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MATHEMATICAL CONSTRUCTION OF THE COOLING CURVE CHARACTERIZING CRYSTALLIZATION FROM A SUPERCOOLED MELT

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A theoretical model characterizing the explosive crystallization from a supercooled melt has been proposed and analyzed. Taking account of the specific features of the cluster-coagulation model of crystallization and the specific features of the experiment has made it possible to construct cooling curves adequate to the experimental ones.

Numerous experimental data [1–5], including those obtained by us [6–10], point to the fact that a considerable number of substances begin to crystallize at a temperature T_m lower than the melting temperature T_{liq}. In so doing, the degree of supercooling of melts $\Delta T = T_{liq} - T_m$ for samples of mass from 0.1 mg to a few grams under normal conditions and at cooling rates from 0.001 to 10 K/sec can reach dozens of degrees, e.g., for Bi, Sb, Sn, Te, S, InSb, H_2O, C_6H_5OH, $C_6H_4(OH)_2$, etc.

To mathematically describe the cooling curve in the coordinates of $T(\tau)$ covering the region of supercooled melt crystallization, let us consider the schematical experimental cooling curves (Fig. 1a and b) registered by the method of cyclic thermal analysis (CTA) [6–10]. Figure 1 also shows their corresponding curves obtained by differential-thermal analysis (DTA) (Fig. 1c and d). The ABC section in Fig. 1a corresponds to the melt cooling down to some temperature $T_m < T_{liq}$. The melt stays in the supercooled state for time τ_1 (section BC). Upon cooling down to the minimum temperature T_m, the sample is spontaneously heated to T_{liq} in time τ_2 (line CD). The rapid rise in the CD section points to the proceeding in the bulk of the superheated melt of the initial stage of crystallization with release of heat Q promoting rapid heating of the whole sample by ΔT^-. Further solidification of the sample (section DE) occurs isothermally at T_{liq} for time τ_3. Upon solidification, the substance is cooled (section EF). Thus, the total crystallization time $\tau' = \tau_1 + \tau_2 + \tau_3$. We call the kind of crystallization given in Fig. 1a nonequilibrium-explosive crystallization (NEEC).

The cooling curve in Fig. 1b (GHKL) corresponds to quasi-equilibrium crystallization (QEC) with insignificant supercooling. As a rule, QEC is observed for melts that are not superheated to a temperature higher than some critical temperature $T_{cr}^+ > T_{liq}$. The melt heated to above T_{cr}^+ crystallizes with supercooling ΔT^-, whose mean value is practically independent of the degree of superheating of the melt. Experiments show [6–10] that the total solidification time τ'' under QEC is always shorter than the total time τ' under NEEC.

In [11, 12], solutions of the thermal problems describing the cooling curves with crystallization are given. However, they neglected the features of the cluster-coagulation models of crystallization of supercooled melts [7], in particular, the explosive character of crystallization at the initial stage in time τ_2, the rapid temperature rise from T_m to T_{liq}, the difference between τ' and τ'' under QEC and NEEC, etc.

The aim of the present paper is to describe mathematically the cooling curve covering the crystallization region (Fig. 1), taking into account the features of the cluster-coagulation model, which will be presented in the course of the problem solution.

Consider the test specimen–furnace system with temperature T_f. Denote the heat-transfer coefficient at the specimen–furnace boundary as ζ. The ambient temperature (outside the furnace) is T_0. Assume that the specimen has a spherical form of radius R. Then the heat-conduction equation in the spherical system of coordinates with re-

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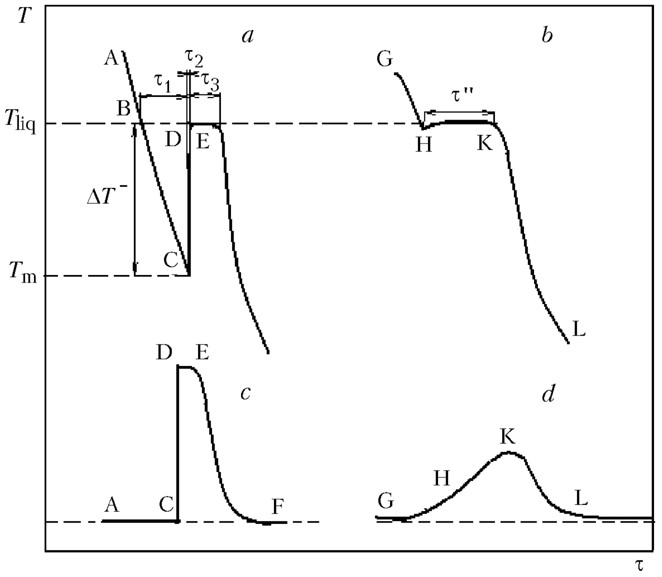

Fig. 1. Cooling curves of pyrocatechol of volume 0.8 cm^3 characterizing crystallization with supercooling (a) and without supercooling (b) obtained by the CTA method and their corresponding DTA curves (c, d).

gard for the invariability in the considered temperature range of the heat-conduction coefficient λ of the specimen is of the form

$$c_p m_0 \frac{\partial T(r,t)}{\partial t} = \lambda \left(\frac{\partial^2 T(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial T(r,t)}{\partial r} \right) V_0 + Q(r,t) , \quad t \geq 0 , \quad 0 \leq r \leq R , \tag{1}$$

where $T(r, t)$ is the temperature at each point of the specimen depending on the radius r and the time t and $Q(r, t)$ is the function of the heat-release sources inside the specimen. The boundary conditions for (1) are as follows:

$$T(r,0) = T_{\mathrm{liq}} , \quad \lambda \left(\frac{\partial T}{\partial r} \right)_{r=R} = - \left(\zeta (T - T_{\mathrm{f}}) + \sigma \varepsilon (T^4 - T_{\mathrm{f}}^4) \right)_{r=R} . \tag{2}$$

Here the first and second terms on the right side of the second expression represent the heat exchange of the specimen with the furnace according to the Newton and Stefan–Boltzmann laws, respectively.

Let us write the heat-release function as

$$Q(r,t) = \Delta H_{\mathrm{liq}} \frac{dm}{dt} = \Delta H_{\mathrm{liq}} m_0 \frac{d\eta}{dt} , \tag{3}$$

where $\eta = m(t)/m_0$ is the degree of crystallinity. In this case, $Q(r, t)$ is the heat released under crystallization of the mass dm of the melt in the time dt.

Taking into account the slow cooling of the massive furnace with a miniature specimen, we can neglect the characteristics of the thin-walled crucible (heat conductivity, heat capacity, etc.) and the processes occurring at the crucible–specimen boundary. Neglecting the temperature difference between the center of the specimen and its boundary and the second coordinate-derivatives, in view of (2), we can simplify expression (1). This is admissible, since in our experiments the sizes of specimens (~1 cm) are much smaller than the furnace sizes. In [13], it was shown that the use of small masses (up to 1 g) is fairly correct for these purposes. Thus, Eq. (1) with the boundary conditions (2) will reduce to the relation

$$\frac{dT}{dt} = -\frac{2}{\rho c_p R}\left(\zeta\,(T - T_f) + \sigma\varepsilon\,(T^4 - T_f^4)\right) + \frac{\Delta H_{\text{liq}}}{c_p}\frac{d\eta}{dt}\,, \quad T(0) = T_{\text{liq}}\,. \tag{4}$$

In the DE section (Fig. 1a) crystallization occurs at an invariable temperature T_{liq}, and the degree η of solid phase build-up obeys the Johnson–Mehl–Avrami equation [14]

$$\eta = 1 - \exp\left(-Z\,(t - \tau_1 - \tau_2)^n\right)\,, \quad t \geq \tau_1 + \tau_2\,, \tag{5}$$

where τ_1 is the incubation period of nucleation; τ_2 is the time of explosive crystallization at the initial stage of solidification.

In the case of NEEC, for sections BC, CD, DE, and EF (Fig. 1a) expression (5) is unacceptable, since it describes the monotonic change in the phase and ignores the initial (explosive) crystallization in the CD section in the time τ_2. According to the cluster-coagulation model of crystallization [7, 15], in the melt, upon reaching under some physical supercooling ΔT^- the critical concentration in some region V_{cr} (of mass m_{cr}) of the melt, the nuclei close with one another, orient themselves with respect to one another, and coagulate in the time τ_2. This is accompanied by a release of heat $Q = m_{\text{cr}}\Delta H_{\text{liq}}$, which leads to a heating of the whole specimen by a value of ΔT^- from T_{m} to T_{liq} at a rate v = 20–50 K/sec. Taking into account that the cooling rate of the furnace $v_{\text{c}} << v$, one can give the heat-balance equation without allowance for the heat loss as

$$m_{\text{cr}}\Delta H_{\text{liq}} = m_0 c_p \Delta T^-\,. \tag{6}$$

Then the relative portion β of the crystallized region in which the critical density of nuclei was concentrated will be equal to

$$\beta = \frac{m_{\text{cr}}}{m_0} = \frac{c_p \Delta T^-}{\Delta H_{\text{liq}}}\,. \tag{7}$$

Upon coagulation of nuclei in the time τ_2, their number in the volume V_{cr} rapidly decreases, forming the initial solid conglomerate. The process of unification of nuclei (in the CD section) in a time from τ_1 to $\tau_1 + \tau_2$ can be described by the equation [16]

$$n_k = n_{k0} \exp\left(-k\,(t - \tau_1)\right)\,, \tag{8}$$

where $n_{k0} = N_k/V_{\text{cr}}$ is the concentration of nuclei in the volume V_{cr} at the onset of coagulation; N_k is the number of nuclei before their coagulation; n_k is the concentration of nuclei after the time $t - \tau_1$ from the onset of coagulation. The coagulation constant k can be determined from the thermogram (Fig. 1a) by the dynamics of the temperature in the CD section in a time from τ_1 to $\tau_1 + \tau_2$; $k = \frac{1}{\tau_2}\ln\,(n_{k0}/n_k)$. For example, if $n_k/n_{k0} = 0.001$ and $\tau_2 = 0.2$ sec, then $k = 26\ \text{sec}^{-1}$.

On the basis of the foregoing, expression (5) can be generalized with allowance for the fast crystallization at the initial stage of solidification of the supercooled melt;

$$\eta = \alpha + \beta\,\left(1 - \exp\left(-k\,(t - \tau_1)\right)\right)\,\Theta\,(t - \tau_1) + (1 - \alpha - \beta)\,\left(1 - \exp\left(-Z\,(t - \tau_1 - \tau_2)^n\right)\right)\,\Theta\,(t - \tau_1 - \tau_2)\,, \tag{9}$$

where α is the portion of the specimen formed from nuclei before their coagulation in the time τ_1.

The presence of the Θ-function is due to the fact that heat release begins sharply at the instant of time τ_1. The parameters Z and n are determined by taking twice the logarithm of (9) [17]. The quantity α can be estimated on the basis of the data on the isothermal crystallization times τ'' at QEC and τ_3 at NEEC. The quantity $\xi = \tau_3/\tau''$ is the nonsolidified portion of the specimen immediately after explosive crystallization; then

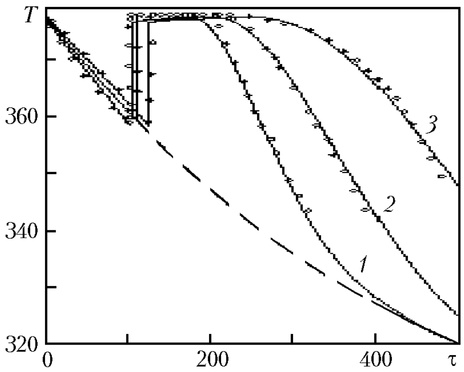

Fig. 2. Cooling curves of pyrocatechol specimens of various volumes [1) V_0 = 0.35; 2) 0.8; 3) 1.5 cm^3)] at a cooling rate of 0.13 K/sec. T, K; τ, sec.

$$\alpha = 1 - \beta - \xi \,. \tag{10}$$

Taking into account the small difference between the temperatures of the furnace T_f and the specimen T, one can neglect the second term on the right side of Eq. (4) [18]:

$$\frac{dT}{dt} = -\gamma (T - T_\text{f}) + \frac{\Delta H_\text{liq}}{c_p} \frac{d\eta}{dt} \,, \quad T(0) = T_\text{liq} \,, \tag{11}$$

where

$$\frac{d\eta}{dt} = \beta k \Theta (t - \tau_1) \exp [- k (t - \tau_1)] + (1 - \alpha - \beta)\, Zn\, (t - \tau_1 - \tau_2)^{n-1}\, \Theta (t - \tau_1 - \tau_2) \exp [- Z (t - \tau_1 - \tau_2)^n] \;;$$

$$\eta = \begin{cases} \alpha \,, & t = \tau_1 \;; \\ 1 \,, & t \to \infty \;; \end{cases} \qquad \frac{d\eta}{dt} = \begin{cases} k\beta \,, & t = \tau_1 \;; \\ 0 \,, & t \to \infty \;; \end{cases} \qquad \gamma = \frac{2\zeta}{c_p \rho R} \,.$$

Furnace cooling occurs by the law

$$T_\text{f} = T_0 + (T_\text{liq} - T_0) \exp (- \gamma_\text{f} t) \,. \tag{12}$$

Solving problem (11), we obtain the equation

$$T(t) = T_1 + \frac{\Delta H_\text{liq}}{c_p} \exp (- \gamma (t - \tau_1)) \int\limits_{\tau_1}^{t} \frac{d\eta}{dt} \exp (\gamma (\tau - \tau_1))\, d\tau \,, \tag{13}$$

where

$$T_1 = T_0 + (T_\text{liq} - T_0) \left(\left(1 + \frac{\gamma}{\gamma_\text{f} - \gamma} \right) \exp (- \gamma t) + \frac{\gamma}{\gamma - \gamma_\text{f}} \exp (- \gamma_\text{f} t) \right).$$

The cooling parameters of the furnace γ_f and the specimen γ are determined from the experimental cooling curves. Under our conditions, usually $\gamma_\text{f} << \gamma$, and the function of T_1 practically coincides with the furnace cooling function T_f.

The value of η was determined by the DTA curves according to the method of [19]. However, because of the exponential character of function (9), the error in calculating coefficients α, β, Z, and n leads to noticeable discrepancies between the model and experimental curves. On the other hand, by the CTA cooling curves one can determine

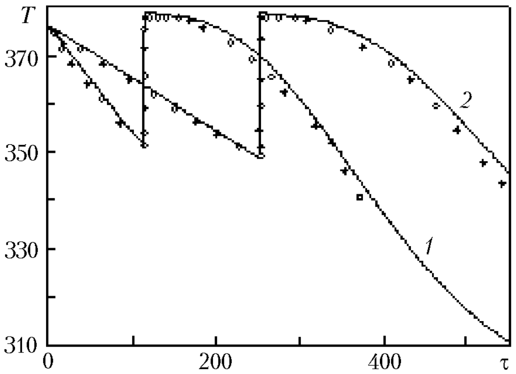

Fig. 3. Cooling curves of the pyrocatechol specimen of volume 1.5 cm^3 at various cooling rates: 1) v_c = 0.24; 2) 0.12 K/sec. T, K; τ, sec.

fairly exactly the derivative of $d\eta/dt$ in the DE section (Fig. 1) that enters into solution (13). Consider Eq. (11). Since in this section $dT/dt = 0$, in view of (12) we obtain

$$\frac{d\eta}{dt} = \frac{\gamma c_p^*}{\Delta H_{\text{liq}}} (T_{\text{liq}} - T_0)\,(1 - \exp(-\gamma_f t)) + k\beta \exp(-k(t - \tau_1))\,, \quad \tau_1 \le t \le \tau_1 + \tau_2 + \tau_3\,. \tag{14}$$

Integrating (14), we find the empirical time dependence of the degree of transformation η in the DE section:

$$\eta = \alpha + \beta\,(1 - \exp(-k(\tau - \tau_1))) + \frac{\gamma c_p^*}{\Delta H_{\text{liq}}} (T_{\text{liq}} - T_0) \left(\tau - \tau_1 + \frac{1}{\gamma_f} (\exp(-\gamma_f t) - \exp(-\gamma_f \tau_1)) \right), \tag{15}$$

where c_p^* is the mean value of the specific heat capacity of the liquid and solid phases ($c_{p\text{liq}}$ and $c_{p\text{s}}$ near T_{liq}). With a correction reducing η to unity at $\tau > \tau_1 + \tau_2 + \tau_3$, this method permits more exact determination of the degree of transformation.

As an example, Fig. 2 shows the cooling curves of pyrocatechol of various volumes at an equal mean cooling rate of 0.13 K/sec and at supercooling ΔT^- = 18 K (dots show the experimental data, the dashed curve corresponds to the furnace cooling curve, and the solid curves are model curves calculated on the basis of solution (13) and expression (14) by means of the Maple 6 mathematical system).

The calculated curves $T = f(t)$ of pyrocatechol of volume 1.5 cm^3 at difference cooling rates are given in Fig. 3 (dots show the experimental data).

As is seen from the figures plotted on the basis of the solution of Eq. (11) in the form of (13), in view of (14) and the experimental data for determining the degree of transformation, the model cooling curves agree fairly well with the experimental ones. The good convergence of the theoretical curves and experimental data is provided by the determination of the proposed model parameters by the CTA and DTA curves.

NOTATION

c_p, specific heat capacity, J/K; $c_{p\text{liq}}$ and $c_{p\text{s}}$, heat capacities of the liquid and solid phases in the vicinity of the melting temperature, J/K; ΔH_{liq}, specific melting heat, J/kg; k, coagulation constant, sec^{-1}; m_{cr}, mass of the region with a critical concentration of nuclei c_0, kg; m_0, mass of the whole specimen, kg; Q, heat released in the process of coagulation of nuclei, J; R, specimen radius, cm; T, specimen temperature, K; T_{m}, minimal temperature of supercooled melt, K; T_{liq}, melting temperature, K; T_{f}, furnace temperature, K; T_0, ambient temperature, K; T_{cr}^+, temperature of critical superheating of melt, K; t, time; Z and n, crystallization constant and index of the form of nuclei (have fractional dimensions); V_{cr}, volume of the region with a critical concentration of nuclei, cm^3; V_0, specimen volume, cm^3; v_c, specimen cooling rate, K/sec; α, portion of nuclei in the supercooled melt formed before coagulation; β, portion of melt solidified in the course of explosive crystallization under coagulation of nuclei; ξ, portion of melt isothermally solidified upon explosive crystallization; γ, specimen cooling parameter; sec^{-1}; γ_f, furnace cooling parameter, sec^{-1}; ε, emissive factor; ζ, heat-transfer coefficient at the specimen–furnace boundary, J/(m^2·sec·K); η, degree of crystallinity; $\Theta(t)$, Heaviside function; λ, heat-conductivity coefficient, J/(m·K·sec); ρ, density, kg/m^3; σ, Stefan–Boltzmann constant, J/(m^2·sec·K^4); τ_1, τ_2, and τ_3, incubation period, explosive crystallization time, and isothermal crystallization time, sec. Subscripts: cr, critical; liq, liquid; m, minimum; c, cooling; f, furnace; p, isobaric process; s, solid.

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