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ANALYSIS OF CRYSTALLIZATION OF A SUPERCOOLED MELT BY THE INTEGRAL BALANCE METHOD

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Using the integral-balance method, the Stefan problem is solved for simply shaped crystals (a prism, a cylinder, and a sphere) grown in a supercooled melt. It is shown that the rate of crystal growth increases with the surface-to-volume ratio (in passage from a prism to a cylinder and a sphere). For all the three shapes of crystals studied the dependence of the speed of motion of the crystallization front on the supercooling is nonlinear and is characterized by a progressive increase.

Formulation of the Problem. According to the general principles of thermodynamics, growth of crystals in a melt is possible only if there is local supercooling of the liquid phase directly in front of the phase interface. At the same time, in formulating the problem of solidification of a melt, i.e., the so-called Stefan problem, the local supercooling of the melt in front of the crystallization front is usually neglected [1, 2]. Recently a new scientific direction has arisen in metallophysics that is related to the technological process of metal-bath hardening [3]. Analysis of crystallization of a highly supercooled melt is the key problem in the theory of this process. Supercooling of a melt is also to be taken into account in analyzing dendrite crystallization of metals and alloys [4]. In works devoted to the theory of dendrite growth [5–7], the complex geometrical situation of the temperature field in the vicinity of the growing (head) part of a dendrite crystal is considered [5–7]. However, not all aspects of crystallization of a supercooled melt have been sufficiently well studied even in solidification of melted bodies of the simplest configurations: a prism, a cylinder, and a sphere.

In what follows, using an approximate method of integral balance, we consider the problem of the dynamics of advance of the phase interface in a supercooled melt for bodies of simple shape. This method was suggested in 1937 by L. S. Leibenzon and later gained rather wide application, in particular, in solving problems with a moving phase interface [8–12].

The scheme given in Fig. 1 makes the formulation of the problem clearer. At the initial instant of time t_0, the melt is cooled below the equilibrium melting point of the substance to the temperature $T_m < T_{mel}$; the quantity $\Delta T = T_{mel} - T_m$ is called the supercooling of the melt. The layer of the melt adjacent to the crystallization front turns out to be heated higher than the melt temperature on account of the evolution of the heat of phase change. This allows a layer of melt of finite thickness $s = b - \varepsilon$ where the melt temperature varies within the limits from T_{mel} (at $r = \varepsilon$) to T_m (at $r = b$) to be singled out near the phase interface. In the sequel we will call this layer of the melt the warmup zone. The problem of nonstationary heat conduction for the warmup zone is formulated using the energy-transfer equation

$$\rho c \frac{\partial \theta}{\partial t} = \mathrm{div}\,(\lambda\ \mathrm{grad}\ \theta) \tag{1}$$

and the boundary conditions

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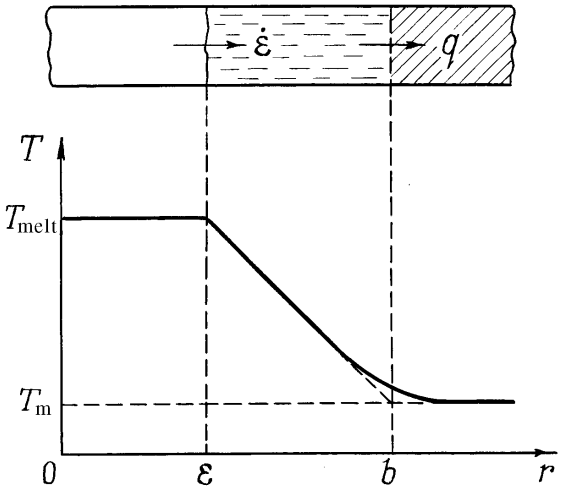

Fig. 1. Schematic diagram of the temperature distribution in the warmup zone ($\varepsilon \le r \le b$) near the phase interface.

$$\theta = T_{\rm mel} - T_{\rm m} \quad \text{for} \quad r = \varepsilon\,, \tag{2}$$

$$-\lambda \frac{\partial \theta}{\partial r} = \rho L \frac{d\varepsilon}{dt} \quad \text{for} \quad r = \varepsilon\,, \tag{3}$$

where $\theta = T(r,\, t) - T_{\rm m}$. The layer thickness $s = b - \varepsilon$ of the warmup zone is assumed to be known, with the heat-flux density on the boundary $r = b$ being equal to

$$q = -\lambda \left(\frac{\partial \theta}{\partial r} \right)_{r=b} . \tag{4}$$

Equations (1)–(4) should be supplemented with the initial conditions (the temperature distribution and the location of the boundaries of the warmup zone at the instant of time t_0, taken as the initial instant); this yields a closed system of equations that characterizes the thermal regime of the warmup zone, which influences the speed of motion of the phase interface. Below, for the case of the growth of simply shaped crystals we give a simplified solution of the above-formulated problem (the so-called Stefan problem) performed by the method of integral balance assuming a stabilized temperature distribution over the cross section of the warmup zone.

Prismatic Crystal. We assume that the temperature field changes along one coordinate r that coincides with the longitudinal axis of a crystal that has the shape of a prism (slab), with the phase interface $r = \varepsilon$ located in the plane normal to the r axis. The heat-conduction equation (1) then becomes

$$\rho c \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial r} \left(\lambda \frac{\partial \theta}{\partial r} \right) . \tag{5}$$

We integrate both sides of Eq. (5) along the coordinate r within the warmup zone, i.e., from ε to b. This yields

$$\rho c \int_{\varepsilon}^{b} \frac{\partial \theta}{\partial t}\, dr = \left(\lambda \frac{\partial \theta}{\partial r} \right)_{r=b} - \left(\lambda \frac{\partial \theta}{\partial r} \right)_{r=\varepsilon}$$

or, with account for the boundary conditions (3) and (4),

$$\rho c \int_{\varepsilon}^{b} \frac{\partial \theta}{\partial t}\, dr = \rho L \frac{d\varepsilon}{dt} - q\,. \tag{6}$$

According to a well-known relation of integral calculus,

$$\frac{d}{dt}\int_{\varepsilon}^{b} \theta\, dr = \int_{\varepsilon}^{b} \frac{\partial \theta}{\partial t}\, dr + \theta\,(b)\,\frac{db}{dt} - \theta\,(\varepsilon)\,\frac{d\varepsilon}{dt}\,,$$

with $\theta(b) = 0$ and $\theta(\varepsilon) = \Delta T$; therefore

$$\int_{\varepsilon}^{b} \frac{\partial \theta}{\partial t}\, dr = \frac{d\Psi}{dt} + \Delta T \frac{d\varepsilon}{dt}\,, \tag{7}$$

where the notation $\Psi = \int_{\varepsilon}^{b} \theta dr$ is introduced.

We substitute the expression for the integral (7) into the left-hand side of Eq. (6):

$$\rho\,(L - c\Delta T)\,\frac{d\varepsilon}{dt} = q + \rho c \frac{d\Psi}{dt}\,. \tag{8}$$

This is the integral balance relation for the warmup zone that is close to the region of the plane crystallization front. We assume further that the crystal grows under stationary conditions characterized by the following features:

a) the temperature of the melt around the growing crystal remains unchanged with time (T_{m} = const);

b) the temperature drop over the cross section of the warmup zone does not change with time (ΔT = const);

c) the thickness of the warmup-zone layer $s = b - \varepsilon$ remains unchanged with time (s = const);

d) the temperature distribution over the cross section of the warmup zone has the stabilized form

$$\theta\,(r) = \Delta T \frac{b - r}{b - \varepsilon}\,. \tag{9}$$

Employing Eq. (9), we calculate the integral Ψ:

$$\Psi = 0.5 s \Delta T \tag{10}$$

and also the density of the heat flux from the warmup zone to the surrounding melt:

$$q = \lambda \Delta T / s\,. \tag{11}$$

Substituting expressions (10) and (11) into the general balance equation (8), we find an expression for the speed of motion of the crystallization front:

$$\frac{d\varepsilon}{dt} = \frac{\lambda \Delta T}{\rho s\,(L - c\Delta T)}\,. \tag{12}$$

We introduce the dimensionless variables

$$y = \varepsilon/s\,, \quad \tau = \lambda t/(\rho c s^2)\,, \quad \Theta = \Delta T/(\Delta T_* - \Delta T)\,, \tag{13}$$

where $\Delta T_* = L/c$. As a result, the expression for the crystallization rate (12) is as follows:

$$dy = \Theta d\tau\,.$$

The integral of the latter equation is

$$y - y_0 = \Theta\tau\,, \tag{14}$$

in which the initial condition $y(0) = y_0$ is taken into account.

Cylindrical Crystal. The heat-conduction equation (1) for an axisymmetric circular field of the excess temperature $\theta(r, t)$ has the form

$$\rho c \frac{\partial\theta}{\partial t} = \lambda \left(\frac{\partial^2\theta}{\partial r^2} + \frac{1}{r}\frac{\partial\theta}{\partial r} \right)$$

or

$$\rho c r \frac{\partial\theta}{\partial t} = \lambda \frac{\partial}{\partial r}\left(r \frac{\partial\theta}{\partial r} \right). \tag{15}$$

We integrate both sides of Eq. (15) along the coordinate r within the warmup zone:

$$\rho c \int_\varepsilon^b r \frac{\partial\theta}{\partial t}\, dr = \lambda \left(r \frac{\partial\theta}{\partial r} \right)_{r=b} - \lambda \left(r \frac{\partial\theta}{\partial r} \right)_{r=\varepsilon}$$

or with conditions (3) and (4) taken into account

$$\rho c \int_\varepsilon^b r \frac{\partial\theta}{\partial t}\, dr = \rho L \varepsilon \frac{d\varepsilon}{dt} - qb\,. \tag{16}$$

Since

$$\frac{d}{dt}\int_\varepsilon^b \theta r dr = \int_\varepsilon^b r \frac{\partial\theta}{\partial t}\, dr + b\theta\,(b)\,\frac{db}{dt} - \varepsilon\theta\,(\varepsilon)\,\frac{d\varepsilon}{dt}\,,$$

with $\theta(b) = 0$ and $\theta(\varepsilon) = \Delta T$, Eq. (16) is reduced to the form

$$\rho\,(L - c\Delta T)\,\varepsilon \frac{d\varepsilon}{dt} = bq + \rho c \frac{d\Psi}{dt}\,, \tag{17}$$

in which $\Psi = \int_\varepsilon^b r\theta dr$.

Using the above assumptions of a steady-state regime of crystallization and the stabilized temperature distribution (9), we obtain an expression for the integral of Ψ:

$$\Psi = \Delta T \left(0.5bs - \frac{1}{3} s^2 \right)$$

and then (assuming that s = const)

$$\frac{d\Psi}{dt} = 0.5s\Delta T \frac{d\varepsilon}{dt} .$$

As a result, the balance equation (17) takes the form

$$\rho\,(L - c\Delta T)\,\varepsilon \frac{d\varepsilon}{dt} = 0.5\rho c\Delta Ts \frac{d\varepsilon}{dt} + \lambda \frac{(\varepsilon + s)\,\Delta T}{s} . \tag{18}$$

Separating the variables in Eq. (18) and using the notation (13), we obtain the following differential equation:

$$dy - \chi \frac{d\,(1+y)}{1+y} = \Theta d\tau , \tag{19}$$

in which the parameter $\chi = (\Delta T_* - 0.5\Delta T)/(\Delta T_* - \Delta T) = 1 + 0.5\Theta$ is introduced. Integration of Eq. (19) with the initial condition $y(0) = y_0$ yields

$$(y - y_0) - \chi \ln \frac{1+y}{1+y_0} = \Theta\tau . \tag{20}$$

Spherical Crystal. The heat-conduction equation (1) for an excess-temperature field $\theta(r, t)$ with central spherical symmetry has the form

$$\rho c \frac{\partial\theta}{\partial t} = \lambda \left(\frac{\partial^2\theta}{\partial r^2} + \frac{2}{r}\frac{\partial\theta}{\partial r} \right)$$

or

$$\rho c r^2 \frac{\partial\theta}{\partial t} = \lambda \frac{\partial}{\partial r}\left(r^2 \frac{\partial\theta}{\partial r} \right). \tag{21}$$

Integrating both sides of Eq. (21) along the coordinate r within the warmup zone with account for Eqs. (3) and (4), we obtain

$$\rho c \int_{\varepsilon}^{b} r^2 \frac{\partial\theta}{\partial t}\, dr = \rho L\varepsilon^2 \frac{d\varepsilon}{dt} - qb^2 . \tag{22}$$

Transforming the integral on the left-hand side of Eq. (22) in the way described above, we arrive at the integral balance relation

$$\rho\,(L - c\Delta T)\,\varepsilon^2 \frac{d\varepsilon}{dt} = b^2 q + \rho c \frac{d\Psi}{dt} , \tag{23}$$

TABLE 1. Thermophysical Properties and Maximum Supercoolings of a Melt for a Number of Metals (according to data of [13–15])

Metal	$\Delta T_{\max}$, deg	L, kJ/kg	c, kJ/(kg·K)	$\Delta T_* = L/c$, deg	$\Delta T_{\max}/\Delta T_*$
Sb	135	160	0.257	623	0.217
BI	90	52.3	0.152	344	0.262
Ga	76	80.3	0.399	201	0.380
Pb	80	26.4	0.148	178	0.455
Sn	118	60.5	0.250	242	0.488
Au	230	67.5	0.148	456	0.504
Cu	236	212	0.493	430	0.548
Ag	227	105	0.283	371	0.611
Ni	319	305	0.655	466	0.684
Fe	295	272	0.785	346	0.853

in which $\Psi = \int_{\varepsilon}^{b} r^2\theta dr$.

Using the stabilized distribution of the excess temperature (9), we find

$$\Psi = \Delta T \left(\frac{1}{2} b^2 s + \frac{1}{4} s^3 - \frac{2}{3} b s^2 \right)$$

and then (for s = const)

$$\frac{d\Psi}{dt} = \Delta T \left(\varepsilon + \frac{1}{3} s \right) s \frac{d\varepsilon}{dt} .$$

Substitution of this equation into the balance equation (23) yields

$$\rho (L - c\Delta T) \varepsilon^2 \frac{d\varepsilon}{dt} = \rho c \Delta T \varepsilon s \frac{d\varepsilon}{dt} + \frac{1}{3} \rho c \Delta T s^2 \frac{d\varepsilon}{dt} + (\varepsilon + s)^2 \lambda \Delta T / s . \tag{24}$$

Separating the variables in Eq. (24) and using the notation (13), we obtain

$$dy - (2 + \Theta)\, d \ln (1 + y) + \left(1 + \frac{2}{3} \Theta \right) \frac{dy}{(1 + y)^2} = \Theta d\tau . \tag{25}$$

Integration of Eq. (25) with the initial condition $y(0) = y_0$ yields the solution in the form

$$(y - y_0) - (2 + \Theta) \ln \frac{1 + y}{1 + y_0} + \left(1 + \frac{2}{3} \Theta \right) \left(\frac{1}{1 + y_0} - \frac{1}{1 + y} \right) = \Theta \tau . \tag{26}$$

Analysis and Correlation of the Solutions. According to expression (12), for crystals of prismatic shape the speed of the phase interface is directly proportional to the criterion $\Theta = \Delta T/(\Delta T_* - \Delta T)$, and it depends on the relation between the supercooling of the melt ΔT and the parameter $\Delta T_* = L/c$, which is a function of the physical properties of the material. Table 1 lists maximum values of the supercooling for a number of metals $\Delta T_{\max}$ obtained by the method of small drops [13–15]. It also lists the physical properties of the metals (L, c) and the ratios $\Delta T_{\max}/\Delta T_*$. We see that the greatest values of $\Delta T_{\max}/\Delta T_*$ are obtained for nickel and iron (0.684 and 0.853), whereas for metals with a comparatively low melting temperature the value of $\Delta T_{\max}$ does not exceed half the value of ΔT_*.

According to the solution (12), it is to be expected that the rate of growth of crystals of prismatic shape will depend linearly on the supercooling $\Delta T (d\varepsilon/dt \sim \Delta T)$ for small values of the supercooling ($\Delta T << \Delta T_*$). But for large supercoolings, where ΔT is of the same order as the parameter ΔT_*, the dependence of the rate of crystal growth on ΔT is characterized by a progressive increase. Denoting the ratio $\Delta T/\Delta T_*$ by φ and using the first several terms of the expansion into the series $(1-\varphi)^{-1} = 1+\varphi+\varphi^2+ +\varphi^3+...$, we can represent the solution (12) in a form that clearly demonstrates this property of progressive increase:

$$\frac{d\varepsilon}{dt} = \frac{\lambda \Delta T}{\rho L s}(1+\varphi+\varphi^2+...) \, . \tag{27}$$

In [16] it is found experimentally that the dependence of the speed of motion of the crystallization front of gallium on the supercooling at ΔT = 10–15 deg can be expressed by a linear law:

$$\dot{\varepsilon} = d\varepsilon/dt = K\Delta T \, , \tag{28}$$

in which $K = 5.3 \cdot 10^{-2}$ m/(sec·K).

For gallium, from Table 1 we have $L/c = \Delta T_* = 201$ deg, and the ratio $\Delta T/\Delta T_*$ for these supercoolings is small (0.05–0.075); therefore we can restrict ourselves to the first term in expansion (27):

$$\dot{\varepsilon} = d\varepsilon/dt \cong \lambda \Delta T/(\rho L s) \, . \tag{29}$$

Comparing the right-hand sides of relations (28) and (29), we can obtain an expression for evaluating the layer thickness of the warmup zone:

$$s \cong \lambda/(\rho L K) \, . \tag{30}$$

Assuming for gallium that $\lambda = 30.6$ W/(m·K), $\rho = 6120$ kg/m^3, and $L = 80.84$ kJ/kg, we find $s = 1.17 \cdot 10^{-6}$ m.

With such a small thickness of the warmup zone layer ($s \sim 10^{-4}$ cm) the dimensionless quantities τ and y attain very large values (10^4–10^6), which makes analysis of the solutions (14), (20), and (26) difficult.

Suppose, for example, an iron crystal grows in a supercooled melt for 1 sec; assuming $\lambda/(\rho c) = 0.05$ cm^2/sec and $s = 10^{-4}$ cm, we find $\tau = 5 \cdot 10^6$. To represent the solutions (14), (20), and (26) in a form more convenient for analysis, we introduce a new geometric dimension R as a scale unit (for example, the quantity R can be selected equal to the maximum possible linear dimension of the crystal). We will use the new dimensionless variables

$$x = \varepsilon/R = \eta y \, , \quad \tau^* = \eta^2 \tau \, , \tag{31}$$

where $\eta = s/R$ (a small quantity). The solutions (14), (20), and (26) in terms of the new variables x and τ^* are transformed to the form (for $y_0 = 0$):

a) for a prism

$$\eta x = \Theta \tau^* \, , \tag{32}$$

b) for a cylinder

$$\eta x - (1+0.5\Theta)\,\eta^2 \ln(1+x/\eta) = \Theta \tau^* \, , \tag{33}$$

TABLE 2. Comparison between the Values of the Dimensionless Duration of Growth τ^* of Prismatic (A), Cylindrical (B), and Spherical (C) Crystals for Prescribed $\Theta = \eta = 0.1$ (I) and 0.01 (II)

x	A	B		C	
		I	II	I	II
0.2	0.2	0.16840	0.08465	0.14839	0.04041
0.4	0.4	0.36268	0.23101	0.33518	0.14736
0.6	0.6	0.55869	0.39529	0.52725	0.28279
0.8	0.8	0.75584	0.56929	0.72162	0.43340
1.0	1.0	0.95362	0.74822	0.91720	0.29341

c) for a sphere

$$\eta x - (2 + \Theta)\,\eta^2 \ln (1 + x/\eta) + \left(1 + \frac{2}{3}\,\Theta\right)\eta^2 \frac{x}{x + \eta} = \Theta\tau^* . \tag{34}$$

Table 2 presents results of calculations by formulas (32)-(34) for two values of the parameters Θ and η, namely, $\Theta = \eta = 0.01$ and $\Theta = \eta = 0.1$. It is seen that passage from the prism to a cylinder and then to a sphere is characterized by a decrease in the dimentionless duration of the growth τ^*, i.e., in the time t that corresponds to the increase in the prescribed (the same for the crystals of all of the configurations indicated) thickness of the solid crust. For example, when $\Theta = \eta = 0.1$ is assigned, the following values of the criterion τ^* correspond to a relative thickness of the solid crust $\varepsilon/R = 0$: $\tau^* = 0.4$ for a prismatic crystal, $\tau^* = 0.36268$ for a cylindrical crystal, and $\tau^* = 0.33518$ for spherical crystal. Thus, the rate of crystal growth increases with the ratio of the surface of the crystal to its volume (which occurs in passage from the prism to a cylinder and a sphere), which seems to be due to more favorable conditions for removing the heat of the phase change from the phase interface to the surrounding melt.

NOTATION

T, temperature; T_{mel}, melting temperature; T_{m}, temperature of the supercooled melt; ΔT_*, ratio of the latent heat of crystallization to the heat capacity; θ, excess temperature; t, time; t_0, initial instant of time; λ, ρ, and c, thermal conductivity, density, and heat capacity, respectively; L, latent heat of crystallization; r, runninf coordinate; s, layer of melt in the temperature interval $T_{\text{melt}} - T_{\text{m}}$ (warmup zone); ε and b, coordinates of the supercooled melt and the warmup zone, respectively; $\dot{\varepsilon}$, speed of motion of the crystallization front; q, heat-flux density; y, dimentionless coordinate, $y = \varepsilon/s$; y_0, initial dimensionless coordinate; τ, dimensionless time, $\tau = \lambda t/\rho c s^2$; Θ, dimensionless temperature; χ, dimensionless parameter, $\chi = 1 + 0.5\Theta$; η and τ^*, dimensionless variables; R, scale unit; φ, relative supercooling; K, coefficient. Subscripts: mel, melting; m, melt; 0, initial value.

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