Journal of Applied Mechanics and Technical Physics, Vol. 42, No. 1, pp. 97–102, 2001

PHASE TRANSITION UPON SOLIDIFICATION FROM A LIQUID STATE

A. I. Fedorchenko

UDC 537.525.1:621.793.7

A criterion that allows one to predict a priori *a mechanism (equilibrium or nonequilibrium) according to which the phase transition upon solidification of a melt from a liquid state will occur is obtained. The fundamental possibility of experimental determination of the kinetic constant and the energy of activation is shown on the basis of the phase-transition criterion obtained and the solution of the problem of sequential nonequilibrium crystallization.*

Introduction. Solidification from a liquid state underlies many methods of producing new materials with unique properties. The high cooling rate of a melt in such processes makes it possible to obtain nonequilibrium structures such as metal glasses, microcrystalline alloys, and supersaturated solid solutions. It follows from results of experimental studies on crystallization of droplets of metal melts [1–3] that supercooling of metal drops of diameter 20–500 μm can reach hundreds of degrees. To study the physical specific features of solidification processes under given conditions (the cooling rate is of the order of 10^6–10^8 K/sec and the supercooling is 100–300 K), it is necessary to take into account the kinetics of solidification.

Zhukov et al. [4] proposed a model of equilibrium solidification of the drops of metal melts upon impact with a massive substrate. Calculation results, related experimental data [5, 6] and the values of the impact parameters are given in Table 1 ($\bar{h}_{\text{exp}}$ and $\bar{h}_{\text{calc}}$ are the experimental and calculated values of the height of the solidificated drop referred to the drop diameter D_p, T_p^0 and T_b^0 are the initial temperatures of the drop and the substrate, respectively, and U_p is the velocity of the drop). Table 1 shows that together with the satisfactory correspondence of the theoretical and experimental data for Al–Al and Al–Ag systems, the calculated values exceed the experimental ones. One can assume that this difference is due to the fact that the model of equilibrium crystallization cannot be applied to all the modes of drop–substrate interaction considered.

Equilibrium crystallization occurs when the supercooling at the crystallization front is equal to zero, which usually takes place for a certain time interval after the beginning of the phase transition, for example, far from the cooling surface. In the case of solidification of the laminas of melts we consider here, this condition cannot be realized. Therefore, a criterion that allows one to predict *a priori* a mechanism (equilibrium or nonequilibrium) according to which the phase transition will occur is necessary. To do this, we consider the problem of solidification of a melt drop within the framework of the model of nonequilibrium crystallization.

Formulation of the Problem. It is known that the main difference between the models of sequential equilibrium and nonequilibrium crystallization consists of the absence or presence of supercooling at the crystallization front. In accordance with this, the equations determining the motion of the crystallization front also change. However, it follows from the general physical considerations that the driving force of any phase transition is the deviation of the thermodynamic parameters of a system from their equilibrium values, i.e., the presence of supersaturation, the role of which is played, in the case of melt–crystal phase transition, by supercooling at the crystallization front $\Delta T = T_m - T$, where T_m is the equilibrium melting (crystallization)

Kutateladze Institute of Thermal Physics, Siberian Division, Russian Academy of Sciences, Novosibirsk 630090. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 42, No. 1, pp. 108–114, January–February, 2001. Original article submitted November 30, 1999; revision submitted June 14, 2000.

TABLE 1

Drop material	Substrate material	D_p, μm	U_p, m/sec	T_p^0, K	T_b^0, K	$\bar{h}_{\text{exp}}$	$\bar{h}_{\text{calc}}$
Ag	Ag	162	30	1234	573	0.1111	0.1883
Al	Ag	180	30	933	673	0.0667	0.0858
Cu	Ag	120	30	1353	573	0.0833	0.1404
Ni	Ag	80	30	1726	673	0.0625	0.1177
Fe	Ag	80	30	1803	773	0.0625	0.1160
Ti	Ag	90	30	1943	573	0.0555	0.0900
Zr	Ag	150	30	2023	473	0.0667	0.1107
Al	Al	240	30	933	673	0.0500	0.0606

point. The velocity of motion of the phase-transition front for metal melts upon supercooling at the front is described by the law of normal growth

$$v = K\Delta T, \tag{1}$$

where K is the kinetic coefficient dependent on the properties of the melt material. Here the thermal-balance conditions

$$\rho L v = [q]_f \tag{2}$$

should be satisfied at the phase-transition front. Here ρ is the density, L is the specific heat of the phase transition, and $[q]_f$ is the jump of thermal fluxes at the crystallization front.

Since it is assumed that $\Delta T = 0$ in the case of an equilibrium phase transition, Eq. (2) determines the velocity of motion of the crystallization front; here Eq. (1) degenerates. However, the case of equilibrium crystallization can be formally included in the model of sequential nonequilibrium crystallization by means of the following limit transition:

$$v_{\text{eq}} = \lim_{\substack{\Delta T \to 0 \\ K \to \infty}} K\Delta T. \tag{3}$$

Here v_{eq} is the equilibrium velocity of the phase-transition front.

In addition, the rate of decrease in supercooling depends on the phase-transition heat and the heat-transfer coefficient β at the crystallization front. If one uses the phase-transition volume heat $L_v = \rho L$ instead of the specific heat L, the unique dimensionless combination

$$\Omega = \frac{\beta}{L_v K} \tag{4}$$

can be composed of the parameters β, L_v, and K.

An important conclusion follows from (3) and (4): the condition $\Omega \ll 1$ corresponds to the case of equilibrium crystallization. Thus, the quantity Ω can serve as a criterion that indicates *a priori* a mechanism according to which the phase transition will occur.

Model of Sequential Nonequilibrium Phase Transition. We consider the impact of a melt drop of diameter D_p heated to the melting point T_m with a flat solid substrate with velocity U_p. With the delay time τ_{d} from the moment of impact in the plane $z = 0$ coinciding with the substrate plane, the phase transition whose front $\zeta(t, r)$ moves in the positive direction of the z axis toward the top of the spreading drop $z_p(t)$ begins. The delay time τ_{d} is determined by the expectation time for the appearance of the first critical nucleus in the melt. It is assumed that the heterogeneous nucleation occurs. In the approximation of nonequilibrium crystallization, the velocity of motion of the phase-transition front depends on supercooling at the crystallization front, i.e., $d\zeta(t, r)/dt = f(\Delta T)$, where the form of the function $f(\Delta T)$ depends on the mechanism of crystal growth (normal or stratified). For metal melts, one can adopt the normal mechanism of growth [7] described by the equation $d\zeta(t, r)/dt = K\Delta T$.

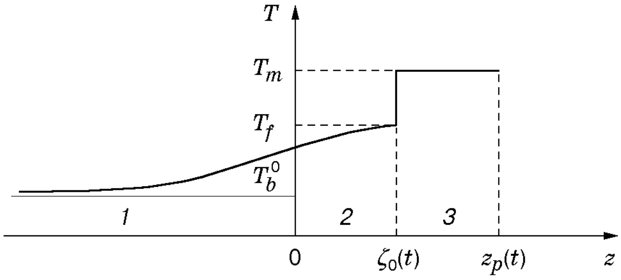

Fig. 1. Temperature distribution upon deformation and solidification of the drop on the substrate: 1) substrate; 2) crystal; 3) melt.

In the first approximation, we assume that the coefficient K does not depend on supercooling and a completely solidificated drop is shaped like a flat disk. This allows us to determine the moment of complete solidification of the drop t^*:

$$\zeta(t^*, 0) = \zeta_0(t^*) = z_p(t^*). \tag{5}$$

Here $z_p(t)$ is the coordinate of the moving top of the drop.

For conditions corresponding to the modes of solidification from a liquid state (the velocity of the drops is 20–100 m/sec and the linear sizes are 10–100 μm), the substrate can be assumed to be semi-infinite and to occupy the half-space $-\infty < z < 0$. One can also consider that the constant temperature T_m is kept in the liquid part of the drop owing to the convective transfer of the melt to the solidification front. Figure 1 shows the temperature distribution for the given formulation of the problem.

We write the heat-conduction equation for the substrate and the solidificated part of the drop for $r = 0$, ignoring the radial heat transfer:

$$\partial_t T_b = a_b \partial_{zz} T_b, \qquad \partial_t T_p^{(s)} = a_p^{(s)} \partial_{zz} T_p^{(s)}. \tag{6}$$

Here the superscript s corresponds to the solid state of the drop material; a_b and a_p are the diffusivities of the substrate and the drop, respectively.

In the plane $z = 0$, we have

$$T_b(t, 0) = T_p^{(s)}(t, 0), \qquad \lambda_b (\partial_z T_b)_{z=0} = \lambda_p^{(s)} (\partial_z T_p^{(s)})_{z=0}. \tag{7}$$

Here λ_b and λ_p are the heat conduction of the substrate and the drop, respectively.

The thermal-balance condition at the crystallization front is written in the form

$$\lambda_p^{(s)} (\partial_z T_p^{(s)})_{z=\zeta_0(t)} = \rho_p^{(s)} L \,\frac{d\zeta_0(t)}{dt} + \beta(T_m - T_f), \tag{8}$$

where T_f is the temperature of the crystallization front.

Expressions (5)–(8) and the condition at infinity $T_b(t, -\infty) = T_b^0$ close the formulation of the problem.

We reduce the initial system to a dimensionless form, using the values of D_p, T_m, and U_p as scale values:

$$\begin{gathered} \frac{\partial \theta_b}{\partial\,\mathrm{Fo}} = a_{b,p} \frac{\partial^2 \theta_b}{\partial \bar z^2}, \quad \frac{\partial \theta_p^{(s)}}{\partial\,\mathrm{Fo}} = \frac{\partial^2 \theta_p^{(s)}}{\partial \bar z^2}, \quad \theta_b(0, \mathrm{Fo}) = \theta_p^{(s)}(0, \mathrm{Fo}), \quad \lambda_{b,p} \frac{\partial \theta_b}{\partial \bar z}\Big|_{\bar z=0} = -\frac{\partial \theta_p^{(s)}}{\partial \bar z}\Big|_{\bar z=0}, \\ \theta_f = 1 - R \,\frac{d\bar\zeta}{d\,\mathrm{Fo}}, \quad \frac{\partial \theta_p^{(s)}}{\partial \bar z}\Big|_{\bar z=\bar\zeta} = (\mathrm{Ku} + \lambda_p^{(l,s)} \,\mathrm{Nu}\, R) \,\frac{d\bar\zeta}{d\,\mathrm{Fo}} = L_{\text{eff}} \,\frac{d\bar\zeta}{d\,\mathrm{Fo}}. \end{gathered} \tag{9}$$

Here $\bar z = z/D_p$, $\theta = T/T_m$, $\mathrm{Fo} = a_p^{(s)} t/D_p^2$ is the Fourier number, $R = a_p^{(s)}/(D_p K T_m)$ is the ratio of the diffusion and kinetic velocities, $\lambda_{b,p} = \lambda_b/\lambda_p^{(s)}$, $\lambda_p^{(l,s)} = \lambda_p^{(l)}/\lambda_p^{(s)}$, $a_{b,p} = a_b/a_p^{(s)}$, $\mathrm{Ku} = L/(c_p^{(s)} T_m)$ is Kutateladze's criterion, $\mathrm{Nu} = \beta D_p/\lambda_p^{(l)}$ is the Nusselt criterion, and $L_{\text{eff}} = \mathrm{Ku} + \lambda_p^{(l,s)} \,\mathrm{Nu}\, R$ is the effective dimensionless heat of melting; the superscript l refers to the liquid state of the drop material.

System (9) was solved analytically by Lyubov [7]; therefore, omitting intermediate calculations, we give only the final results. The dimensionless coordinate of the phase-transition front is determined from the relation $\bar{\zeta} = 2\gamma\sqrt{\mathrm{Fo}}$, where the constant γ is found from the characteristic equation

$$\frac{1-\theta_b^0}{\mathrm{Ku} + \lambda_p^{(l,s)}\,\mathrm{Nu}\,R} = \sqrt{\pi}\gamma[K_\varepsilon + \mathrm{erf}\,(\gamma)]\,\mathrm{e}^{\gamma^2}. \tag{10}$$

Here $K_\varepsilon = \sqrt{\lambda_p^{(s)}\rho_p^{(s)}c_p^{(s)}/(\lambda_b\rho_b c_b)}$ and $\theta_b^0 = T_b^0/T_m$. It follows from expression (10) that the effect of the kinetics itself on the process of crystallization is determined by the criterion

$$\Omega = \lambda_p^{(l,s)}\,\frac{\mathrm{Nu}\,R}{\mathrm{Ku}} = \frac{\beta}{L_v K} \qquad (L_v = \rho_p^{(s)}L), \tag{11}$$

whose form coincides with relation (4) obtained in terms of the similarity and dimensionality theory.

With allowance for (11), Eq. (10) is written in the form

$$\frac{1-\theta_b^0}{\mathrm{Ku}\,(1+\Omega)} = \sqrt{\pi}\gamma[K_\varepsilon + \mathrm{erf}\,(\gamma)]\,\mathrm{e}^{\gamma^2}. \tag{12}$$

According to (3), upon equilibrium crystallization, the condition $K \to \infty$ should be satisfied and, hence, $\Omega \ll 1$. Therefore, one can ignore the value of Ω compared to unity in Eq. (12). In this case, the dynamics of the crystallization front will be completely determined by the criterion of equilibrium phase transition Ku. Otherwise, for $\Omega \gg 1$, the dynamics of the phase transition will depend significantly on the kinetics of the process.

We consider the problem of determining the height of the solidificated drop. As done in [4], assuming that the velocity of the drop top is a constant magnitude on the time interval considered, we obtain the following equation which determines the time of complete solidification of the drop:

$$1 - \delta\,\mathrm{Pe}\,\mathrm{Fo} = 2\gamma\,\mathrm{Fo}^{1/2}, \tag{13}$$

where $\delta = a_p^{(l,s)}$, $\mathrm{Pe} = U_p D_p/a_p^{(l)}$ is the Peclet number, γ is the root of the transcendental equation (12), and $a_p^{(l,s)} = a_p^{(l)}/a_p^{(s)}$.

We write the solution of Eq. (13) in the form $\mathrm{Fo}^* = (2\gamma^2 + \delta\,\mathrm{Pe} - 2\gamma\sqrt{\gamma^2 + \delta\,\mathrm{Pe}}\,)/(\delta\,\mathrm{Pe})^2$. Therefore, the dimensionless height of the solidificated drop is $\bar{h} = h/D_p = 1 - \delta\,\mathrm{Pe}\,\mathrm{Fo}^*$.

To use the resulting expressions, it is necessary to calculate the average value of the Nusselt number and the kinetic constant K.

Convective Heat Transfer in the Vicinity of the Critical Point. We consider the axisymmetrical nonisothermal flow of an incompressible liquid in the vicinity of the critical point and determine the contribution from the convective component to the heat transfer at this point.

Since for metal melts, the Prandtl number is $\mathrm{Pr} \approx 10^{-2}$–$10^{-3}$, to determine the velocity component u normal to the substrate, one can use the solution of the problem of ideal spreading of a liquid in the vicinity of the critical point $u = -2\alpha z$, where α is a constant quantity, which will be determined below. Then, the boundary-value problem of convective heat transfer takes the form

$$\partial_t T - 2\alpha z\,\partial_z T = a\,\partial_{zz}T, \qquad T(t,\infty) = T(0,z) = T_{p0}, \qquad T(t,0) = T_{b0}. \tag{14}$$

We reduce problem (14) to a dimensionless form, introducing the following dimensionless variables: $\theta = (T - T_{p0})/(T_{b0} - T_{p0})$, $\eta = z(2\alpha/a)^{1/2}$, and $\tau = 2\alpha t$. We obtain

$$\partial_\tau\theta - \eta\,\partial_\eta\theta = \partial_{\eta\eta}\theta, \tag{15}$$

$$\theta(\tau,\infty) = \theta(0,\eta) = 0, \qquad \theta(\tau,0) = 1. \tag{16}$$

To solve problem (15), (16), we introduce the self-similar variable $\varphi = \eta/f(\tau)$ with an unknown function $f(\tau)$. Then, Eq. (15) takes the form

$$\frac{d^2\theta}{d\varphi^2} + \varphi(ff' + f^2)\,\frac{d\theta}{d\varphi} = 0, \tag{17}$$

where $f' = df/d\tau$.

We require that the bracketed expressions in Eq. (17) be equal to unity. Whence we find the explicit form of the function $f(\tau)$:

$$f(\tau) = [1 - \exp(-2\tau)]^{1/2}. \tag{18}$$

The solution of the resulting equation

$$\frac{d^2\theta}{d\varphi^2} + \varphi\,\frac{d\theta}{d\varphi} = 0$$

subject to the boundary conditions $\theta(\infty) = 0$ and $\theta(0) = 1$ takes the form

$$\theta(\varphi) = 1 - \sqrt{\frac{2}{\pi}} \int\limits_0^{\varphi} \exp\Big(-\frac{x^2}{2}\Big)dx. \tag{19}$$

Now we find the local value of the Nusselt number

$$\mathrm{Nu} = \beta D_p/\lambda_p^{(l)}. \tag{20}$$

Presenting (20) in the form

$$\mathrm{Nu} = \frac{qD_p}{\lambda_p^{(l)}(T_{p0} - T_{b0})} = \frac{D_p}{T_{p0} - T_{b0}}\,\frac{\partial T}{\partial z}\Big|_{z=0}$$

and using expressions (18) and (19) for calculation of the derivative, we obtain

$$\mathrm{Nu} = \sqrt{\frac{4\alpha}{\pi a}}\,\frac{D_p}{\sqrt{1 - \exp(-2\tau)}}. \tag{21}$$

We determine the coefficient α in formula (21) as follows [8]:

$$\alpha = U_p/(2D_p). \tag{22}$$

With allowance for (22), expression (21) takes the form

$$\mathrm{Nu} = \sqrt{\frac{2\,\mathrm{Pe}}{\pi}}\,\frac{1}{\sqrt{1 - \exp(-2\tau)}}.$$

Averaging the local number Nu over the characteristic time of drop deformation D_p/U_p to which the dimensionless time $\tau = 1$ corresponds, we obtain $\overline{\mathrm{Nu}} = \sqrt{5.5\,\mathrm{Pe}/\pi}$.

Discussion of Calculation Results. At present, reliable experimental data permitting one to find the values of K for melts of metals or alloys are lacking, whereas the theoretical values obtained on the basis of one or another model concepts of the rate of crystal growth differ greatly. This is connected with the fact that the values of certain parameters used in theoretical studies are approximate. In the present work, to determine K, the expression

$$K = \frac{D_L \Delta H_a}{d_a k T_m^2}, \tag{23}$$

where $D_L = D_0 \exp[-E/(kT_m)]$ is the self-diffusion coefficient, d_a is the effective diameter of a molecule (atom), E is the energy of activation of a viscous flow, ΔH_a is the enthalpy of melting per molecule (atom), and k is the Boltzmann constant, was used. In formula (23), the values of the preexponential factor D_0 included in the self-diffusion coefficient and the energy of activation of a viscous flow are approximate. Therefore, we perform calculations according to the proposed model for Ag, Al, Cu, and Ni drops (see Table 1), for which exact values of D_0 and E are known [9]. The data used for calculation of the process of drop solidification according to the model of nonequilibrium crystallization are given in Table 2.

TABLE 2

Melt	d_a, 10^{-10} m	D_0, 10^{-7} m^2/sec	E, 10^{-20} J/atom	ΔH_a, 10^{-20} J/atom
Ag	2.68	0.9	6.0	1.87
Al	2.67	2.0	4.2	1.75
Cu	2.38	0.7	6.6	2.15
Ni	2.33	1.8	9.15	2.95

TABLE 3

Drop material	Substrate material	$\bar{h}_{\rm exp}$	$\bar{h}_{\rm eq}$	$\bar{h}_{\rm neq}$	Ω
Ag	Ag	0.1111	0.1883	0.1173	1.13
Al	Ag	0.0667	0.0858	0.0805	0.18
Cu	Ag	0.0833	0.1404	0.0774	1.56
Ni	Ag	0.0625	0.1177	0.0785	0.57
Al	Al	0.0500	0.0606	0.0605	0.16

The calculation results obtained for the dimensionless height of solidificated drops according to the nonequilibrium model and the values of the phase-transition criterion Ω are listed in Table 3 ($\bar{h}_{\rm eq}$ and $\bar{h}_{\rm neq}$ refer to the calculation according to the equilibrium and nonequilibrium models, respectively).

An analysis of the results obtained allows us to make the following conclusions. According to (4), one can use the equilibrium model for $\Omega \ll 1$. The values of the phase-transition criterion $\Omega = 0.18$ and 0.16 correspond to the modes of Al–Ag and Al–Al interaction. Here the calculation results obtained according to the equilibrium and nonequilibrium models almost coincide and agree well with the experimental data.

With increase in Ω, the difference between $\bar{h}_{\rm neq}$ and $\bar{h}_{\rm eq}$ also increases; however, the values of $\bar{h}_{\rm neq}$ and $\bar{h}_{\rm exp}$ are, as before, in good agreement.

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