

Article

Anomalous Dynamics of Recalescence Front in Crystal Growth Processes: Theoretical Background

Dmitri V. Alexandrov ¹, Peter K. Galenko ^{1,2,*} and Liubov V. Toropova ^{2,3}

¹ Laboratory of Multi-Scale Mathematical Modeling, Department of Theoretical and Mathematical Physics, Ural Federal University, Lenin Ave., 51, Ekaterinburg 620000, Russia

² Otto-Schott-Institut für Materialforschung, Friedrich-Schiller-Universität-Jena, 07743 Jena, Germany

³ Laboratory of Mathematical Modeling of Physical and Chemical Processes in Multiphase Media, Department of Theoretical and Mathematical Physics, Ural Federal University, Lenin Ave., 51, Ekaterinburg 620000, Russia

* Correspondence: peter.galenko@uni-jena.de

Abstract: A theory for crystal nucleation and growth with the recalescence front is developed. The theory is based on the saddle-point technique for evaluating a Laplace-type integral as well as the small parameter method for solving the moving boundary heat transfer problem. The theory developed shows the U-shaped behavior of the growth velocity–melt undercooling curve. The ordinary upward branch of this curve is caused by the growth dictated by heat transport and the predominant crystal growth, while the unusual downward branch demonstrates the anomalous behavior caused by the predominant nucleation and attachment kinetics of the growing crystals to the phase interface. Such a U-shaped behavior of the growth velocity–melt undercooling curve is consistent with experimental data carried out on the ground, under reduced gravity during parabolic flights, and in the microgravity conditions onboard the International Space Station [M. Reinartz et al., JOM 74, 2420 (2022); P.K. Galenko et al., Acta Mater. 241, 118384 (2022)].



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1. Introduction

The solid–liquid interface dynamics in the phase transformation processes from an undercooled liquid to a solid state completely determine the direction and velocity of crystallization as well as the properties of the solidifying material. A mathematical model of such a process was first formulated in Stefan's pioneering works [1,2], and the thermodiffusion problem with a moving phase transformation interface is now called the Stefan problem [3–5]. In general, a non-stationary Stefan-type problem with a moving curved boundary of the phase transformation (crystallization front) has no exact analytical solution. As this takes place, one can find a single integro-differential equation for the interface function that defines the time-dependent position of a curvilinear crystallization front. This approach, or the boundary integral theory, is based on Green's function technique [6–9]. However, a direct solution of a thermodiffusion differential model with a moving phase transformation interface or the boundary integral equation can be solved analytically only in cases of quasi-stationary interface growth having a known shape (i.e., planar, spherical, or paraboloidal) [10–15]. In natural processes and technological conditions, the crystallization phenomenon can be complicated by the fact that the liquid phase (solution or melt) before the solid/liquid phase interface may contain microcrystals from the solid phase. In this case, a simultaneous effect of growth and the nucleation of crystals exists during crystallization [16–21]. This effect leads, for example, to the U-shape behavior of the recalescence front velocity–melt undercooling curve [20,21]. At a glance, such behavior seems to be non-trivial. To explain why the front velocity decreases and increases with undercooling,

we need to describe the process of crystal nucleation within a thin, undercooled two-phase layer ahead of the phase interface. This theory is developed below.

This paper is organized as follows: A theoretical model describing the nucleation and growth of crystals in an undercooled two-phase layer is given in Section 2 based on classical nucleation theory [22–28]. A numerical example of the nucleation and growth of crystals is considered in Section 3, where the interface motion is analyzed for the obtained driving force (melt undercooling). Our conclusions are formulated in Section 4.

2. Theoretical Modeling

In this section, we formulate the integro-differential model describing the evolution of a crystal assemblage in an undercooled liquid and obtain an analytical solution to this model using the small parameter method.

2.1. The Model of Crystal Ensemble Nucleation

We consider a single-component melt that occupies a half-space $\xi > 0$. At the time $\tau = 0$, the melt's initial temperature T_l is higher than the temperature of the phase transition T_p . Then, the boundary temperature at $\xi = 0$ goes to a value of $T_0 < T_p$. As a result of heat transfer, the undercooling temperature $\Delta T = T_p - T$ goes into the liquid phase, occupying the region $0 < \xi < \Sigma(\tau)$. Here, τ is the time variable, and $\Sigma(\tau)$ is the moving phase transition boundary, where $T = T_l = T_p$ (T and T_l denote temperatures in the regions $0 < \xi < \Sigma(\tau)$ and $\xi > \Sigma(\tau)$, respectively). Solid-phase nuclei occur at a rate of $I(\Delta T)$ in the undercooled layer $0 < \xi < \Sigma(\tau)$. Note that the undercooling $\Delta T = 0$ at the phase transition boundary $\xi = \Sigma(\tau)$. In addition, the latent heat released during the phase transition reduces the undercooling but does not entirely compensate for it (see Figure 1).

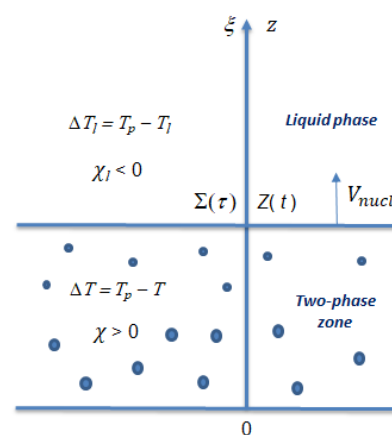


Figure 1. An illustration of the phase transition process where nucleation and growth of crystallites of different sizes (filled circles) are taking place. The crystallization process moving with velocity V_{nucl} is directed along the spatial axis ξ . The two-phase layer–liquid phase boundary $\Sigma(\tau)$ moves due to the predominant nucleation of crystals. Symbols z and $Z(t)$ designate dimensionless values of ξ and $\Sigma(\tau)$, respectively. The dimensionless melt undercooling in the two-phase layer ($\chi = \Delta T / \Delta T_0$) and liquid phase ($\chi_l = \Delta T_l / \Delta T_0$) becomes zero at the phase transition boundary $\xi = \Sigma(\tau)$ (or $z = Z(t)$). Here, T_p and T_0 are the phase transition and initial temperatures, respectively; T and T_l are the current temperatures in the two-phase layer and liquid phase, respectively.

Further, we assume the quasi-stationary growth velocity of single spherical crystals [29–32], i.e.,

$$\frac{dr}{d\tau} = \frac{\beta_* \Delta T}{1 + \beta_* q r'} \quad (1)$$

where r is the crystal radius, β_* is the kinetic parameter, and $q = \frac{L_V}{\lambda_l}$ with L_V representing the latent heat of the crystallization and λ_l as the thermal conductivity of the liquid. Let

us note that Expression (1) can be derived when considering the stationary temperature conductivity equation in liquid. Note as well that a generalization of the growth law (1) to the unsteady temperature field around the growing crystal can be constructed. Such a generalization has been completed in Refs. [33–35] for undercooled single/binary melts and supersaturated solutions.

There are two modes of crystal growth that depend on the particle radius r . When it is small enough, $r \ll \frac{1}{\beta_* q}$, the crystal growth rate does not depend on r , and the growth mode can be called “kinetic”; however, when the rate of particle growth is controlled by the rate of heat removal, $r \gg \frac{1}{\beta_* q}$, the regime is called “diffusion-controlled growth”.

Let us consider the well-known nucleation rate that depends only on melt undercooling [36]

$$I(\Delta T) = \begin{cases} I_* \exp \left[-p \left(\frac{\Delta T_0}{\Delta T} \right)^2 \right], & \text{WVZ kinetics} \\ I_*(\Delta T)^p, & \text{Meirs kinetics} \end{cases}, \quad (2)$$

where the acronym WVZ means the Weber–Volmer–Frenkel–Zeldovich nucleation kinetics, I_* is the pre-exponential factor, and ΔT_0 represents the initial undercooling of the melt [36]. Parameter $p = \frac{16\pi\gamma_i^3 T_p}{3L_V^2 \Delta T_0^2 k_B}$ (where γ_i is the surface tension, and k_B is the Boltzmann constant) is a dimensionless Gibbs number in the case of the WVZ kinetics and an empirical constant in the case of the Meirs kinetics.

The particle-radius distribution function $\phi(\tau, \xi, r)$ in the moving two-phase layer filled with nucleating and growing crystals satisfies the kinetic equation

$$\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial r} \left(\frac{dr}{d\tau} \phi \right) = 0, \quad 0 < \xi < \Sigma(\tau), \quad r > 0, \quad \tau > 0. \quad (3)$$

The temperature field in the moving layers $0 < \xi < \Sigma(\tau)$ and $\xi > \Sigma(\tau)$ is defined by the heat transfer equations

$$\rho c \frac{\partial T}{\partial \tau} = \lambda \frac{\partial^2 T}{\partial \xi^2} + \frac{4\pi L_V}{3} \frac{\partial}{\partial \tau} \int_0^\infty r^3 \phi dr, \quad 0 < \xi < \Sigma(\tau), \quad \tau > 0, \quad (4)$$

$$\rho_l c_l \frac{\partial T_l}{\partial \tau} = \lambda_l \frac{\partial^2 T_l}{\partial \xi^2}, \quad \xi > \Sigma(\tau), \quad \tau > 0. \quad (5)$$

Here, ρ and ρ_l represent the densities of the two-phase layer and liquid phase, c and c_l define their heat capacities, and λ and λ_l determine their heat conductivity coefficients, respectively, where subscript l designates the liquid layer. Note that newly born crystals within the layer $0 < \xi < \Sigma(\tau)$ release latent crystallization heat, leading to the integral source term in Equation (4).

These equations need to be completed by the boundary and initial conditions at $r = 0$, $\tau = 0$, $\xi = 0$, and $\xi \rightarrow \infty$, as well as the phase transition boundary $\xi = \Sigma(\tau)$ of the form

$$\frac{dr}{d\tau} \phi = I(\Delta T), \quad r = 0, \quad \tau > 0; \quad \phi = 0, \quad \tau = 0, \quad 0 < \xi < \Sigma(\tau); \quad (6)$$

$$T = T_0, \quad \xi = 0, \quad \tau > 0; \quad T_l \rightarrow T_\infty, \quad \xi \rightarrow \infty, \quad \tau > 0; \quad (7)$$

$$T = T_l = T_p, \quad \frac{\partial T}{\partial \xi} = \frac{\partial T_l}{\partial \xi}, \quad \xi = \Sigma(\tau), \quad \tau > 0; \quad T_l = T_\infty, \quad \tau = 0. \quad (8)$$

2.2. Analytical Solution

For convenience, we use the following dimensionless values

$$\begin{aligned} D_f &= \ell^4 \phi, \quad \sigma = \frac{r}{\ell}, \quad z = \frac{\xi}{\ell}, \quad \chi = \frac{\Delta T}{\Delta T_0}, \quad \chi_l = \frac{\Delta T_l}{\Delta T_0}, \\ \gamma &= \frac{\lambda \tau_0}{\rho c \ell^2}, \quad Z = \frac{\Sigma}{\ell}, \quad t = \frac{\tau}{\tau_0}, \quad b = \frac{4\pi L_V}{3\rho c \Delta T_0}, \\ \alpha_* &= \beta_* q \ell, \quad \tau_0 = \frac{\ell}{\beta_k \Delta T_0}, \quad \ell = \left(\frac{\beta_k \Delta T_0}{I_0} \right)^{1/4}, \end{aligned} \quad (9)$$

where $\Delta T_0 = T_p - T_0$ and $\Delta T_l = T_p - T_l$ are the initial and current undercoolings, respectively. Let us specifically highlight that D_f represents the dimensionless particle-radius distribution function, σ stands for the dimensionless radius of the crystals, z represents the dimensionless crystallization axis plotted in Figure 1, t is the dimensionless time variable, and χ and χ_l mean the dimensionless undercoolings in the layer of nucleation $0 < z < Z(t)$ and the liquid phase $z > Z(t)$.

Rewriting now the model expressions and boundary conditions in dimensionless variables, we arrive at the kinetic equation and the boundary and initial conditions for the dimensionless distribution function D_f in a two-phase layer $0 < z < Z(t)$, which reads as

$$\frac{\partial D_f}{\partial t} + \chi \frac{\partial}{\partial \sigma} \left(\frac{D_f}{1 + \alpha_* \sigma} \right) = 0, \quad \sigma > 0, \quad t > 0, \quad (10)$$

$$D_f = \frac{1}{\chi} \exp[p g(\chi)], \quad \sigma = 0; \quad D_f = 0, \quad t = 0, \quad (11)$$

where

$$g(\chi) = g(t, z) = \begin{cases} 1 - \chi^{-2}, & \text{WVZ nucleation kinetics} \\ \ln \chi, & \text{Meirs nucleation kinetics} \end{cases}. \quad (12)$$

Applying the Laplace integral transform to the model (10) and (11) regarding t , we obtain the distribution function of particles along the radius in the form of

$$D_f = (1 + \alpha_* \sigma) \varphi(x(t, z) - y(\sigma)) \eta(x(t, z) - y(\sigma)), \quad (13)$$

where

$$\varphi(t, z) = \frac{1}{\chi} \exp(p g(t, z)), \quad x(t, z) = \int_0^t \chi(t_1, z) dt_1, \quad y(\sigma) = \sigma + \frac{\alpha_* \sigma^2}{2}, \quad (14)$$

and η represents the Heaviside function.

Then, substituting the dimensionless parameters and variables (9) into Expressions (4) and (5) and the boundary conditions (7) and (8), we obtain

$$\frac{\partial \chi}{\partial t} = \gamma \frac{\partial^2 \chi}{\partial z^2} - b \frac{\partial}{\partial t} \int_0^t h(v, t, z) \exp(p g(v, z)) dv, \quad 0 < z < Z(t), \quad t > 0, \quad (15)$$

$$\frac{\partial \chi_l}{\partial t} = \gamma \frac{\partial^2 \chi_l}{\partial z^2}, \quad z > Z(t), \quad t > 0, \quad (16)$$

$$\chi = 1, z = 0, t > 0; \chi_l \rightarrow \chi_\infty = \frac{T_p - T_\infty}{\Delta T_0}, z \rightarrow \infty, t > 0; \quad (17)$$

$$\chi = \chi_l = 0, \frac{\partial \chi}{\partial z} = \frac{\partial \chi_l}{\partial z}, z = Z(t), t > 0; \chi_l = \chi_\infty, t = 0, \quad (18)$$

where we suppose that $\rho = \rho_l$, $\lambda = \lambda_l$, and $c = c_l$. We notice that the integral included in the right-hand side of Formula (15) is written according to the previously described theory [36], in which the variable v fulfills formulas $x(v, z) = x(t, z) - y(\sigma)$ and $h(v, t, z) = \alpha_*^{-3} \left[\sqrt{1 + 2\alpha_*(x(t, z) - x(v, z))} - 1 \right]^3$.

The integral term in Expression (15) can be estimated given the fact that the dimensionless variable p is significantly greater than unity for a large variety of undercooled melts [36]. This integral can then be calculated using the saddle-point method for the Laplace integral [37,38]. Equation (12) shows that $\partial g / \partial v = (dg/d\chi) \partial \chi / \partial v < 0$ for the two kinetic mechanisms under question: the WVFZ and Meirs ($dg/d\chi > 0$ and $d\chi/dv < 0$). This is due to the fact that the function g reaches a maximum value at the boundary point $v = 0$. Estimating the derivatives χ on v using Equation (15), we find that the first three of them become zero at $v = 0$, and the fourth derivative is $-12b$ in the case of the WVFZ and $-6b$ in the case of the Meirs kinetics. Keeping just the main term of the asymptotic expansion in (15), we obtain [37,38]

$$\frac{\partial \chi}{\partial t} = \gamma \frac{\partial^2 \chi}{\partial z^2} - A \varrho(\chi, t, z), t > 0, 0 < z < Z(t), \quad (19)$$

where

$$\varrho(t, z) = \frac{\chi(t, z) \left[\sqrt{1 + 2\alpha_* x(t, z)} - 1 \right]^2}{\sqrt{1 + 2\alpha_* x(t, z)}}, A = \frac{3b^{3/4} \Gamma(1/4)}{b_0 \alpha_*^2 p^{1/4}}, \quad (20)$$

and Γ represents the Euler gamma function, $b_0 = 2^{7/4}$ (the WVFZ), and $b_0 = 4^{3/4}$ (the Meirs kinetics).

Let us further discuss two crystal growth modes: the kinetic ($\alpha_* \ll 1$, KG) and diffusion-controlled ($\alpha_* \gg 1$, DCG) ones. For these cases, we obtain from (20)

$$\varrho(t, z) \approx \begin{cases} \alpha_*^2 x^2(t, z) \chi(t, z), & \text{KG} \\ \sqrt{2\alpha_* x(t, z)} \chi(t, z), & \text{DCG}. \end{cases} \quad (21)$$

Now combining expressions (19)–(21), we have

$$\frac{\partial \chi}{\partial t} = \gamma \frac{\partial^2 \chi}{\partial z^2} - \varepsilon \Phi(\chi, x), t > 0, 0 < z < Z(t), \quad (22)$$

where

$$\varepsilon = \begin{cases} \alpha_*^2 A, & \text{KG} \\ \sqrt{2\alpha_*} A, & \text{DCG} \end{cases} \quad \text{and} \quad \Phi(\chi, x) = \begin{cases} x^2 \chi, & \text{KG} \\ \sqrt{x} \chi, & \text{DCG} \end{cases}. \quad (23)$$

Below, we search for the solution to (16)–(18), (22), and (23) as a power expansion with a small parameter ε

$$\chi = \chi_0 + \varepsilon \chi_1 + \dots, Z = Z_0 + \varepsilon Z_1 + \dots \quad (24)$$

By substituting Formula (24) into Expressions (16) and (22), expanding the boundary conditions at $z = Z(t)$ in the Taylor series, and equating terms with the same power of ε ,

we come to the conclusion that the problem can be solved using the following self-similar variables

$$\chi_0 = f_0(\zeta), \quad \zeta = \frac{z}{\sqrt{t}}, \quad Z_0(t) = \alpha\sqrt{t}, \quad (25)$$

$$\chi_1 = \begin{cases} f_1(\zeta)t^3, & \text{KG} \\ f_1(\zeta)t^{3/2}, & \text{DCG} \end{cases} \quad \text{and} \quad Z_1(t) = \begin{cases} \beta t^{7/2}, & \text{KG} \\ \beta t^2, & \text{DCG} \end{cases}.$$

In this case, α and β are the constant coefficients determining the phase transition boundary $Z(t)$. Functions $f_0(\zeta)$ and $f_1(\zeta)$ will be introduced later. Consequently, the governing equations and boundary conditions, (16)–(18), (22), and (23), can be written as

$$\gamma \frac{d^2 f_0}{d\zeta^2} = -\frac{\zeta}{2} \frac{df_0}{d\zeta}, \quad \gamma \frac{d^2 f_1}{d\zeta^2} = \Psi(\zeta) - \frac{\zeta}{2} \frac{df_1}{d\zeta}, \quad \gamma \frac{d^2 \chi_l}{d\zeta^2} = -\frac{\zeta}{2} \frac{d\chi_l}{d\zeta}, \quad (26)$$

$$f_0 = 1, \quad f_1 = 0, \quad \zeta = 0; \quad \chi_l \rightarrow \chi_\infty, \quad \zeta \rightarrow \infty; \quad (27)$$

$$f_0 = 0, \quad f_1 + \beta \frac{df_0}{d\zeta} = 0, \quad \chi_l = 0, \quad \frac{df_0}{d\zeta} = \frac{d\chi_l}{d\zeta}, \quad \frac{df_1}{d\zeta} = 0, \quad \zeta = \alpha, \quad (28)$$

where

$$\Psi(\zeta) = \begin{cases} 4K^2(\zeta)\zeta^4 f_0(\zeta), & \text{KG} \\ \sqrt{2K(\zeta)}\zeta f_0(\zeta), & \text{DCG} \end{cases} \quad \text{and} \quad K(\zeta) = \int_{\zeta}^{\infty} \frac{f_0(\zeta_1)}{\zeta_1^3} d\zeta_1.$$

The analytical solution to the problem presented in (26)–(28) can be expressed as

$$f_0(\zeta) = 1 - \frac{\operatorname{erf}\left(\frac{\zeta}{2\sqrt{\gamma}}\right)}{\operatorname{erf}\left(\frac{\alpha}{2\sqrt{\gamma}}\right)}, \quad f_1(\zeta) = \int_0^{\zeta} (\Omega(\zeta_1) - \Omega(\alpha)) \exp\left(-\frac{\zeta_1^2}{4\gamma}\right) d\zeta_1, \quad (29)$$

$$\chi_l(\zeta) = \chi_\infty \left[1 - \frac{\operatorname{erfc}\left(\frac{\zeta}{2\sqrt{\gamma}}\right)}{\operatorname{erfc}\left(\frac{\alpha}{2\sqrt{\gamma}}\right)} \right], \quad \Omega(\zeta) = \frac{1}{\gamma} \int_0^{\zeta} \Psi(\zeta_1) \exp\left(-\frac{\zeta_1^2}{4\gamma}\right) d\zeta_1. \quad (30)$$

Constants α and β must be found from the following expressions

$$\operatorname{erfc}\left(\frac{\alpha}{2\sqrt{\gamma}}\right) + \chi_\infty \operatorname{erf}\left(\frac{\alpha}{2\sqrt{\gamma}}\right) = 0, \quad (31)$$

$$\beta = \sqrt{\pi\gamma} \operatorname{erf}\left(\frac{\alpha}{2\sqrt{\gamma}}\right) \exp\left(\frac{\alpha^2}{4\gamma}\right) f_1(\alpha). \quad (32)$$

3. Numerical Example

In this section, we obtain the melt undercooling that drives the crystallization process and takes the phase interface motion into account; i.e., we consider a simultaneous process of bulk nucleation and the growth of crystals. In this case, the melt undercooling as well as the crystallization velocity contain two contributions associated with these two process modes.

Since solidification kinetics are experimentally defined by the phenomena of crystal nucleation and growth, the theoretical explanation should include both of these processes as well. Therefore, the process mode contains the two-phase layer with the bulk nucleation of crystals (see Figure 2a). Since, in solidification experiments of undercooled droplets, the whole system shown in Figure 2a is in motion due to the crystal growth of the solid phase

(motion of the recalescence front), we are switching to a moving frame of reference. In this case, we have the combined bulk nucleation and growth of crystals shown in Figure 2b. In other words, the whole growth rate contains two contributions appearing from the bulk nucleation (V_{nucl}) and crystal growth (V_{front}). The recalescence front velocity is given by $V_{rec} = |V_{nucl}| + V_{front}$.

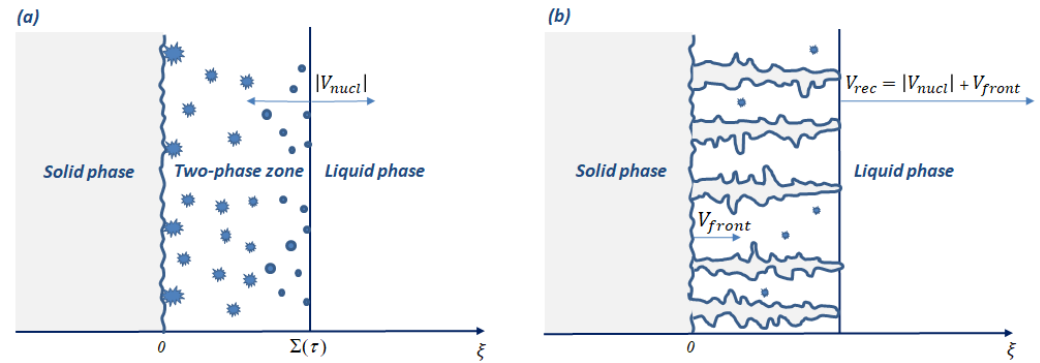


Figure 2. An illustration showing the moving two-phase zone along the spatial coordinate ξ at time τ . Panel (a) demonstrates the bulk phase transition process described in Section 2. Panel (b) illustrates a combined effect of the bulk and crystallization from an undercooled melt.

For the sake of convenience, we use dimensional variables to describe the main parameters that characterize the motion of the recalescence front: its growth velocity V_{rec} , time τ , and the melt undercooling ΔT . First, we define the undercooling balance ΔT as the sum of nucleation and the front undercoolings

$$\Delta T = \Delta T_{nucl} + \Delta T_{front}, \quad (33)$$

$$\Delta T_{nucl} = \Delta T_0 \left[f_0(\xi, \tau) + \varepsilon I_0^{k/4} \beta_*^{3k/4} \Delta T_0^{3k/4} \tau^k f_1(\xi, \tau) \right], \quad (34)$$

$$\Delta T_{front} = \left(\frac{V}{\mu_k} \right)^{1/l}, \quad (35)$$

where μ_k is the kinetic coefficient for undercooling, and l is a constant parameter. The velocity of the recalescence front reads as

$$V_{rec} = |V_{nucl}| + V_{front}, \quad (36)$$

$$V_{nucl} = \left(\frac{\beta_* \Delta T_0}{I_0} \right)^{1/4} \left[\frac{\alpha I_0^{1/8} \beta_*^{3/8} \Delta T_0^{3/8}}{2\sqrt{\tau}} + \frac{7}{2} \varepsilon \beta \tau^{5/2} I_0^{7/8} \beta_*^{21/8} \Delta T_0^{21/8} \right], \quad (37)$$

$$V_{front} = \mu_k \Delta T^l. \quad (38)$$

Here, Expressions (34) and (37) follow from Equation (24).

In previous studies [20,21,39,40], anomalous behavior of the “melt undercooling–recalescence front velocity” curve was observed using electromagnetic levitation experiments for the Al-rich Al–Ni alloys. Namely, a decreasing branch of the solidification (recalescence front) velocity for the increasing melt undercooling was detected. Below, we explain this behavior using an active nucleation process ahead of the growing solid phase.

Our calculations, based on the model under question in kinetic growth mode, have shown that the nucleation front velocity V_{nucl} gradually decreases with time and changes its sign from positive to negative (Figure 3). In this pure nucleation growth mode, shown in Figure 2a, the process has two stages. During the first of these, Stage (i), the crystals actively nucleate and start to grow ($\Sigma(\tau)$ increases with time and $V_{nucl}(\tau) > 0$). During the second stage, which is Stage (ii), the crystals already release a sufficient amount of the latent crystallization heat and thus partially compensate for the melt undercooling ($\Sigma(\tau)$ decreases with time and $V_{nucl}(\tau) < 0$). When dealing with the simultaneous operation of bulk nucleation and crystal growth (Figure 2b), the solid-phase–two-phase zone boundary is moving with the velocity V_{front} induced by the driving force similar to what occurs during the solidification of undercooled droplets in an electromagnetic levitation facility. From the physical point of view, we are shifting to the reference frame moving at the speed V_{front} in Figure 2a and thus obtaining the combined process illustrated in Figure 2b. In this case, as before, we have the two aforementioned stages of the combined process of bulk nucleation and the growth of crystals. When dealing with Stage (i), the recalescence front velocity V_{rec} is a sum of two additive contributions connected with the front propagation due to bulk nucleation, V_{nucl} , and the crystal growth V_{front} . When dealing with Stage (ii), the velocity V_{nucl} is directed towards the front, which is accelerated by the effect of the crystals sticking to the interfacial boundary. As a result, the recalescence front velocity V_{rec} is also the sum of V_{front} and $|V_{nucl}|$. Therefore, we have (36) in both cases.

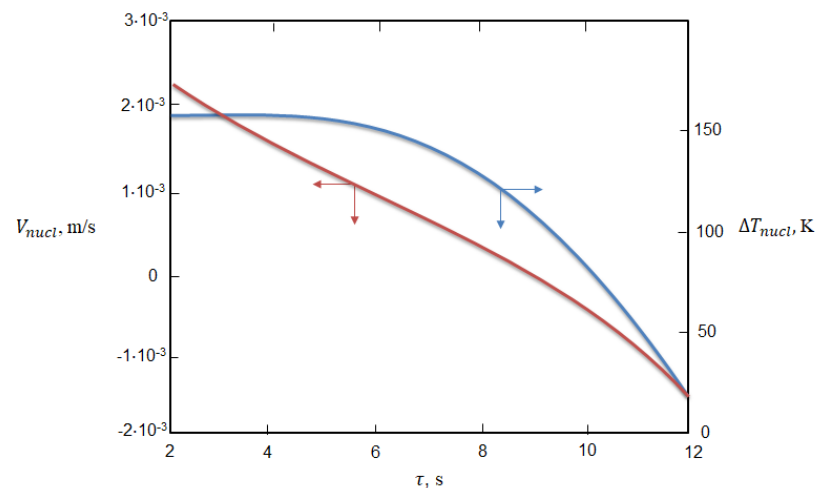


Figure 3. The bulk crystallization velocity V_{nucl} (red line) and melt undercooling ΔT_{nucl} (blue line) as functions of time τ for pure nucleation mode. Physical parameters used for calculations are: $\Delta T_0 = 400$ K, $I_0 = 10^{11} \text{ m}^{-3} \text{ s}^{-1}$, $\beta_* = 2 \cdot 10^{-7} \text{ m s}^{-1} \text{ K}^{-1}$, $\tau_0 = 2.1$ s, $\zeta = 10^{-4}$ m, $\varepsilon = 0.1$, $\alpha = 52.46$, $\beta = 0.1$, $k = 1$, $\gamma = 3 \cdot 10^3$, $p = 8$.

Eliminating the time variable τ from the blue and red curves, $V_{nucl}(\tau)$ and $\Delta T_{nucl}(\tau)$, plotted in Figure 3, we obtain $V_{nucl}(\Delta T)$. By adding $V_{front}(\Delta T)$ from Equation (38) to this relationship, we come to the U-shaped curve $V_{rec}(\Delta T)$ demonstrated in Figure 4. Its minimum point (marked by the vertical dotted line in Figure 4) divides two different regimes of the crystallization process: (i) frontal growth + nucleating crystals ahead of the front and (ii) frontal growth accelerated by the attachment kinetics of particles sticking to the phase interface. The second stage is connected to the narrowing of the nucleation region due to a partial reduction in the melt undercooling as the crystals grow and release latent solidification heat. The theory under consideration qualitatively describes the experimental data for Al-rich Al-Ni alloys solidified in the electromagnetic levitation facility on the ground, under reduced gravity during parabolic flights, and under microgravity conditions onboard the International Space Station [20,21,39,40].

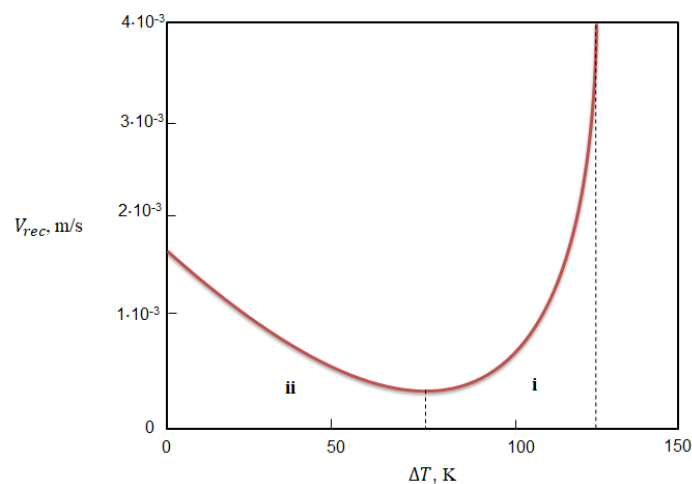


Figure 4. The recalescence front velocity V_{rec} as a function of melt undercooling ΔT . Region (i) describes predominant crystal growth in comparison to the nucleation of crystals ahead of the phase interface while Region (ii) corresponds to propagation of the recalescence front due to predominant contribution of nucleation of crystals over their growth (with the attachment of crystals to the phase interface). Physical parameters used for calculations correspond to Figure 3 and $l = 1$, $\mu_k = 5 \cdot 10^{-6} \text{ m s}^{-1} \text{ K}^{-1}$.

4. Conclusions

In summary, a model of combined bulk nucleation and crystal growth is developed to describe the evolution of the recalescence front. To do this, we first consider a pure bulk crystallization scenario in which newly born crystals grow in the phase transition layer extending/suppressing its thickness Σ with a time τ . This problem, described by the aforementioned integro-differential model, has been solved by the small parameter method. Then, we move the phase transition layer along a spatial direction and thus obtain two contributions: the undercooling balance and the recalescence front velocity $V_{rec} = |V_{nucl}| + V_{front}$ (Figure 2). As a result, the problem of combined bulk nucleation and crystal growth [20] has been described analytically by Expressions (33) and (36). The combined effect of these modes leads to the U-shaped dynamics of the recalescence front velocity. As this takes place, the right (upward) branch in Figure 4 is connected with the predominant crystal growth and intense nucleation mode, and the left (downward) branch describes the predominant nucleation of the crystals with their attachment to the interface. These are due to the fact that the crystals grow and release the latent solidification heat, which partially compensates for the melt undercooling, suppresses the nucleation domain, and induces crystals to stick to the moving front. These two modes of the crystallization process are divided by the minimum point in Figure 4. The U-shaped behavior of the “recalescence front–melt undercooling” curve is in qualitative agreement with the experimental data from Refs. [20,21].

Let us especially note that this paper deals with the anomalous law of motion for the phase transformation boundary resulting from crystallization with a planar front and also nucleation and crystal growth ahead of this front. In many scientific papers devoted to similar problems, the simultaneous operation of these two mechanisms of the crystallization process is not considered (see, among others, [27,41–45]). For a more detailed description of the simultaneous growth and nucleation modes, it is necessary to consider both processes in a non-stationary mode. In other words, to the directional, unsteady crystallization from a cooled wall, one must additionally consider the process of nucleation and bulk crystal growth in front of the crystallization interface (solid phase–two-phase zone interface) [46–50]. To solve such a highly nonlinear problem with a moving boundary, the saddle-point technique can be used to construct an approximate solution to the bulk crystallization problem ahead of the moving interface [26–28], and then the differential series method can be applied to construct an approximate solution to the crystallization problem [33–35]. The

solution to such an urgent problem, which is a subject of future research, is necessary for a more accurate explanation of the U-shaped behavior of the “crystallization velocity–melt undercooling” relationship.

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