EVOLUTION OF A SYSTEM OF NUCLEI IN A SUPERCOOLED BINARY MELT*

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Growth of fluctuationally emerging nuclei of a new phase is considered by the example of the process of volume crystallization of a supercooled binary melt. The evolution of the size distribution function for crystals, the kinetics of removal of supercooling, and the change in impurity concentration and temperature in the melt are investigated on the basis of a nonlinear system of mass balance and heat balance equations and the kinetic equation for the crystal size distribution density function. Asymptotic representations for the basic macroscopic characteristics of the process are obtained.

Phase transitions from the liquid to the solid state, proceeding in the volume of a supercooled melt (solution), form the basis of many technologies for production, separation, and purification of various substances in the metallurgy and chemical industry [1, 2]. These transitions usually occur as a result of growth of solid phase particles on nuclei emerging either by fluctuation (homogeneous nucleation) or on foreign crystallization centers (heterogeneous nucleation) in the volume of a supercooled melt or solution (volume crystallization). The quality of the solid materials produced is governed by the conditions of the volume crystallization process, and therefore determination of the basic characteristics of the process is necessary for development of optimum methods for controlling crystallizers of various types.

One usually distinguishes three stages when investigating the process of volume crystallization. The distination is explained by different characteristic times of relaxation in each stage [3]. In the initial stage fluctuational emergence of small aggregations of a new phase occurs in the medium, i.e., nuclei. This stage is investigated in great detail in numerous works based on Ya. B. Zel'dovich's theory [4, 5], in which the dependence of the nucleation rate on the degree of metastability of the maternal phase is determined. The final stage (the stage of Ostwald maturation) is a process of recrystallization. The supercooling in this stage is slight and the fluctuational emergence of nuclei can be ignored. Of crucial importance in this stage is the process of "eating" of small particles by large ones, i.e., the growth of larger particles owing to dissolution of small particles. I. M. Lifshits and V. V. Slezov [6] realized an approach to the problem with a series of simplifying assumptions. They obtained an asymptotic law of size distribution ($t \to \infty$) of particles, independent of the initial (at the moment of onset of the Ostwald maturation stage) distribution. Investigation of the intermediate stage when both the influence of growing particles on the state of the ambient medium and persisting nucleation are simultaneously important is a rather complex problem, to which a series of works have been devoted recently [7, 8]. However, as far as the authors know, the intermediate stage of the process of crystallization in binary systems has not been studied before. This investigation is needed because it is a natural stage in studying directed hardening of binary melts, which is often accompanied by formation of thermally or concentrationally supercooled zones in which nucleation and crystal growth occur.

The aim of the present work is to determine the kinetics of change of the basic characteristics of a supercooled binary melt in the intermediate. The investigations are based on a method proposed in [8].

We consider the process of growth of a suspension of solid spherical particles in a binary melt. At the initial moment $\tau = 0$ a melt having the impurity concentration σ_0 will be considered to be cooled down to the temperature θ_0, which is lower than the phase transition temperature $\theta_l (\sigma_0)$ for the given impurity concentration. Then in the melt nuclei of the solid phase continuously emerge, which grow and form a suspension of solid spherical particles, which is macroscopically homogeneous. The evolution of this system is described by a kinetic equation for the particle radius distribution density function $f(\tau, r)$, a heat balance equation for the melt temperature θ_1, and a mass balance equation for the impurity concentration σ. Neglecting random fluctuations of the rate of particle growth, these equations can be written in the following form:

$$\frac{\partial f}{\partial \tau} + \frac{\partial}{\partial r}\left(\frac{dr}{d\tau} f\right) = 0, \quad \tau > 0, \quad r > r_*,$$

$$\rho_m C_m \frac{d\theta_1}{d\tau} = \rho L \int\limits_0^\infty 4\pi r^2 \frac{dr}{d\tau} f \, dr, \tag{1}$$

$$\frac{d\sigma}{d\tau} = (1 - k) \sigma \int\limits_0^\infty 4\pi r^2 \frac{dr}{d\tau} f \, dr.$$

Here ρ_m and ρ are the mixture and solid material density, respectively (we will further assume that $\rho_m = \rho$); k is the effective coefficient of trapping, defined as the ratio of the impurity concentration in the crystal to the average impurity concentration in the volume of the maternal medium. We will regard k as a constant value and r_* as so small that it can be assumed equal to zero. For simplicity we also assume that ρ_m, ρ, and C_m are independent of the temperature and the volume concentration of the solid phase.

The system of equations (1) satisfies the following initial and boundary conditions:

$$f = 0, \quad \theta_1 = \theta_0, \quad \sigma = \sigma_0 \quad \text{when} \quad \tau = 0; \tag{2}$$

$$\frac{dr}{d\tau} f = J(\Delta\theta_1) \quad \text{when} \quad r = 0, \tag{3}$$

$$\Delta\theta_1 = \theta_* - m\sigma - \theta_1, \tag{4}$$

where J is the nucleation frequency; $dr/d\tau$ is the particle growth rate; θ_* is the crystallization temperature for the pure substance; m is the slope of the liquidus line. Condition (3) determines a flow of nuclei with the critical radius and shows that the distribution of crystals depends strongly on the supercooling $\Delta\theta_1$.

To close problem (1)-(4), concrete representations are needed for the nucleation frequency and the crystal growth rate. In work we will assume for definiteness that

$$\frac{dr}{d\tau} = \frac{\beta \Delta\theta_1}{1 + \beta(\rho L/\lambda) r}. \tag{5}$$

This formula is valid in rather wide parameter ranges and corresponds to the isotropic stationary approximation [9], where β is some kinetic coefficient and λ is the thermal conductivity of the liquid phase.

For the nucleation frequency we will make of use the expression

$$J = B \exp\left[-p/(\Delta\theta_1^2/\theta_0^2)\right], \tag{6}$$

where B is the nucleation rate at the initial moment, corresponding to the supercooling $\Delta\theta_0$, $\Delta\theta_0 = \theta_* - m\sigma_0 - \theta_0$. Expression (6) for the nucleation frequency is valid both for homogeneous and heterogeneous nucleation [10]. The parameter p is equal to [4]

$$p = \frac{W_c}{k_b \theta_l} .$$

For convenience in further discussion we represent B in the form

$$B = J_0 \exp (p) .$$

We introduce the natural scales of length and time

$$l_0 = (\beta \Delta \theta_0)^{1/4} J_0^{-1/4} , \quad \tau_0 = (\beta^3 \Delta \theta_0^3 J_0)^{-1/4} ,$$

as well as the dimensionless variables and parameters

$$t = \tau/\tau_0 , \quad s = r/l , \quad U = \Delta \theta_1/\Delta \theta_0 , \quad T = \theta_1/\Delta \theta_0 ,$$

$$T_* = \theta_*/\Delta \theta_0 , \quad F = f l_0^4 , \quad \alpha = \frac{\beta L \rho}{\lambda} l_0 , \quad K_1 = \frac{4 \pi L}{C_m \Delta \theta_0} ,$$

$$T_0 = \theta_0/\Delta \theta_0 , \quad C = \frac{\sigma}{\sigma_0} , \quad M = \frac{m \sigma_0}{\Delta \theta_0} , \quad K_2 = 4 \pi (1 - k) . \tag{7}$$

In the variables of (7) the basic equations of the system take the form

$$\frac{\partial F}{\partial t} + \frac{\partial}{\partial s} \left(\frac{\partial s}{\partial t} F \right) = 0 , \tag{8}$$

$$\frac{dT}{dt} = K_1 \int_0^\infty s^2 \frac{ds}{dt} F \, ds , \tag{9}$$

$$\frac{dC}{dt} = K_2 C \int_0^\infty s^2 \frac{ds}{dt} F \, ds , \tag{10}$$

$$U = T_* - MC - T , \tag{11}$$

$$\frac{ds}{dt} = \frac{U}{1 + \alpha s} , \tag{12}$$

$$UF|_{s=0} = \exp \left[- \frac{1 - U^2}{U^2} p \right] , \tag{13}$$

$$F = 0 , \quad U = 1 , \quad T = T_0 , \quad C = 1 \quad \text{at} \quad t = 0 . \tag{14}$$

The solution of Eq. (8) with the initial condition from (14) is expressed by the relation

$$F (t , s) = (1 + \alpha s) \varphi [x (t) - y (s)] \eta [x (t) - y (s)] , \tag{15}$$

where

$$x (t) = \int_0^t U (t) \, dt , \quad y (s) = \int_0^s (1 + \alpha s) \, ds ,$$

and the function φ is determined by the boundary condition (13)

$$\varphi\left(x\left(t\right)\right) = \frac{1}{U\left(t\right)} \exp\left[-\frac{1-U^2\left(t\right)}{U^2\left(t\right)} p\right], \tag{16}$$

$\eta(x)$ is the Heaviside function, equal to zero for negative values of the argument and to unity for positive ones.

Relation (12) can be integrated (we employ the initial condition $s = 0$ at $t = v$). We have

$$\alpha s = [1 + 2\alpha\left(x\left(t\right) - x\left(v\right)\right)]^{1/2} - 1. \tag{17}$$

At $t = 0$, (17) determines in dimensionless form the radius $s_m(t)$ of crystals that had emerged at the initial moment at the moment t.

Relation (15) specifies the function F in implicit form; however, it makes it possible to simplify Eqs. (9) and (10) considerably. We substitute (15) into the integral in the right-hand side of Eqs. (9) and (10) and replace the integration variable s for any fixed t by a new variable v using the equality $x(v) = x(t) - y(s)$. We obtain the following equations:

$$\frac{dT}{dt} = K_1 U \int\limits_0^t h\left(v, t\right) \exp\left[pg\left(v\right)\right] dv, \tag{18}$$

$$\frac{dC}{dt} = K_2 UC \int\limits_0^t h\left(v, t\right) \exp\left[pg\left(v\right)\right] dv, \tag{19}$$

where

$$h\left(v, t\right) = \alpha^{-2} \frac{\left([1 + 2\alpha\left(x\left(t\right) - x\left(v\right)\right)]^{1/2} - 1\right)}{[1 + 2\alpha\left(x\left(t\right) - x\left(v\right)\right)]^{1/2}}, \quad g\left(v\right) = -\frac{1-U^2\left(t\right)}{U^2\left(t\right)}.$$

To further simplify the functional integral equations, we employ the following method. We note that the integral in the right-hand side of Eqs. (9) and (10) is the Laplace integral and it would be reasonable to use the Laplace method [11] for its approximate calculation. It is easy to verify that

$$\frac{dg}{dt} = 2U^{-3}\frac{dU}{dt} < 0,$$

i.e., the maximum of the function g is attained on the boundary $t = 0$ of domain of definition its and that only its forth derivative is different from zero at the point $t = 0$ and it is equal to $-4MK_1 - 4K_2$. Taking into account only the dominant term of the asymptotic expansion of the integral in (18) and (19), we have [11]

$$\int\limits_0^t h\left(v, t\right) \exp\left[pg\left(v\right)\right] dv \approx 1/4\Gamma\left(1/4\right) \left[\frac{-4!}{p\left(-4MK_1 - 4K_2\right)}\right]^{1/4} h\left(0, t\right) \exp\left[pg\left(v\right)\right], \tag{20}$$

where $\Gamma(x)$ is the Euler gamma-function.

The order of the integrodifferential equations (18) and (19) can be lowered by using the transformations

$$\frac{dC}{dt} = \frac{\partial C}{\partial x}\frac{dx}{dt} = \frac{\partial C}{\partial x} U, \quad \frac{dT}{dt} = \frac{\partial T}{\partial x}\frac{dx}{dt} = \frac{\partial T}{\partial x} U,$$
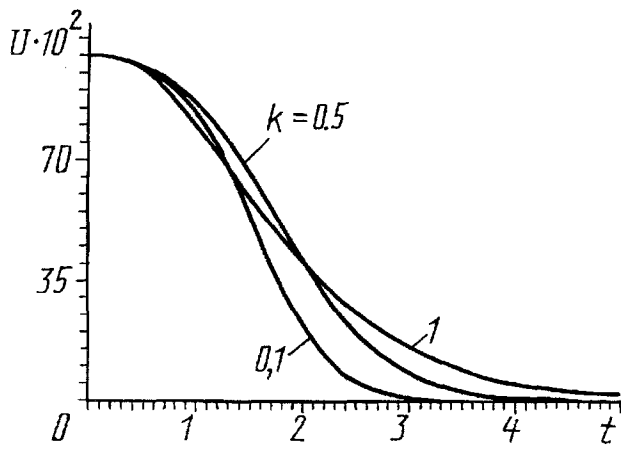
after which they are reduced to the equations
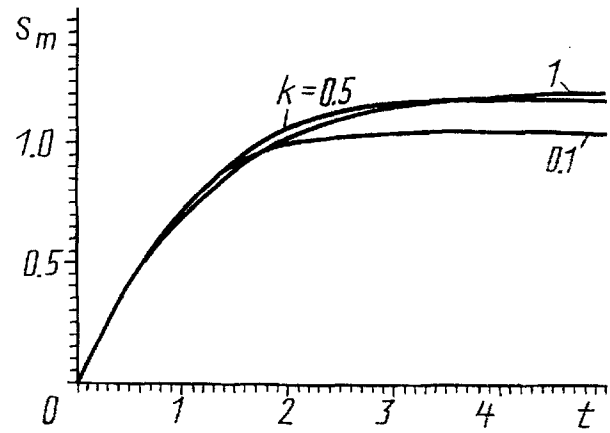
Fig. 1. Kinetics of removal of supercooling vs. time t.

Fig. 2. Maximum radius of crystals s_m vs. time t.

$$\frac{\partial T}{\partial x} = K_1 \varepsilon \, \alpha^{-2} \frac{\left([1 + 2\alpha x \, (t)]^{1/2} - 1\right)^2}{[1 + 2\alpha x \, (t)]^{1/2}}, \qquad (21)$$

$$\frac{\partial C}{\partial x} = K_2 C \, \varepsilon \, \alpha^{-2} \frac{\left([1 + 2\alpha x \, (t)]^{1/2} - 1\right)^2}{[1 + 2\alpha x \, (t)]^{1/2}}, \qquad (22)$$

where

$$\varepsilon = 1/4\Gamma \, (1/4) \left[\frac{6}{p \, (MK_1 + K_2)}\right]^{1/4}.$$

The solutions of Eqs. (21) and (22) with the initial conditions from (14) are

$$T = T_0 + \frac{K_1 \, \varepsilon \, \alpha^{-3}}{3} \, [(1 + 2\alpha x)^{1/2} - 1]^3, \qquad (23)$$

$$C = \exp \left(\frac{K_2 \, \varepsilon \, \alpha^{-3}}{3} \, [(1 + 2\alpha x)^{1/2} - 1]^3\right). \qquad (24)$$

Then (11) immediately yields an expression that determines the kinetics of removal of supercooling as a function of the modified time x:

$$U = T_* - M \exp \left(\frac{K_2 \, \varepsilon \, \alpha^{-3}}{3} \, [(1 + 2\alpha x)^{1/2} - 1]^3\right) - \left\{T_0 + \frac{K_1 \, \varepsilon \, \alpha^{-3}}{3} \, [(1 + 2\alpha x)^{1/2} - 1]^3\right\}. \qquad (25)$$

Replacing U by dx/dt leads to a nonlinear differential equation that can easily be integrated numerically. After this the relative supercooling U as a function of the real time t can be found directly (see Fig. 1). All the calculations hereinafter were performed for the following values of the parameters: $p = 5$, $\Delta\theta_0 = 10$; $T_* = 150$, $T_0 = 148.9$, $M = 0.1$, $\alpha = 1$, and $K_1 = 1$.

The obtained modified time x as a function of the time t makes it possible to determine the change in the maximum radius of the crystals (see (17)). The plot of $s_m(t)$ for different coefficients of trapping of the impurity is given in Fig. 2, and Fig. 3 illustrates the values of concentration and temperature as functions of k as $t \to \infty$.
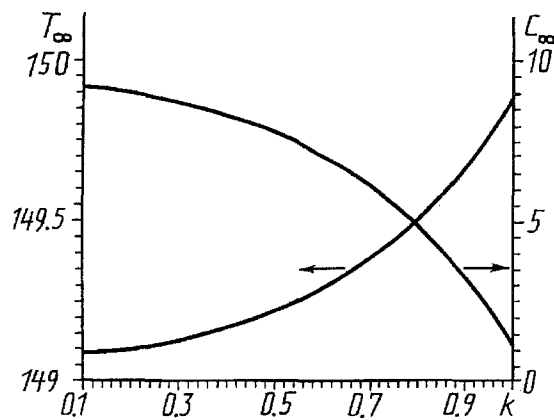
Fig. 3. Temperature T_∞ and impurity concentration in the melt C_∞ vs. coefficient of trapping of the impurity k.
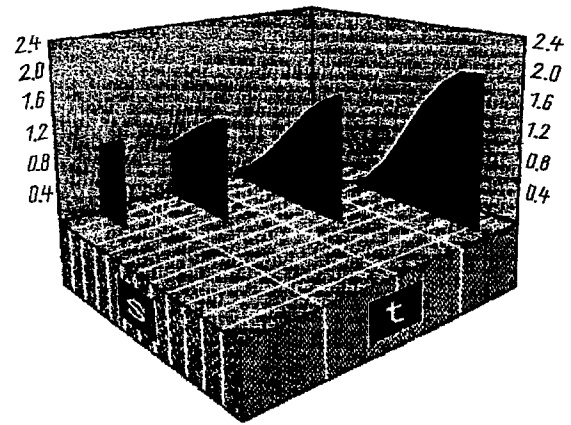
Fig. 4. Evolution of the distribution density function in time ($t = 0.25$, 0.5, 1, 5); the calculations were performed at $k = 0.1$; the maximum radius for each moment is $s_m = 0.2$, 0.4, 0.7, 1.04.

The evolution of the crystal radius distribution density function is determined by formula (15) (see Fig. 4). A distinguishing feature of the obtained distribution consists in the presence of a maximum at $s = s_m$. When the function $F(t, s)$ passes the maximum value at $s = s_m$ it drops to zero in a jump. We also note that from some moment the nucleus size distribution function undergoes only insignificant changes. For the values of the parameters used in the present work, the distribution function remains practically unchanged starting with $t = 5$.

Thus, the formulated problem of a theoretical determination of the kinetics of removal of supercooling and the size distribution of crystals in a supercooled binary melt is completely solved.

In conclusion, we note that the obtained asymptotic size distribution of crystals can be considered as the initial distribution for the final stage of recrystallization.

NOTATION

τ, time; θ_0, σ_0, temperature and impurity concentration in the melt at $\tau = 0$; $\theta_l(\sigma)$, phase transition temperature for the impurity concentration σ; $f(\tau, r)$, distribution density function of particles by radii r; θ_1, melt temperature; r_*, critical nucleus radius (the minimum crystal size); C_m, specific heat of the mixture; ρ_m and ρ, densities of the mixture and the solid material; L, specific heat of melting; k, effective coefficient of trapping of the impurity; $\Delta\theta_1$, supercooling of the melt; θ_*, phase transition temperature of the pure substance; β, some kinetic coefficient; λ, thermal conductivity of the liquid phase; B, nucleation rate at the initial moment; W_c, work of formation of the critical nucleus, corresponding to the supercooling $\Delta\theta_0$; k_b, Boltzmann constant; J and p, constants, determining the nucleation frequency; l_0 and τ_0, natural scales of length and time; t and s, dimensionless time and radius of crystals; T_*, dimensionless temperature of phase-transition of a pure substance; T and U, dimensionless temperature and subcooling of the melt; F, dimensionless distribution function; C, dimensionless impurity concentration; α, K_1, M, and K_2, dimensionless parameters; $s_m(t)$, maximum crystal size at the moment t.

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