International Journal of Heat and Mass Transfer 52 (2009) 3290–3296

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Theory of volumetric crystallization of the undercooled melt

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ARTICLE INFO

Article history:
Received 29 December 2008
Available online 13 March 2009

Keywords:
Spontaneous crystallization
Melt
Undercooling

ABSTRACT

The model of volumetric crystallization of the undercooled melt is presented. This model consists in proper consideration of heat release, caused by phase transition, by means of substitution of real distribution of the temperature field, formed in the melt around the growing sites of a new phase, into the kinetic equations describing the process. Numerical solution to the problem was derived at the example of metal melt crystallization. The current model is compared with the isothermal model and the model, based on consideration of heat release in balance relationships.

1. Introduction

In general, phase transitions occur by means of nucleation and growth of the new phase sites. Hence, total kinetics of this process is determined by nucleation frequency and the rate of nucleus growth. The values of these characteristics relate to the complex of thermodynamic and kinetic parameters, available under the given conditions, and a degree of medium metastability. The important task is determination of dependence between the part of transformed volume, time, number of the formed sites of a new phase, duration of transformations, etc. The problems of this type were solved repeatedly with regard to crystallization of the undercooled melts [1,2]. However, it should be noted that latent heat of phase transition was not considered in these works because of assumption of the isothermal character of the process or it was considered integrally, using the balance relationships and assuming melt undercooling, uniform over the whole volume at any time moment. This model is true only for times, when the length of a heat wave around nuclei exceeds their sizes significantly, and melt undercooling near crystallization fronts is almost equal to its initial undercooling (the stage of non-equilibrium crystallization). With the nucleus growth, heat near their surfaces is accumulated gradually, the melt temperature approaches the equilibrium temperature of phase transition, and a quasistationary temperature boundary layer is formed around the nuclei (the stage of equilibrium crystallization). Because of a strong dependence of nucleation frequency on undercooling, the probability of nucleation of new crystallization sites near the growing crystals decreases drastically, and this will significantly effect kinetics of volumetric transformation. This requires some additions to the existing models of phase transitions. The current work deals with the description of total volumetric crystallization with consideration of the abovementioned factors.

2. Problem statement

Let us consider the melt volume, which is cooled fast at the initial moment to some temperature $T_0 < T_{mel}$, where T_{mel} is the equilibrium crystallization temperature. At this the cooling rate $q = -dT/dt$ is so high that at this stage there are no any nuclei of the crystalline phase, formed within the melt volume. This can be expressed by the condition [3] $V \int_{T_{mel}}^{T_0} (J/q) dT < 1$, where V_0 is the initial volume of melt; J is nucleation frequency. This situation may occur, for instance, at high-speed collision of metal melt droplets with a cold heat-conducting substrate [4]. When the melt is cooled to a given temperature, its crystallization starts. This process is assumed adiabatic.

The main goal of this work is determination of dependence between the part of a crystalline mass and time $X(t) = V(t)/V_0$ where $V(t)$ is the volume of a crystallized matter; number of generated crystallization sites $N(t)$; duration of transformation. The final number of crystallites and their size distribution function will probably determine the microstructure of solidified material. Let us think that the density of matter in both phases is the same. In particular, we will neglect matter shrinkage during solidification process.

Before problem statement let us consider the mechanisms of crystal nucleation and growth in the undercooled melt and briefly consider the models of volumetric crystallization currently available in the literature.

2.1. Mechanism of crystal growth

To describe the growth of a crystal ensemble, this work uses the following "cellular" model. The whole volume of melt is divided into areas: spherical cells, where one crystal grows in the center

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doi:10.1016/j.ijheatmasstransfer.2009.01.023

Nomenclature

a	thermal diffusivity
a^*	dimensionless coefficient
c	heat capacity
d_m	diameter of molecule
f	size distribution of nuclei
G	Gibbs number
h	Plank constant
J	nucleation frequency
J_0	nucleation frequency at initial undercooling
K	kinetic coefficient
Ku	Kutateladze number
k	dimensionless coefficient
k_B	Boltzmann constant
L	specific melting heat
N	number of crystals per a volume unit
N_m	number of molecules per a unit of melt volume
N_p	number of impurity particles per a volume unit
N_{max}	number of nuclei, formed during the process per a volume unit
n^*	number of molecules per a critical nucleus
n_i	number of molecules on the surface of the *i*th impurity particle
q	cooling rate
R	crystal radius
R^*	radius of critical nucleus
r	radial coordinate
r_c	cell size
r_T	thickness of temperature boundary layer around a crystal
r_{cr}	average size of solidified material grain
r_0	typical size
T	temperature
T_{mel}	melting temperature
T_0	initial temperature of melt
ΔT	melt undercooling, $T_{mel} - T$
ΔT_0	initial undercooling of melt
t	time
t_e	lag time
t^*	typical time of nucleation expectation
t_{cr}	time of crystallization
t_0	typical time
U	activation energy
V	crystal volume
V_T	volume of “stagnation area” around crystal
V_0	initial volume of melt
v_0	typical rate of crystal growth
W^*	work of critical nucleation in homogeneous process
X	part of crystalline mass
X_T	total volume of “stagnation area”
X_{max}	final part of crystalline mass

Greek symbols

λ	heat conductivity
ρ	density
σ	surface tension at melt-crystal interface
φ_i	equilibrium wetting angle of the *i*th impurity particle surface
ψ	function of φ
χ	proportionality coefficient

of every cell. There is no heat flux at the cell boundary because of symmetry. The process of crystal growth in this statement is described by the following boundary problem [1].

Let a spherical crystal grows in the melt with temperature $T_0 < T_{mel}$. Temperature field $T(r,t)$ around a crystal is described by the equation of heat conductivity, illustrating spherical symmetry of the problem

$$\frac{\partial T}{\partial t} = \frac{a}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right), \tag{1}$$

where $a = \lambda/(\rho c)$ is thermal diffusivity of the melt; ρ, λ, c are density, heat conductivity, and heat capacity, respectively.At the initial moment

$$T(r,0) = T_0. \tag{2}$$

The boundary conditions on the crystal surface are as follows:

- the heat balance condition

$$\rho L\frac{dR}{dt} = -\lambda\left(\frac{\partial T}{\partial r}\right)_{r=R}, \tag{3}$$

- the equation, describing kinetics of phase transition (the mechanism of crystal growth is considered normal, i.e., the rate of its growth is assumed proportional to melt undercooling at the front of crystallization) [5,6]

$$\frac{dR}{dt} = K(\Delta T)_{r=R}, \tag{4}$$

where R is the crystal radius; L is specific heat of crystallization; $\Delta T = T_{mel} - T$ is melt undercooling; $K = (d_m^4\rho L)/(hT_{mel})\ \exp(-U/(k_B T_{mel}))$ is kinetic coefficient characterizing frequency of molecule bonding from the melt to the crystal; k_B is Boltzmann constant; h is Plank constant; d_m is diameter of matter molecule; U is activation energy.

The condition at the cell boundary

$$\left(\frac{\partial T}{\partial r}\right)_{r=r_c} = 0, \tag{5}$$

where r_c is the cell radius, which will be determined below.

Let us turn to the following dimensionless variables (hereinafter the dimensionless variables will be written with a superscript stroke): $\overline{T} = T/T_{mel};\ \bar{r} = r/r_0; \bar{t} = t/t_0$,where $r_0 = a/(K\,T_{mel})$; $t_0 = a/(K\,T_{mel})^2$. Then the boundary problem (1)–(5) will be written as

$$\frac{\partial\overline{T}}{\partial\bar{t}} = \frac{1}{\bar{r}^2}\frac{\partial}{\partial\bar{r}}\left(\bar{r}^2\frac{\partial\overline{T}}{\partial\bar{r}}\right); \tag{6}$$

$$\overline{T}(\bar{r},0) = \overline{T}_0; \tag{7}$$

$$\frac{d\overline{R}}{d\bar{t}} = -Ku^{-1}\left(\frac{\partial\overline{T}}{\partial\bar{r}}\right)_{\bar{r}=\overline{R}};\quad \frac{d\overline{R}}{d\bar{t}} = (\Delta\overline{T})_{\bar{r}=\overline{R}}; \tag{8}$$

$$\left(\frac{\partial\overline{T}}{\partial\bar{r}}\right)_{\bar{r}=\bar{r}_c} = 0, \tag{9}$$

where $Ku = L/(c\,T_{mel})$ is Kutateladze number.

If the crystal size is considerably less than cell size $R/r_c \ll 1$, boundary condition (9) can be substituted by the condition of infinity, consisting in equality of the initial melt temperature at a large distance from the crystal

$$T(r\to\infty,t) = T_0. \tag{10}$$

As it is shown below the process of nucleation occurs only at the initial stage of crystallization, therefore application of boundary condition (10) for its description can be quite reasonable. For later time intervals condition (9) should be used.

Using the common theory of solution to heat conductivity equations within domains with moving boundaries, we can find the solution, which meets equation (6) and conditions (7), (8), and (10) [7]

$$\overline{T}(\bar{r},\bar{t}) = \overline{T}_0 + \frac{Ku}{2\sqrt{\pi\bar{r}}}\int_0^{\bar{t}} \frac{\overline{R}(\bar{\tau})\frac{d\overline{R}}{d\bar{\tau}}}{\sqrt{\bar{t}-\bar{\tau}}}\left\{\exp\left(-\frac{[\bar{r}-\overline{R}(\bar{\tau})]^2}{4(\bar{t}-\bar{\tau})}\right)\right.$$
$$\left.-\exp\left(-\frac{[\bar{r}+\overline{R}(\bar{\tau})]^2}{4(\bar{t}-\bar{\tau})}\right)\right\}d\bar{\tau}; \quad \frac{d\overline{R}}{d\bar{t}} = 1-\overline{T}(\overline{R},\bar{t}).$$

The solution to boundary problem (7), (8), and (10) becomes easier, if there is the crystallization state, when the temperature changes are so slow that we can assume $dT/dt \approx 0$. This approximation is quite reasonable for low rates of crystal growth. In this case the solution takes the following form [1]

$$\overline{T}(\bar{r},\bar{t}) = \overline{T}_0 + \frac{\Delta\overline{T}_0 Ku^{-1}\left(\sqrt{1+2Ku\Delta\overline{T}_0\bar{t}}-1\right)^2}{\bar{r}\sqrt{1+2Ku\Delta\overline{T}_0\bar{t}}}; \tag{11}$$

$$\overline{R}(\bar{t}) = Ku^{-1}\left(\sqrt{1+2Ku\Delta\overline{T}_0\bar{t}}-1\right). \tag{12}$$

It follows from Eqs. (11) and (12) that for $t << (2Ku\Delta\overline{T}_0)^{-1}$ the process of crystallization occurs as the isothermal one, and the rate of crystal growth is determined by kinetics of phase transition: $\overline{R}(\bar{t}) \approx \Delta\overline{T}_0\bar{t}$ (the same relationship can be also obtained for the isothermal model of crystal growth, turning value Ku to zero in Eq. (12)). For higher time ranges ($t \gg (2Ku\Delta\overline{T}_0)^{-1}$) heat is accumulated near the crystal surface, and finally the melt temperature near its surface becomes equal to the equilibrium temperature of phase transition. In this case heat removal becomes predominant in the process of crystallization: $\overline{R}(\bar{t}) \approx \sqrt{\bar{a}^*\bar{t}}$, where $\bar{a}^* = 2Ku^{-1}\Delta\overline{T}_0$; and quasistationary temperature boundary layer $\Delta\overline{T}(\bar{r}) \approx \Delta\overline{T}_0(1-\overline{R}/\bar{r})$ is formed around a crystal. Namely for these time ranges the model of volumetric crystallization, based on consideration of heat release in balance relationships, is inappropriate because in this case the temperature field in the melt is significantly nonuniform.

2.2. Nucleation rate

Let us define nucleation frequency J by the classic kinetic theory of Frenkel–Zeldovich [8,9]

$$J = N_m J^* \exp(-W^*/k_BT) + \sum_{i=1}^{N_p} n_i J^* \exp(-W^*\psi(\varphi_i)/k_BT), \tag{13}$$

The first term in the right part of Eq. (13) characterizes frequency of homogeneous nucleation (in a pure melt), and the second term characterizes frequency of heterogeneous nucleation (on impurity particles and foreign debris). Here, $W^* = 16\pi\sigma^3T_{mel}^2/(3\rho^2L^2\Delta T^2)$ is the work of critical nucleation in a homogeneous process (the radius of a critical nucleus at homogeneous nucleation is determined by expression $R^* = 2\sigma T_{mel}/(\rho L\Delta T)$; the model of heterogeneous nucleation uses the same value of the curvature radius of a domed nucleus surface as the model of homogeneous process); σ is the surface tension at the melt–crystal interface; $J^* = (2d_m/h)(\sigma k_BT)^{1/2}\exp(-U/(k_BT))$; N_m is the number of molecules per a unit of melt volume; n_i is the number of molecules on the surface of the ith impurity particle (foreign surface), which can be the nucleation sites; N_p is the number of impurity particles per a unit of melt volume; $\psi(\varphi_i) = (1/4)(1-cos\varphi_i)^2(2+cos\varphi_i)$, φ_i is the equilibrium wetting angle for the surface of the ith impurity particle.

It should be noted that in the current work we have used the dependence for stationary nucleation frequency because according to the estimates of [9] typical lag time (time of state stabilization) $t_e \approx n_*^{4/3}(h/(k_BT))\exp(U/k_BT)$, where n^* is the number of molecules per a critical nucleus, is essential only for the high-viscous melts (at viscosities close to the values of the amorphous state of matter), not considered in the current work.

According to analysis of relationship (13), at small undercooling nucleation occurs predominantly at the heterogeneous sites, and the lower the wetting angle of impurity particle surfaces, the higher the rate of nucleation. With a rise of undercooling the role of homogeneous nucleation increases and finally it becomes predominant. It is easy to determine the value of critical undercooling ΔT^*, corresponding to transition from the mechanism of heterogeneous nucleation to the mechanism of homogeneous nucleation: $\Delta T^* = T_{mel}(\frac{G(1-\psi)}{\ln(N_m/N_pn)})^{1/2}$, where $G = 16\pi\sigma^3/(3\rho^2L^2k_BT)$ is the Gibbs number. When deriving the latter relationship, it was assumed for simplicity that in the melt there were impurity particles only of one kind.

Generally speaking, a priori description of heterogeneous nucleation is significantly complicated by the fact that dependence for nucleation frequency includes some values of complex determination. Therefore, we will confine ourselves to the description of homogeneous crystallization.

In dimensionless variables frequency of homogeneous nucleation $\bar{J} = J/J_0$ takes the form

$$\bar{J} = \exp\left(G(\Delta\overline{T}_0^{-2} - \Delta\overline{T}^{-2})\right),$$

Here, $J_0 = J(\Delta T_0)$ is typical nucleation frequency (in our case this is frequency of homogeneous nucleation at initial undercooling).

2.3. Isothermal model of spontaneous crystallization

This model does not consider the release of the latent heat of phase transition during the crystalline mass growth. This means that melt undercooling during crystallization is constant and, hence, nucleation frequency and crystal growth rate also stay constant.

One of the first works, where the solution to the given problem was suggested, is the work of Kolmogorov [10]. It is shown there that dependence of crystalline mass X on time is determined by relationship

$$X(t) = 1 - \exp\left(-\int_0^t J(\tau)V(t-\tau)d\tau\right) = 1 - \exp(-(\pi/3)J_0v_0^3t^4), \tag{14}$$

where V is the volume of crystal, nucleated at time moment τ; $J_0 = J(\Delta T_0)$ is nucleation frequency; $v_0 = K\varDelta T_0$ is the rate of crystal growth. The densities of liquid and solid phases are assumed to be equal in this model. The mechanism of growing site "collision" is not considered there.

It follows from (14) that the part of the crystalline mass approaches one asymptotically (i.e., time of phase transition tends to infinity), and this does not corresponds to physics of the process because it is obvious that for the final rate of crystal growth and final nucleation frequency time of phase transition will be finite if even a single nucleus is generated in a volume. It is always possible that there will be no even one nucleus, but for an isolated system with finite volume V_0 this "possibility" tends to zero "catastrophically" at $t \gg t^* = 1/(JV)$ (t^* is typical time of nucleation expectation).

In this connection, when developing the non-isothermal model of volumetric crystallization, we will use the results taken from [11], where the isothermal model is developed on the basis of ideas different from the Kolmogorov's theory. The main idea of this work is as follows. Let there is a volume occupied by some metastable phase of some matter. During the process of phase transition this volume is gradually filed with a new phase (stable in this state). At this nucleation is possible only within the area, which is still in the previous phase state. Hence, time dependence of the part of volume X, occupied by a new phase, is described by integral equation

$$X(t) = \int_0^t J(\tau)(1 - X(\tau))V(t - \tau)d\tau. \quad (15)$$

Number of nuclei N formed during time t in a volume unit is determined by expression

$$N(t) = \int_0^t J(\tau)(1 - X(\tau))d\tau. \quad (16)$$

In case of constant melt undercooling an analytical solution to Eq. (15) can be found

$$X(t) = 1 - \cos\left\{(2\pi J_0 \upsilon_0^3)^{1/4} t\right\} \cosh\left\{(2\pi J_0 \upsilon_0^3)^{1/4} t\right\}. \quad (17)$$

It follows from relationship (17) that the time of complete crystallization of the melt is finite, and dependences $X(t)$, calculated by formulas (17) and (14), coincide only at the initial stage of the process.

The maximal number of nuclei formed during the whole process $N_{max} \approx 0.8(J_0/v_0)^{3/4}$ can be determined from Eq. (16) with consideration of (17). We should note that according to Kolmogorov's theory, despite the time of melt crystallization tends to infinity, the number of forming nuclei is finite and equals $N_{max} \approx 0.9(J_0/v_0)^{3/4}$.

It is obvious that a miss of latent heat of phase transition in solutions to the problems of volumetric transformation leads to significant errors.

2.4. The model of spontaneous crystallization based on consideration of heat release in balance relationships

According to this model, heat, released in phase transition, is spread uniformly over the whole volume of the melt, the melt temperature increases gradually during the process, and the temperature field stays uniform in the whole melt volume at any moment of time. Time dependence of a part of the crystalline mass and the number of generated nuclei are also described by Eqs. (15) and (16). However, in contrast to the isothermal model, nucleation frequency and the rate of crystal growth depend on time because melt undercooling reduces gradually. At this melt undercooling is determined from the equation of energy balance

$$\Delta\overline{T} = \Delta\overline{T}_0 - KuX.$$

2.5. Kinetics of volumetric phase change

Let us try to solve the stated problem from the point of model concept different from the above mentioned. As it was already noted, a temperature boundary layer is formed around the growing crystals due to release of the latent heat of phase transition. At this, probability of nucleation of the new crystallization sites near the existing ones will be considerably lower than that far from the existing sites because of the strong dependence of nucleation frequency on undercooling. We can accept that some "stagnation" area is formed around the crystals, and new crystallization sites are not formed there. It is shown schematically in Fig. 1. To take this fact into the account, let us substitute real dependence of nucleation frequency around crystals $J(r)$ by the stepped one, considering that within the "stagnation" area nucleation does not occur, whereas beyond this area nucleation frequency equals frequency at initial undercooling. We will determine the size of a "step" (thickness of temperature boundary layer r_T) from the condition that typical times of nucleation expectation in a cell at stepped and real dependences $J(r)$ should be equal, and this considers the above substitution correctly:

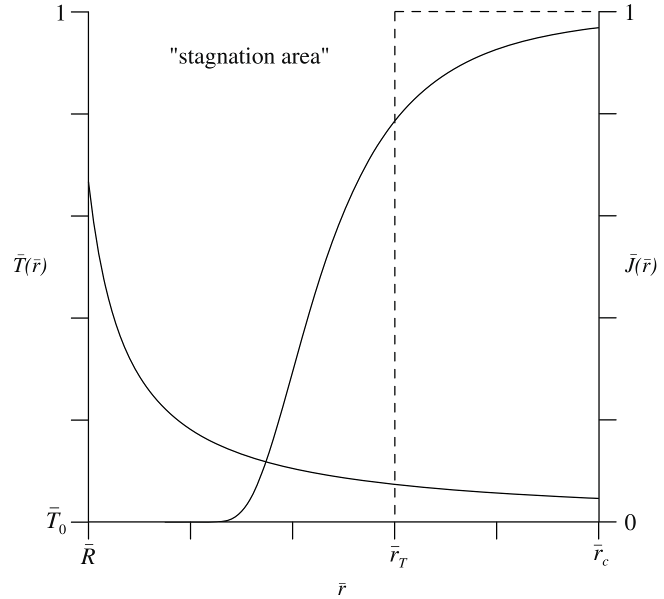

Fig. 1. Scheme of the process: 1, crystal; 2, "stagnation" area around crystal; 3, melt.

$$\bar{r}_T = \left(\bar{r}_c^3 - 3\int_{\bar{R}}^{\bar{r}_c} \bar{J}(\bar{r})\bar{r}^2 d\bar{r}\right)^{1/3}.$$

Let us take cell size r_c proportional to the size of crystals: $r_c = \chi R$. This condition is quite grounded because the thickness of temperature boundary layers, formed around the crystals, is proportional to the size of crystals (11) and (12). Proportionality coefficient χ is determined from the condition that cells occupy the whole volume

$$N(4\pi/3)\chi^3 \int_0^R R^3 f(R)dR = 1,$$

where $f(R) = N^{-1}(dN/dR)$ is the function of size distribution of nuclei. Here, N is the number of crystallites per a volume unit, generated by time moment t. We should note that both distribution function $f(R)$ and coefficient χ depend on time.Considering the abovementioned, the total volume of "stagnation" area X_T in a unit of matter volume vs. the number of all crystallites generated by time moment $\bar{t}$ is determined by the following integral equation

$$X_T(\bar{t}) = k\int_0^{\bar{t}} \bar{J}(1 - X_T(\bar{\tau}))\overline{V}_T(\bar{t} - \bar{\tau})d\bar{\tau}, \quad (18)$$

where $\overline{V}_T = (4\pi/3)\bar{r}_T^3$ is the volume of "stagnation" area around the crystal, nucleated at time moment $\bar{\tau}$; $k = J_0 r_0^3 t_0$ is a dimensionless coefficient. Eq. (18) is modification of the equation for time dependence of the crystalline mass part, obtained in the framework of the isothermal model in [11]. There is an analogy between the volume occupied by the crystalline phase, where nucleation of new sites is excepted (in the isothermal model), and the volume of "stagnation" area of the given non-isothermal model. We should note that in Eq. (18) $\bar{J}$ does not depend on time because it is dimensionless nucleation frequency at initial undercooling (for only homogeneous nucleation $\bar{J} = 1$).

Time dependence of the part of the crystallized volume will be described by relationship

$$X(\bar{t}) = k\int_0^{\bar{t}} \bar{J}(1 - X_T(\bar{\tau}))\bar{V}(\bar{t} - \bar{\tau})d\bar{\tau},$$

where $\overline{V} = (4\pi/3)\overline{R}^3$ is the volume of crystal, nucleated at time moment $\bar{\tau}$. We should note that function $X(\bar{t})$ tend asymptotically to $X_{max} = Ku^{-1}\Delta\overline{T}_0$, determined from the condition that melt crystallization stops, when heat of phase transition eliminates its undercooling. The melt crystallizes completely, when $\Delta\overline{T}_0 > Ku$.

Number of nuclei N formed during time $\bar{t}$ in a volume unit is determined by expression

$$N(\bar{t}) = (k/r_0^3)\int_0^{\bar{t}} \bar{J}(1 - X_T(\bar{\tau}))d\bar{\tau}.$$

We should note that the nucleation rate of new crystallization site dN/dt is important only at the initial stage of the process. This is caused by the fact that formation even of a small part of the crystalline mass is enough to eliminate melt undercooling and reduce nucleation frequency by several orders in comparison with the initial one. In terms of the considered model this means that the thickness of temperature boundary layers, formed around crystals, is significantly larger than the size of crystals, and the total volume of "stagnation" area X_T tends to one even at small values of X. At this the rate of new site nucleation reduces drastically. Following crystallization occurs due to the growth of the existing sites.

The average size of crystallized grains is $r_{cr} = (4\pi N_{max}/3)^{-1/3}$, where N_{max} is the number of crystallites formed during the whole process. Since nucleation occurs only at the initial stage, all grains of crystallized matter will have almost the same size, close to their average value, and the final function of distribution will be relatively narrow.

The developed system of equations completely determines crystallization dynamics of undercooled melt with consideration of real distribution of the temperature field, formed in the melt volume during crystal nucleation and growth; this system also allows determination for the crystallized matter microstructure.

3. Calculation results

Numerical calculations at the example of crystallization of the undercooled metal melt were carried out using the considered model. Results of calculations were compared with data obtained by the known models, described above. It was assumed that the melt is so pure that nucleation in the considered range of undercooling has the homogeneous nature. Aluminum was chosen as the studied material. This is caused by the fact that all its thermal–physical and kinetic properties, required for calculations, are well studied. Besides, purely homogeneous nucleation, considered in the paper, is most often for various technological processes related to crystallization of pure metals and alloys. The following thermal–physical and kinetic properties of the matter were used in calculation: $T_{mel} = 933$ K; $\rho = 2700$ kg/m^3; $\lambda = 209$ W/(m K); $c = 880$ J/(kg K); $L = 361$ kJ/kg; $\sigma = 0.093$ N/m; $d_m = 2.6\cdot10^{-10}$ m; $U = 4.15 \times 10^{-20}$ J/mol. Let us introduce the scale values and similarity criteria: typical size $r_0 \approx 3.3 \times 10^{-7}$ m; typical time of stabilization of equilibrium crystal growth $t_0 \approx 1.2 \times 10^{-9}$ s; Kutateladze number $Ku = 0.44$; Gibbs number $G = 1.1$. The low boundary of the range of considered undercooling meets the situation, when frequency of homogeneous nucleation becomes essential, and the upper boundary corresponds to typical undercooling of aluminum melt, which can be obtained by the known methods of quenching, when no sites are nucleated in the melt at cooling [4]. For clear understanding of the considered phenomenon results of calculations are presented then in dimensional variables.

Time dependence of the number of crystallization sites nucleated during the process is shown in Fig. 2a. Initial undercooling of the melt was assumed 130 K. According to the figure, at initial times dependence $N(t)$ is close to the linear one. This means that crystals, nucleated at this stage, do not effect the rate of nucleation of the new ones. With a growth of the crystalline mass total volume of "stagnation" area X_T increases, nucleation rate of new crystallization sites dN/dt decreases and, finally, vanishes. At this the part of the crystalline mass is still low and makes up several percents, and, as it was mentioned above, this is explained by the fact that the size of "stagnation" area around crystals exceeds significantly the sizes of the crystals. Therefore, nucleation occurs only at the initial stage of the process. Dependence $N(t)$ calculated by the model on the basis of heat release consideration in balance relationships is shown in Fig. 2b. In this case, the nucleation rate of crystallization sites dN/dt decreases because of reduction of melt undercooling. Fast transition from the final rate to zero at relatively short times is caused mainly by the strong dependence of nucleation frequency on undercooling (13).

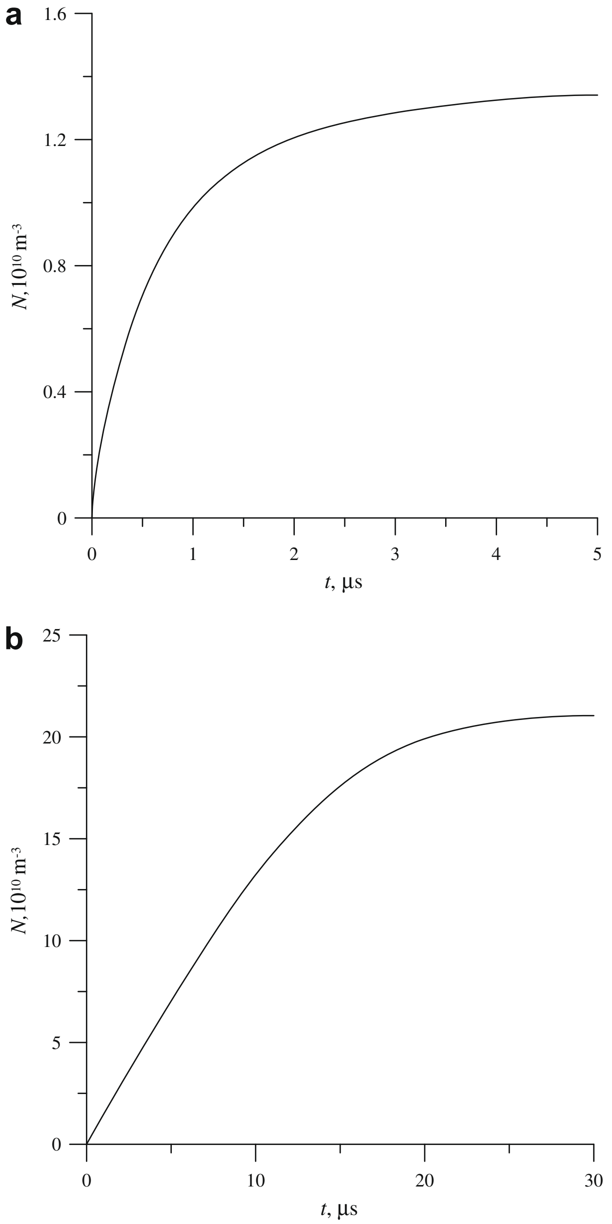

Fig. 2. Number of nucleated crystallization sites vs. time: (a) calculation by the model presented; (b) calculation by the integral model.

Time dependence of the part of the crystalline mass is illustrated in Fig. 3. Initial undercooling of melt was assumed equal to 130 K. According to the figure, curves $X(t)$, calculated by both non-isothermal models, tend asymptotically to 0.32, corresponding to X_{max} for given undercooling, whereas the isothermal model provides complete crystallization of the melt.

We should note that the characters of dependences $N(t)$ obtained by two different non-isothermal models differ, whereas dependences $X(t)$ almost coincide with the only difference that they have different time scale. This is caused by the fact that model difference is mainly shown at the initial stage of the process, when new crystallization sites are nucleated. At the later stage, when the process of volumetric transformation is determined by the growth of the existing sites, the models almost coincide because they use the same mechanism of crystal growth. Differences in time of crystallization are caused by the fact that the number of sites nucleated at the initial time moment is different for different models.

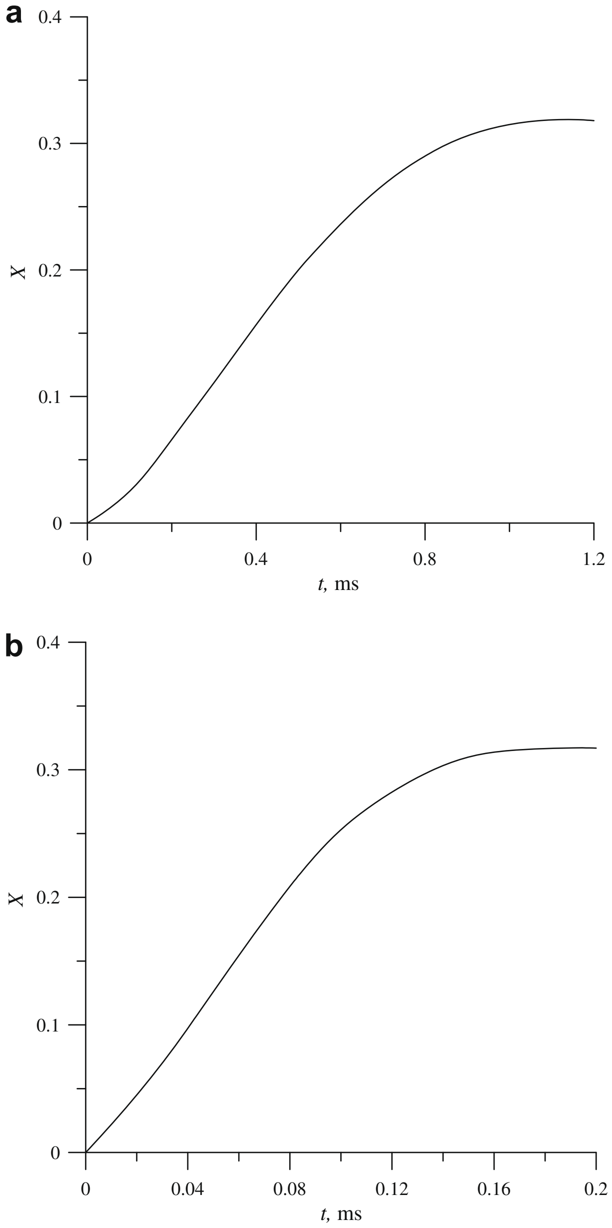

Fig. 3. Part of the crystalline mass vs. time: (a) calculation by the model presented; (b) calculation by the integral model.

Diagrams of dependence between the number of nucleated sites N_{max}, typical time of crystallization t_{cr}, and initial undercooling of melt, plotted by the isothermal and non-isothermal models, are shown in Figs. 4 and 5. Typical time of crystallization was determined as time, when the part of the crystalline mass becomes equal to $0.9X_{max}$. Perhaps, the growth in the number of crystallization sites and reduction of typical time of the process with an increase in initial undercooling of the melt relates to a significant increase in nucleation frequency and rate of crystal growth.

At first sight it may seem that dependences for isothermal and presented non-isothermal models do not differ considerably. However, several factors should be taken into account here. First, nucleation rates differ significantly in the non-isothermal and isothermal models. Thus, in the isothermal model it is significantly higher (12). Second, in the non-isothermal model the area with possible nucleation of new crystallization sites, is significantly smaller (what is connected with the forming boundary temperature layers around the crystals). Third, in the non-isothermal model time of crystallization is considerably longer than typical time of new site nucleation, whereas, in the isothermal model nucleation occurs during the whole process. However, the time of the whole process in the isothermal model is considerably shorter than that in the non-isothermal model, and this levels the differences in the number of nucleated sites. And, finally, in the isothermal model the whole melt should be crystallized in any case, but there is some limitation related to initial undercooling of the melt in the non-isothermal model.

The principle difference of the non-isothermal model of volumetric crystallization based on consideration of heat release in balance relationships from the model presented in the current paper is as follows. In the first model nucleation of new sites stops because of reduction in melt undercooling over the whole volume, what decreases nucleation frequency, and finally vanishes, but in the current model the area, where new crystallite nucleation is possible, becomes smaller (and finally also vanishes). However, in both models nucleation occurs only at the initial stage of the process (at this, typical duration of this stage is considerably shorter then typical time of the whole process), and following melt crystallization is going on due to the growth of existing sites.

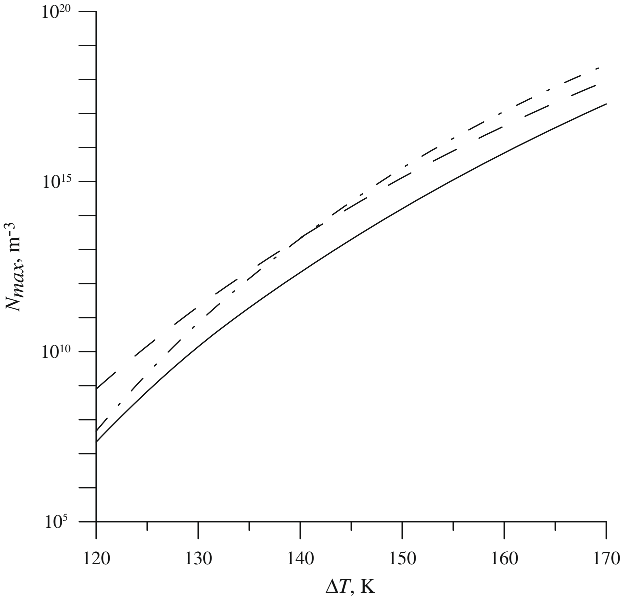

Fig. 4. Number of nucleated crystallization sites vs. initial undercooling of melt: solid line, calculation by the model presented; dashed line, calculation by the integral model; dotted line, calculation by the isothermal model.

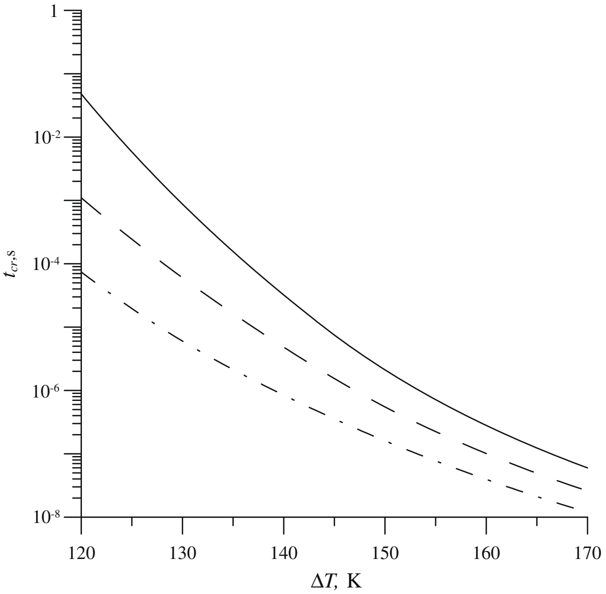

Fig. 5. Typical time of crystallization vs. initial undercooling of melt: solid line, calculation by the model presented; dashed line, calculation by the integral model; dotted line, calculation by the isothermal model.

Considering this fact, the calculation scheme for the whole process can be significantly simplified. When determining of the number of crystallization sites N_{max}, nucleated at the initial stage, by the model presented, dependence of crystalline mass part on time can be calculated from the following relationship $X(t) = N_{max}\,(4\pi/3)\,R^3(t)$. We should note once more that the mechanism of growing site "collision" is not considered by the current model. Dependence $R(t)$ can be obtained from the boundary problem (1)–(5), where the size of a cell around crystal is determined from relationship $r_c = [(4\pi/3)\,N_{max}]^{-1/3}$.

It is also can be seen in Figs. 4 and 5 that difference in dependences of nucleated site number on crystallization time for the non-isothermal models decreases with a rise of initial undercooling. This relates to the fact that at significant undercooling the mechanism of crystal growth approaches the non-equilibrium one. However, in the studied range of undercooling typical dimensionless times, when nucleation occurs, are considerably longer than one. This means that the conditions of nuclei growth differ from the isothermal conditions, and application of the model of volumetric crystallization based on consideration of heat release in balance relationships (and all the more the isothermal model) is not proper.

In conclusion, we should note that direct comparison of calculation results with experimental data is rather complex because in experiment it is difficult to achieve fast required uniform undercooling over the whole volume of the melt. Therefore, to verify the results obtained the corresponding model problem should be solved, e.g., the conjugated problem on crystallization of a metal melt microlayer on a massive substrate.

4. Conclusions

The model of spontaneous crystallization of melt, turned fast into the undercooled state, with consideration of heat release at the growth of new phase sites was developed. Available models of volumetric transformations were analyzed, and their differences from the model presented are shown. It is noted that missing of heat release or its consideration in balance relationships can lead to significant errors. Numerical solution to the problem was obtained at the example of metal melt crystallization. Typical times of the process, number of nucleated crystallization sites and dependence of the crystalline mass part on time were determined.

Acknowledgements

The work was financially supported by the Russian Foundation for Basic Research (Project Code 06-08-00657), the Research Grants Council of the RF President (Grant MK-1714.2007.8), the Foundation of Russian Science Support, in the framework of the State Contract 02.516.11.0003.

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