) - f_{0S}(T) + a_S^2/4b$.

As is evident from (6), the rate as a function of η has a maximum at $\eta = 0$ and two symmetrical minima at $\eta = \pm \eta_0$. The quantity $\Delta(T)$ vanishes at $T = T_e$ and is

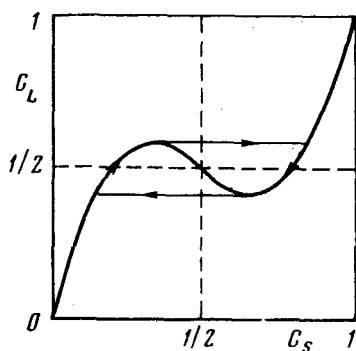


FIG. 2.

positive for $T < T_e$. At the temperature T_s , determined by the condition $\Delta(T_s) = a_s^2/3b$, the solidus lines AM and BN intersect the spinodal lines FM and GN (Fig. 1), and below T_s the rate is positive for all C_s . The dependence $C_L(C_s)$ [Eq. (7)] has the form shown in Fig. 2. As the crystallization temperature decreases, $\Delta(T)$ increases, characterizing the supercooling of the initial phase, and V increases correspondingly. At some temperature, which we shall denote by T_C , C_L becomes a monotonically increasing function of C_s . It is evident that near T_C Eq. (7) can be rewritten in the form

$$C_L - 1/2 = -\epsilon(T)\eta + \frac{2b}{a_L} \eta^3, \quad (8)$$

where $\epsilon(T) \sim (T - T_C)/T_C \ll 1$. Using this infinitesimal quantity, we simplify the problem (1)–(4).

If $C_0 \approx 1/2$, then the characteristic region of variation of C_s is determined by the positions of the maxima and minima on the curve $C_L(C_s)$, i.e., $C_s - 1/2 \sim \epsilon^{1/2}$. In this case $C_L - 1/2 \sim \epsilon^{3/2} \ll C_s - 1/2$. In addition, in the zeroth-order approximation with respect to ϵ the velocity V may be assumed to be independent of C_s , and we can use its value at $C_s = 1/2$. Using these estimates, we retain only the leading terms in (2):

$$D_L \frac{\partial C_L}{\partial z} \simeq V(C_s - 1/2) \equiv V\eta \quad \text{at } z = 0. \quad (9)$$

From this equation it is easy to estimate the characteristic length l of variation in $C_L(z, t)$, namely, $lV|D_L| \sim \epsilon \ll 1$. For this reason, the second term on the right side of Eq. (1) is a factor of ϵ smaller than the first term and we can drop it. This means that when the concentration field is in the liquid phase, the motion of the interface can be ignored. In this case, the solution of Eq. (1) with the condition (9) (Ref. 4) gives for the concentration $C_L(t)$, on the interface the expression

$$C_L - \frac{1}{2} = -V \int_0^t \frac{\eta(t') dt'}{\sqrt{\pi D_L(t - t')}}. \quad (10)$$

For simplicity, we shall examine the case $C_0 = 1/2$. Substituting C_L from Eq. (8) into the left side of (10) and introducing the dimensionless time $\theta = tV^2/\epsilon^2 D_L$, we obtain the integral equation

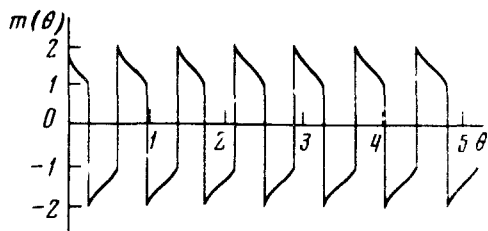


FIG. 3.

$$m(\theta) - \frac{m^3(\theta)}{3} = \int_0^\theta \frac{m(\theta') d\theta'}{\sqrt{\pi(\theta - \theta')}}, \text{ where } m = (C_S - 1/2)(6b/\epsilon a_L)^{1/2}. \quad (11)$$

Equation (11) determines the time dependence of the composition of the solid phase at the interface. The result of a numerical solution of this equation is shown in Fig. 3. The θ dependence of m has the form of discontinuous oscillations with a period $\theta_0 = 0.76$. Correspondingly, the dimensional period is $t_0 = 0.76\epsilon^2 D_L / V^2$. The jumps in C_S occur when the maximum and minimum points are attained, while the entire oscillatory crystallization process follows the trajectory shown by the arrows in Fig. 2. The concentration C_L oscillates with the same period, but remains continuous. Since in the solid phase there is no diffusion, Fig. 3 gives at the same time the simultaneous concentration profile of the layered structure that forms in the solid phase. The period of this structure is $L = Vt_0 = 0.76\epsilon^2 D_L / V$.

At $C_0 = 1/2$, crystallization below T_C occurs in the steady-state regime, for which the constant composition of the solid phase is equal to the initial value $C_S = C_0$. A stability analysis shows that for $\partial C_L / \partial C_S < 0$, the steady-state regime is unstable and in our case the discontinuous oscillatory regime arises. Thus, the curve *MKN* (Fig. 1), on which $\partial C_L / \partial C_S = 0$, is the curve of kinetic transitions from the oscillatory crystallization regime (above this curve) to the stationary regime.

A more detailed analysis of the different crystallization regimes in the entire C_0 - T plane will be given in another publication.

We thank A. A. Chernov, A. A. Migdal, and D. E. Khmel'nitskiĭ for their interest in this work and for useful discussions, and O. L. Shalynin for help in performing the numerical calculations.

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Translated by M. E. Alferieff

Edited by S. J. Amoretty