On heterogeneous nucleation in a supercooled melt

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Abstract. A mathematical model of the heterogeneous nucleation of a solid phase in a melt modified by exogenous refractory nanoparticles is developed. Analytical expressions are obtained for the free energy of formation and the rate of heterogeneous nucleation of the solid phase, taking into account the influence of dimensional and capillary effects. The study is of interest for constructing a mathematical model of heterogeneous crystallization that describes the processes of structure formation in metals and alloys modified by refractory nanoparticles.

1. Introduction
Investigation of a solid crystalline phase nucleation in a melt containing nanoscale particles is important for understanding the mechanisms of structure formation during the solidification of nanomodified metals and alloys. In recent years, more and more attention has been paid to the new technology for processing metals and alloys by modifying the melt with nanopowders of refractory compounds with a characteristic particle size of ~ 100 nm (nanomodification) [1–3]. These particles are characterized by a high specific surface area, are well wetted by the melt and serve as active nanosubstrate for the formation of a solid phase. To predict the influence of such nanomodifiers on the structure and properties of the moulding, it is necessary to study the features of nucleation of a solid phase on an exogenous nanoparticle substrate, depending on its dimensional, morphological, capillary and other properties. An experimental study of these processes under high-temperature conditions is a complex technical and methodological task. Therefore, the most effective method is theoretical research, which requires the development of appropriate physical and mathematical models. Despite a significant number of publications devoted to heterogeneous nucleation [4–13], the problem of nucleation of a solid phase on nanoscale substrate particles introduced into a metallic melt still remains relevant. Below, based on the thermodynamic approach, a study of the heterogeneous nucleation in a supercooled melt on a cubic nanoparticle was carried out, taking into account capillary and dimensional effects.

2. Problem statement
To determine the rate of the heterogeneous nucleation, we assume that the seed nanoparticles have the shape of a cube, whose faces are characterized by the wetting angle $0^\circ < \theta < 90^\circ$. According to Rebinder's ideas [14], refractory nanoparticles are potential centers of crystallization, i.e. seeds on the surface of which separate clusters are formed and under certain conditions are transformed into solid phase nuclei. Consider the kinetics of the formation of such a nucleus, assuming that it has the shape
of a spherical segment (cap) (figure 1). The nuclei forming on the face of a cubic nanoparticle should have a contact spot diameter not exceeding the length \( l_p \) of an edge of a cubic particle [5]:

\[
2R_c \sin \theta \leq l_p
\]  

(1)

where \( R_c \) is the critical radius of the nucleus.

The expression for the free Gibbs energy of nucleation in this case has the form:

\[
\Delta G = \sigma_{12} S_{12} + (\sigma_{23} - \sigma_{13}) \cdot S_{23} - \frac{\kappa \rho \Delta T}{T_s} V
\]  

(2)

Here, \( \Delta T = T_s - T \) is the supercooling, \( T_s \) is the temperature of crystallization, \( T \) is the current temperature, \( \rho \) is the density of the metal, \( \kappa \) is the heat of crystallization, \( \sigma_{23} \) is the surface tension of the melt – substrate, \( \sigma_{13} \) is the surface tension of the nucleus – substrate, \( S_{23} \) is the surface area of the nucleus, \( V \) is its volume, \( S_{12} \) is the contact surface area of the nucleus with the substrate, \( \sigma_{12} \) is the surface tension of the nucleus – melt, whose value, taking into account the size factor, is given by

\[
\sigma_{12} = \sigma_{12}^{\infty} (1 - 2\delta / R) \]  

[15], where \( \delta \) is the Tolman parameter characterizing the size of the interphase transition layer, equal within order of magnitude to the diameter of the melt atom, \( \sigma_{12}^{\infty} \) is the surface tension for flat surface and \( R \) is the radius of curvature of the tension surface.

After substituting the expressions for \( \sigma_{12}, S_{12}, S_{23}, V \) in equation (2) and neglecting terms of the second order of smallness with respect to the quantity \( 2\delta / R \ll 1 \), we obtain

\[
\Delta G = \pi \sigma_{12}^{\infty} R^2 \left( 1 - \frac{2\delta}{R} \right) \left( 2 + \cos \theta \right)
\]  

(3)

Here, \( R_0 = 2\sigma_{12}^{\infty} T_s / (\kappa \rho \Delta T) \) is the radius of the critical nucleus in homogeneous nucleation [16]. At \( 2\delta / R_0 \to 0 \) and \( R = R_0 \), equation (3) takes the known form of the free Gibbs energy of the nucleus on a flat surface without taking into account size effects [16].

The critical radius of heterogeneous nucleus \( R_c \) is determined from the condition

\[
\frac{d\Delta G}{dR} = \pi \sigma_{12}^{\infty} \left( 1 - \cos \theta \right) \left( 2 + \cos \theta \right) \left( 2 R - 2\delta - \frac{2R^2}{R_0} \right) = 0 .
\]

Hence, we obtain at \( 4\delta / R_0 \ll 1 \):

\[
R_c = R_0 \left( 1 + \frac{4\delta}{R_0} \right) \approx R_0 \left( 1 - \frac{\delta}{R_0} \right).
\]  

(4)

Then, we have the critical free energy, up to a small value of \( \delta / R_0 \) of the first order from (3), taking into account (4),

\[
\Delta G^* = \frac{1}{3} \pi \sigma_{12}^{\infty} R_0^2 \left( 1 - \frac{6\delta}{R_0} \right) \left( 1 - \cos \theta \right) \left( 2 + \cos \theta \right).
\]  

(5)

The obtained expression (5) at \( \delta = 0 \) coincides with the known expression for the critical value of the free energy of a spherical cap nucleus on a flat substrate [16].

Figure 1. Diagram of solid phase nucleus on the flat facet of the nanoparticle. 1 – melt, 2 – nucleus, 3 – nanoparticle.
Substituting (4) in condition (1), taking into account the expression for the value of $R_0$, we obtain the relation connecting the supercooling $\Delta T$ with the contact angle $\theta$ and the particle size $l_p$, with accuracy within a small value equal to $2\delta \sin \theta / l_p$:

$$\Delta T \geq B \sin \theta / l_p,$$

where $B = 4\sigma_i^0 T_c / (\kappa_p)$. With the given values of $\theta$ and $l_p$, it determines the minimum supercooling for the formation of the nucleus on the flat face of the nanoparticle.

The probability of the formation of a critical nucleus on one of the faces of the nanoparticle is proportional to $\exp(-\Delta G^*/k_BT)$, where $k_B$ is the Boltzmann constant. According to the theorem for the probabilities addition of compatible events, the number of critical nuclei formed on all facets of the cubic nanoseeds is determined by the formula

$$n = n_f \left[ 6 \exp \left( -\frac{\Delta G^*}{k_BT} \right) - \exp \left( -\frac{6\Delta G^*}{k_BT} \right) \right].$$

Here, $n_f$ is the number of surface atoms of the face per unit volume of the melt:

$$n_f = n_p \left( \frac{l_p}{l_c} \right)^2,$$

where $n_p$ is the number of nanoparticles-seeds per unit volume of the melt, $l_p$ is the size of the seed edge, $l_c$ is the interatomic distance for the seed material. The value of $n_p$ is determined by the mass concentration of seeds in the melt, $m_p \%$, the density of the seed material $\rho_p$ and the melt density:

$$n_p = \frac{m_p \rho}{(100 \rho_p l_p^3)}.$$

Neglecting the second term in square brackets in (6) in comparison with the first one, we obtain

$$n = 6n_f \exp \left( -\Delta G^*/(k_BT) \right).$$

The rate of heterogeneous origin of nuclei is determined by the following equation [17]:

$$I = n_s v_{ls}.$$  

Here, $n_s$ is the number of melt atoms adjacent to the nucleus, and $v_{ls}$ is the frequency of atomic jumps across the liquid-cluster interface.

For the spherical cap nucleus the value of $n_s$ is determined by the formula [17]:

$$n_s = 2\pi R_c^2 (1 - \cos \theta) / l_c^2,$$

where $l_c$ is the diameter of the melt atom. The frequency of the jumps $v_{ls}$ is estimated from relation

$$v_{ls} = \frac{D}{l_c^2}.$$  

Here, $D$ is the diffusion coefficient in the liquid, determined by the Arrhenius equation:

$$D = D_0 \exp \left( -E/k_BT \right),$$

where $D_0$ is the empirical constant, and $E$ is the activation energy of the diffusion process in the melt.

Now, the expression for the rate of heterogeneous nucleation on a cubic nanoseed (10), taking into account expressions (7–9, 11–13) takes the following form:

$$I = n_p \frac{12\pi D_0}{l_c^4} \left( \frac{l_p}{l_c} \right)^2 \left( R_c^2 (1 - \cos \theta) \exp \left[ -\frac{(E + \Delta G^*)}{k_BT} \right] \right),$$

where $0^\circ < \theta < 90^\circ$, the free Gibbs energy $\Delta G^*$ is determined by (5) and the value of $R_c$ is determined by (4).
3. Results and discussion

Numerical calculations were carried out for aluminium modified with titanium nitride in the form of crystals close to cubic. The thermophysical characteristics of the metal [18] and the initial data are taken as follows: $T_s = 933$ K, $\rho = 2600$ kg/m$^3$, $\kappa = 4.02 \times 10^5$ J/kg, $D_0 = 10^{-7}$ m$^2$/s, $E = 4.2 \times 10^{-20}$ J, $\sigma_1^\infty = 0.093$ J/m$^2$, $l_a = 2.86 \times 10^{-10}$ m, $l_c = 4.235 \times 10^{-10}$ m, $l_p = (30–90) \times 10^{-9}$ m, $\rho_p = 5440$ kg/m$^3$, $m_p = 0.1\%$ wt., $k_B = 1.38 \times 10^{-23}$ J/K. The values of supercooling and wetting angle varied with allowance for the experimental data [19].

Figure 2 shows the dependences of the critical Gibbs energy $\Delta G^*$ (a) and the rate of nucleation in a unit volume of the melt $I$ (b) on the contact angle $\theta$. In this case, the size of the nanoparticle was $l_p = 4.23 \times 10^{-8}$ m, supercooling $\Delta T = 2$ K, and calculations were carried out at three values of the relative parameter $2\delta/R_0 = 0; 0.007; 0.05$. It follows from formula (5) that taking into account the size factor in the expression for surface tension should lead to a decrease of the free energy of the heterogeneous nucleus formation, which in turn contributes to an increase of the nucleation rate. The graphs for the first two cases, when the curvature of the melt – nucleus interface was not taken into account ($\delta = 0$) in determining the interfacial energy, or the Tolman parameter was assumed equal within an order of magnitude to the diameter of the melt atom ($\delta = l_a$, $2\delta/R_0 = 0.007$), coincide (curves 1 on figures 2a and 2b). Thus, we can assume that for a very small value of $2\delta/R_0 < 0.01$ the size factor in the expression for surface tension has practically no effect on the energy and rate of nucleation. The value of the dimensionless parameter $2\delta/R_0 = 0.05$ can be considered limiting, since in the derivation of formula (4) this value was imposed on the smallness condition $4\delta/R < 1$. Curves 2 on figures 2a and 2b illustrate the maximum possible influence of the size factor on the critical Gibbs energy and the rate of nucleation. The graphs show that the highest nucleation rates $I >> 10^{10}$ m$^{-3}$s$^{-1}$ occur at wetting angles $\theta < 12^0$. 

![Figure 2](image-url)

**Figure 2.** Dependences of critical Gibbs energy (a) and rate of nucleation (b) on the wetting angle at $2\delta/R_0 = 0.007 – 1$, $2\delta/R_0 = 0.05 – 2$. 


The dependence of the nucleation rate on the size of the nano-substrate (figure 3) was also calculated for three values of the Tolman parameter, the wetting angle was chosen equal to $\theta = 10^0$, and supercooling $\Delta T = 2$ K. Analysis of calculated curves shows that the small Tolman parameter ($2\delta/R_0 < 0.01$) has almost no effect on the rate of nucleation (see figure 3), and the decrease in the size of the cubic nano-substrate at a fixed value of the mass fraction of the substrate material in the melt leads to its growth.

4. Conclusions
A mathematical model of the heterogeneous nucleation of the solid phase on highly activated wettable nanoseeds has been developed. Analytic expressions have been obtained for the critical radius, the formation energy, and the nucleation rate of crystallization centers on ultradispersed seeds (nanoparticles), which allow one to investigate the effect of dimensional and capillary effects on nucleation processes in a supercooled melt. It has been established that taking into account the dimensional dependence of the surface tension at the nucleation-melt interface significantly affects the nucleation processes at the ratio of the Tolman parameter to the critical radius $2\delta/R_0 > 0.01$. Increasing the dispersity of the nanoseeds increases the nucleation rate of the solid phase. However, the wettability of particles has the greatest effect on this value. This necessitates the cladding of particles with appropriate metals, which increase the wettability and adsorption properties of their surfaces.

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