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Abstract

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ON THE THEORY OF NONSTATIONARY GROWTH OF CRYSTALS UNDER NON-ISOTHERMAL CONDITIONS

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The process of growth of crystals from a melt, when the released heat of solidification q and the heat of superheating are removed through a layer of the formed solid phase ψ into the external medium, is a typical case of crystallization occurring, as a rule, under nonisothermal conditions.

The complexity of the mathematical description of such a real process has led to the fact that, in studying its kinetics, two essentially different directions have been clearly distinguished. The first of them is limited to investigating the thermal aspect of the process, assuming that there is no undercooling ΔT at the crystallization front. The second considers only the physicokinetic aspect of the process, for which $\Delta T \neq 0$, but the process itself proceeds under isothermal conditions, where the release of heat q—the principal factor studied in works of the first direction—plays no role. Such separate study of the kinetics of the real growth process is artificial, and a joint consideration of both aspects of the problem is expedient.

The kinetics of the nonstationary growth process of an ideal one-component crystal under isothermal conditions, if the process is carried out through the formation of two-dimensional nuclei on its faces, is conveniently described by the distribution function of nuclei according to the number of atoms n contained in them at a given time t: $Z(n,t)$. If the probability of attachment of one atom to the n-th nucleus is $P_+(n)$, and of detachment is $P_-(n)$, then for $n \gg 1$ (1)

$$\frac{\partial Z(n,t)}{\partial t} = \frac{1}{2}\frac{\partial^2}{\partial n^2}\left\{[P_-(n) + P_+(n)]Z(n,t)\right\} \frac{\partial}{\partial n}\left\{[P_-(n) - P_+(n)]Z(n,t)\right\}.$$

We choose the boundary conditions according to Becker—Döring (2):

$$\begin{aligned} &Z(n,t)=b(n) && \text{for } n=0,\\ &Z(n,t)=0 && \text{for } n\to\infty,\\ &Z(n,t)=0 && \text{for } t=0, \end{aligned} \tag{2}$$

where $b(n)$ is the function of the equilibrium distribution of nuclei.

Equation (1) becomes the equation of Ya. B. Zel' dovich $^{(3)}$ if, to determine $P_{\pm}(n)$, one uses the approximation of the transition-state method $^{(4)}$ and considers the case

$$\frac{1}{2kT}\frac{d\Delta F(n)}{dn} \ll 1;$$

$\Delta F(n)$ is the change in free energy arising upon formation of an n-nucleus in the system.

Since the period of nonstationarity τ is the time required to reach the 99% level of the stationary distribution function of nuclei Z_{st}, its value $^{(5)}$ is determined only by the growth process near the critical size n^*, and it may be estimated using the expression $^{(6)}$

$$\tau = \frac{9V^2kT}{\pi S\omega \exp\left\{-\frac{U}{kT}\right\} d^4}\frac{\beta}{\alpha^2} = \frac{a_1}{\Delta T^2}. \tag{3}$$

Here V, S are shape coefficients of the nucleus; ω is the frequency of oscillation of the atoms; d is the atomic diameter; U is the activation energy for the transition of an atom into the nucleus. α and β are related to $\Delta F(n)$ and are determined as follows: the former by the change in free energy upon transformation of a unit volume of the coexisting phases ΔF_0, the latter by the tension on the surface of the nucleus σ. In the model under consideration, two-dimensional nuclei may conveniently be regarded as flat disks, for which σ is the edge tension.

Taking nonstationarity into account, the differential equation for $Z(n^*,t)$ (7) under isothermal conditions is

$$\tau\frac{dZ(n^*,t)}{dt} + Z(n^*,t) = Z_{\text{st}}. \tag{4}$$

This expression satisfies (2) and determines the complete kinetics of nonstationary crystal growth if, using the continuity equation, one passes in it to the flux of nuclei $I(n^*,t)$ and introduces the magnitude of the growth rate in the direction perpendicular to the moving face of the crystal: $V = dI(n^*,t)$ (1). For isothermal conditions $\tau = \text{const}$ and

$$\tau\, dV/dt + V = V_{\text{st}}. \tag{5}$$

Under nonisothermal conditions $\tau = \tau(T, \Delta T) = \tau(t)$ and

$$\frac{d}{dt}(\tau V) + V = V_{\mathrm{st}}. \tag{6}$$

In equation (6) we assume that, for any temperature, the classical dependence is fulfilled

$$V_{\mathrm{st}} = a_2 \exp\left\{-\frac{a_3}{\Delta T}\right\}. \tag{7}$$

In the overwhelming majority of cases of crystallization from the melt $\Delta T \ll T$, and a_1, a_2, and a_3 may be regarded as constant under nonisothermal conditions.

Equation (6) takes into account the "lag" of the growth rate relative to the change in temperature of the crystallization front, associated with the inertia of the growth process, while expression (7) gives the stationary growth rate, which is realized after a time $t > \tau$ following a change in temperature.

We shall take account of the thermal aspect of the problem under nonisothermal conditions by considering the example of a linear temperature distribution in the growing crystal, which we assume to be maintained despite $\Delta T(t)$. The temperature on the external surface ($x = 0$) of the crystal is taken to be constant. If the fluxes from the melt and into the melt at $\Delta T(t)$ may be neglected in comparison with the heat flux through the crystal, then from the heat-balance equation

$$V = \frac{\lambda}{q\gamma} \left.\frac{\partial T(x,t)}{\partial x}\right|_{x=y(t)} = \delta \left.\frac{\partial T(x,t)}{\partial x}\right|_{x=y(t)}, \tag{8}$$

where λ is the thermal-conductivity coefficient of the crystal; γ is the specific weight; $\delta = \lambda / q\gamma$.

The real process is described sufficiently accurately by such constraints, and, since $V = y'$, from equation (8) we obtain:

$$yy' = \delta(\Delta T_0 - \Delta T); \tag{9}$$

ΔT_0 is the supercooling at the crystallization front at the initial instant of time $t = 0$. All quantities with subscript 0 will refer to this instant of time.

The joint consideration of the physicokinetic and thermal aspects of the problem reduces to solving the system of equations (6) and (9), which will fully describe the growth process with allowance for the constraints made above—

···conditions. The system of equations (6) and (9) leads to the equation

$$\begin{aligned}(\delta\Delta T_0 - yy')y'' + 2y'({y'}^2 + yy'') + \frac{y'}{a_1\delta^2}(\delta\Delta T_0 - yy')^3 &= \\ = \frac{a_2}{a_1\delta}\exp\left\{-\frac{a_3\delta}{\delta\Delta T_0 - yy'}\right\}(\delta\Delta T_0 - yy')^3&.\end{aligned} \tag{10}$$

We seek its solution in the form of a series in powers of the parameter $\delta\Delta T_0$, not necessarily small. It will be valid for those values of t that ensure convergence of such a series. Restricting ourselves only to the linear terms of the series, we obtain

$$y_0 = V_{\text{st.0}}\tau_0\left[e^{-t/\tau_0} + \frac{t}{\tau_0} - 1\right], \qquad V_{\text{st.0}} = V_{\text{st}}(\Delta T_0),$$

$$\begin{aligned}y = y_0 + \delta\Delta T_0 \Bigg[\frac{y_0^3}{\tau_0} - \frac{V_{\text{st.0}}}{\tau_0}y_0^2 t + V_{\text{st.0}}\left(\frac{a_2}{2\Delta T_0} - 1\right) \times \\ \times \left(y_0^2 - \frac{1}{\tau_0}y_0 t^2 - 3V_{\text{st.0}}^2 t^2 + \frac{V_{\text{st.0}}^2}{\tau_0}t^3 + 6V_{\text{st.0}}\tau_0 y_0\right)\Bigg].\end{aligned} \tag{11}$$

From equations (9) and (11) we obtain

$$V = \left[2\frac{V_{\text{st.0}}}{\tau_0}\,\delta(\Delta T_0 - \Delta T)\right]^{1/3}\left[1 - \left(\frac{a_2}{\Delta T_0^2} + \frac{8}{\Delta T_0}\right)(\Delta T_0 - \Delta T)\right]. \tag{12}$$

The limiting transition $\Delta T \to \Delta T_0$ ($t \to 0$) in equation (12) gives $V = 0$, although at the crystallization front the supercooling $\Delta T = \Delta T_0$ has already been attained. Consequently, a lag occurs in accordance with (2).

The joint solution of equations (7) and (9),

$$V = V_{\text{st.0}}\left[1 - \frac{a_2}{\Delta T_0^2}(\Delta T_0 - \Delta T)\right], \tag{13}$$

where the lag is not taken into account, does not satisfy the boundary conditions of problem (2) under the limiting transition $\Delta T \to \Delta T_0$ ($t \to 0$), since here $V \neq 0$. As $\delta \to \infty$, equation (13) passes into the classical expression (7).

When the heat removal is finite, then, as the process proceeds in time, it is necessary to take into account increasingly higher powers of the parameter $\delta\Delta T_0$.

In the limiting case $t \gg \tau_0$, i.e., for large y, the kinetic aspect of the growth process in equation (10) becomes insignificant, and only the thermal aspect remains, which gives the well-known law of crystal growth $\sim \sqrt{t}$. The obtained dependence of the growth rate on the process time as a function of two of its factors—physicokinetic and thermal—corresponds to the real picture of the process.

If, in experimental studies, the instantaneous relation between the rate and the supercooling at the crystallization front is recorded, then it will coincide with the classical relation (7) only under isothermal conditions of transformation and for those instants of time when the "lag" effect has already disappeared. In reality, the actual transformation process is, as a rule, nonstationary and proceeds under nonisothermal conditions. In this case, when carrying out the indicated instantaneous measurements, because of the continuously realized lag effect, it will not be possible to obtain dependence (7). Therefore, in studying the kinetics of growth of crystals from melts, in order to avoid a large scatter of experimental points, it is recommended to strictly monitor the maintenance of isothermal conditions and, at any growth rates, to take into account the additional restriction $t > \tau_0$. This is especially important in the case of small supercoolings, which occur during the crystallization of metals.

The dependence (12) has, in the linear approximation, a maximum at $\Delta T_0 - \Delta T = \frac{1}{4}(a_2/\Delta T_0^2 + 8/\Delta T_0)$, which, for purely physical reasons, will be preserved in any approximation. The ratio of the growth rates calculated from equations (12) and (13) at this point characterizes the influence of the lag effect on the kinetics of the process. For the organic substance salol,

$$V_{\text{st}} = 0.3 \exp\{-3.7/\Delta T\} \text{ cm/sec},$$

for $\Delta T_0 = 1$; 0.8 and 0.6° this ratio is respectively 9; 13; 30. For the metal gallium (^{8}) (face [001])

$$V_{\text{st}} = 7000 \exp\{-13/\Delta T\} \text{ cm/sec},$$

for $\Delta T_0 = 1$; 0.8 and 0.6° the corresponding ratios will be 35; 305; $6.5 \cdot 10^5$. Consequently, the lag effect plays an essential role in the growth of metallic crystals, where large cooling rates are usually realized and the whole process takes place over comparatively short time intervals. Apparently, the quantity τ_0 in this case cannot be neglected. In the growth of organic crystals, as follows from the estimate given above, obtained from a very conditional description of the experimental data, the lag effect is manifested to a considerably smaller extent.

The maximum of the growth rate with allowance for lag in the case of gallium is reached, for $\Delta T_0 = 1^\circ$, at a distance $y \sim 5 \cdot 10^{-4}$ cm. When the supercooling at the crystallization front decreases, this distance increases rapidly and, for real $\Delta T < 0.1^\circ$, becomes very considerable.

A complete calculation of the kinetics of crystal growth under nonisothermal conditions can be obtained from equation (10), using electronic computing devices for its numerical integration.

Thus, in analyzing experimental data on the dependence of the crystal growth rate on supercooling, it should be borne in mind that the effects of nonstationarity and nonisothermality may substantially influence the effective relation between V and ΔT and may obscure the relationships characteristic of the true physical mechanism of the process; consequently, in setting up experiments one should strive to obtain stable isothermal conditions at the crystallization front (for example, by programmatically changing the conditions of heat removal from the crystallization front).

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