Numerical simulation of nucleation and solid phase growth in a nanomodified binary alloy

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Abstract. A mathematical model of solidification of a binary alloy with eutectic-type phase diagram modified by refractory nanoscale particles as nucleation centers of the crystalline phase is proposed. Thermodynamic processes in the melt and solid phase, heterogeneous nucleation and growth of particles of the main ($\alpha$) phase of the crystallizing material are described. The crystal phase origin occurs on the surface of nanoscale particles. The volume of the solid phase grown on separate crystallization centers determines the character of the grain structure in the solidified alloy. On the example of a binary alloy based on iron (Fe-C) numerical simulation of melt solidification in a cylindrical casting is carried out. The features of the kinetics of heterogeneous nucleation and crystallization in the melt were considered. It is determined that the undercooling magnitudes, the conditions of nucleation, the rate of crystallization and solidification time vary significantly inside the casting. It is established that as the melt cools, volume-sequential crystallization takes place. The area with the finest structure of the solidified metal is located near the wall of the mold.

1. Introduction
Among binary metal alloys whose phase diagram has eutectic, Fe-C carbon alloys are of particular interest being the main structural materials in almost all branches of modern production. However, at present, there are still urgent problems to reduce defects and increase the strength of steel castings. One way to solve these problems can be grinding the structure of the hardened metal by adding nanoscale refractory particles to the melt. Heterogeneous nucleation is possible on particles, depending on the size, shape, and wettability of their surface, as well as the consistency of their atomic lattices with the material of the nucleus. The use of this technology allows of increasing the number of crystallization centers and improving the performance properties of the metal [1-4]. Specially prepared particles of materials SiC, TiC, TiN, etc. can serve as modifiers.

In this paper, the process of solidification of a two-component Fe-C alloy modified by refractory nanoscale particles in ceramic mold is considered. The mathematical model describing thermophysical and thermodynamic phenomena in the alloy in liquid and solid state, as well as heterogeneous nucleation and crystallization of the main $\alpha$-phase from the melt is formulated. Kinetics of solid phase growth and temperature regimes in solidifying casting are determined. The numerical simulation results are used to assess the adequacy of the crystallization model in the presence of nanoscale particles in a binary iron alloy.
2. Mathematical model
The solidification process of Fe-C alloy in cylindrical mold is considered. Due to the symmetry of the object, it is sufficient to limit the modeling process only to half of the central longitudinal section of the mold (figure 1).

![Figure 1. Schematic representation of the mold with the melt and the calculated area: 1 - melt, 2 - insulating wall and bottom, 3 - control points at half height from the mold bottom.]

The height of the casting is equal to \( H \), its radius is \( R \), the thickness of the thermal insulation pad in the bottom of the mold is \( h_b \), and the thickness of the side wall is \( h_w \).

The melt is uniformly modified in the volume by refractory nanoscale particles with a characteristic size of \( l_p \), their mass content of \( m_p \) does not exceed 0.05% and, therefore, their influence on the thermophysical characteristics of the melt can be neglected. The thermophysical properties of the metal in the liquid and solid phases are assumed to be constant and equal to the average values in the considered temperature ranges.

We introduce indices \( i=1 \) and \( i=2 \) for the liquid and solid phases of the alloy, respectively, and \( i=3 \) for the mold material. Then, taking into account the above assumptions, the heat transfer in the alloy is described by the following equation in the cylindrical coordinate system \((r, z)\):

\[
c_i \rho_i \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_e \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \lambda_e \frac{\partial T}{\partial z} \right) + \rho_2 \kappa \frac{\partial f_s}{\partial t}, \quad 0 \leq r \leq R, h_b \leq z \leq h_b + H, \tag{1}
\]

where the local values of the coefficients are: \( c_e = c_1, \rho_e = \rho_1, \lambda_e = \lambda_1 \) when \( f_s = 0 \), \( c_e = c_2, \rho_e = \rho_2, \lambda_e = \lambda_2 \), when \( f_s = 1 \) and \( c_e = c_1 (1 - f_s) + c_2 f_s, \rho_e = \rho_1 (1 - f_s) + \rho_2 f_s, \lambda_e = \lambda_1 (1 - f_s) + \lambda_2 f_s \) when \( 0 < f_s < 1 \). Here, \( f_s \) is the fraction of the solid phase in the melt, \( \lambda, c, \rho \) are the thermal conductivity, heat capacity, and density, respectively, \( \kappa \) is the specific heat of melting.

The temperature field in the mold wall is described by equation

\[
c_3 \rho_3 \frac{\partial T}{\partial t} = \lambda_3 \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right), \quad 0 \leq r \leq R + h_w, 0 \leq z \leq h_b; R \leq r \leq R + h_w, h_b \leq z \leq h_b + H. \tag{2}
\]

Heat exchange occurs between the outer surfaces of the mold, the free surface of the melt and the environment, the heat transfer coefficients are constant. On the contact surfaces of the melt with the
form, the thermal resistance, determined by the results of experiments, is taken into account [7]. The melt and mold temperatures at the initial moment are assumed to be the same and equal to a value slightly higher than the crystallization temperature of the pure metal. The model assumes that the wetting refractory nanoscale particles are uniformly distributed over the melt volume. It is shown in [8] that homogeneous nucleation in the process of solidification of such a melt is practically not observed, and the nucleation and growth of the crystalline phase occurs only on the seeds.

According to [5], under the assumption that nanoscale particles have the shape of a cube, the faces of which are characterized by the wetting angle $\theta$, the expression for the rate of nucleation of crystals of the $\alpha$-phase (i.e., iron-based solid solution) has the form:

$$I = n_p \frac{2\pi^2 D_0 R_c^4 (1 - \cos \theta) \sin^2 \theta \exp[-(E + \Delta G^\circ)/ (k_B T)]}{l_p^3 l_c^2}.$$  \hspace{1cm} (3)

Here, $n_p = m_p \rho_p / (100 \rho_p l_p^3)$ is the number of nanoscale particles per unit volume of the melt, $\rho_p$ is the density of the particle’s material, $l_p$ is the length of the edge of nanoparticle, $l_p$, $l_c$ are the interatomic distance in the melt and in the nanoparticle, respectively, $k_B$ is the Boltzmann constant, $D_0$ is the pre-exponent in Arrhenius's law for self-diffusion coefficient of iron in the melt, $E$ is the activation energy of this process. The Gibbs energy $\Delta G^\circ$ of formation of a critical nucleus is equal to

$$\Delta G^\circ = \pi \sigma_{12} R_c (R_c - 6\delta)(1 - \cos \theta) (2 + \cos \theta) / 3;$$

where $R_c$ is the critical radius of the nucleus, determined by relation $R_c = R_0 - \delta$ [6], $\delta$ is the Tolman’s parameter [9], $R_0 = 2\sigma_{12}^0 T_{10} / (\kappa \rho_0 \Delta T_0)$, $\sigma_{12}^0$ is the surface tension at the interface of nucleus-melt, $\Delta T_0 = T_{L0} - T$, $T_{L0}$ is the initial liquidus temperature.

The number of crystals of the $\alpha$-phase formed during the cooling of the liquid metal, starting with the time moment $t_{L0}$, when the temperature fell to the value $T_{L0}$, is equal to

$$N(r, z, t) = \int_{t_{L0}}^{t} I(r, z, \tau) \left[1 - f_s(r, z, \tau)\right] d\tau,$$

where $f_s$ is the fraction of the growing solid phase determined by the relations [10]:

$$f_s(r, z, t) = 1 - \exp(-N_V_t), \quad V_t(r, z, t) = (4\pi / 3)(R^3 - R_{c0}^3),$$

where $V_t$ is the volume of the solid phase growing on a single nanoparticle. Assuming that the solid phase growth obeys the normal mechanism and is determined by the linear dependence of the growth rate on magnitude of undercooling, $\partial R/\partial t = K_\alpha \Delta T$ [11], where $R$ is the radius of the crystal, $K_\alpha$ is the physical constant, $\Delta T = T_L - T$, $T_L$ is the current liquidus temperature, we obtain

$$R(r, z, t) = R_{c0} + \int_{t_{L0}}^{t} K_\alpha \Delta T d\tau,$$

where $R_{c0} = (32\pi)^{1/2} l_p$ is the radius of a spherical particle having a surface area equal to the surface of a cubic particle. To estimate the kinetic constant $K_\alpha$, it is possible to use the formula [12]:

$$K_\alpha = (D \Delta H_a) / (l_c k_B T_A^3),$$

where $\Delta H_a$ is the enthalpy of melting per atom, the diffusion coefficient in the liquid metal $D$ is determined by the Arrhenius equation $D = D_0 \exp[-E/(k_B T)]$. Undercooling of a melt with a variable impurity content $\Delta T = T_L - T$ can be represented as

$$\Delta T = T_A - \beta C_0 \left(1 - f_s\right)^{1-k} - T.$$
of the slope of the liquidus line in the Fe–C state diagram. Concentration of the dissolved component is determined by the non-equilibrium lever rule \( C = C_0/(1-f_s)^{1/4} \) [11], where \( C_0 \) is the initial concentration, \( k \) is the impurity distribution coefficient.

Note that the crystallization of the \( \alpha \)-phase from the melt occurs in the temperature range \( T_{10} \geq T \geq T_E \), where \( T_{10} = \beta C_0 \), \( T_E \) is the eutectic temperature. The solidification rate \( \partial f_s/\partial t \) is determined according to the equation:

\[
\frac{\partial f_s}{\partial t} = [V_s(I - f_s) + 4\pi Nk_n R^2(T_s - T)](1 - f_s) .
\]

(4)

The fraction of the solid phase when cooled to the eutectic temperature \( (T = T_E) \) is equal to \( f_s.E \). After cooling the metal below the eutectic temperature, the eutectic phase solidifies. Since in binary iron-based alloys the eutectic concentration is much higher than the impurity (carbon) content and, consequently, the value of \( f_s \) is close to one, in this model a stepwise increase to one of the fraction of the solid phase is assumed upon cooling below the \( T_E \) point.

3. Results of numerical experiments

In order to test the model, numerical simulation of solidification of Fe-0.49\%C alloy in cylindrical form with introduced refractory TiN particles of 80 nm size in the amount of 0.03% by weight (bulk concentration of nanoparticles \( n_p = 7.65 \times 10^{17} \) m\(^{-3}\)) was carried out. To determine the initial and boundary conditions, we used the description of an experiment in which the crystallization of a cylindrical casting of a similar size was studied [7].

Numerical research of process of crystallization of the modified melt was carried out at following parameters for the mold and alloy Fe-0.49\%C [7, 13-15]: \( c_1 = 680 \text{ J/(kg·K)} \), \( \lambda_1 = 30 \text{ W/(m·K)} \), \( \rho_1 = 7100 \text{ kg/m}^3 \), \( c_2 = 580 \text{ J/(kg·K)} \), \( \lambda_2 = 27 \text{ W/m·K} \), \( \rho_2 = 7450 \text{ kg/m}^3 \), \( \kappa = 2.77 \times 10^3 \text{ J/kg} \), \( T_0 = 1793 \text{ K} \), \( T_L = 1803 \text{ K} \), \( T_{10} = 1758 \text{ K} \), \( T_E = 1420 \text{ K} \), \( \beta = 91.7 \text{ K/\%} \), \( C_0 = 0.49 \text{ wt.\%} \), \( k = 0.4 \), \( K_n = 3.5 \times 10^{-5} \text{ m/(s·K)} \), \( \alpha_1 = 150 \text{ W/(m}^2\cdot\text{K}) \); density of nanoparticles TiN \( \rho_p = 5440 \text{ kg/m}^3 \), \( m_p = 0.03 \text{ wt.\%} \), \( l_p = 8 \times 10^{-8} \text{ m} \), \( l_d = 2.9 \times 10^{-10} \text{ m} \), \( l_s = 8.23 \times 10^{-10} \text{ m} \), \( D_p = 1.4 \times 10^{-7} \text{ m/s} \), \( \Delta H_p = 2.58 \times 10^{-20} \text{ J/atom} \), \( E = 9.6 \times 10^{-20} \text{ J/atom} \), \( \sigma_{12}^{\infty} = 0.2 \text{ J/m}^2 \), \( k_{12} = 1.38 \times 10^{-23} \text{ J/K} \), \( \delta = 1.53 \times 10^{-11} \text{ m} \), \( \theta = 5^\circ \), \( R = 0.017 \text{ m} \), \( H = 0.051 \text{ m} \), \( h_s = 10^2 \text{ m} \), \( h_a = 1.5 \times 10^3 \text{ m} \), \( c_s = 1080 \text{ J/(kg·K)} \), \( \rho_s = 1.65 \times 10^3 \text{ kg/m}^3 \); \( \lambda_3 = 1.28 \text{ W/(m·K)} \), \( \alpha_3 = 150 \text{ W/(m}^2\cdot\text{K}) \), \( R_0 = 10^{-4} \text{ m}^2\cdot\text{K/W}, T_s = 293 \text{ K} \).

A finite difference method was used to implement the (1)-(4) model. The calculated area was divided into \( I \times K \) cells. The steps of the spatial grid \( h_s, h_c \) were chosen from the condition that the contact surfaces of the melt and the mold were located in the middle between the neighboring nodes of the grid. The temperature distribution is described by the values at the grid nodes. The solution of the algebraic system obtained by implicit approximation of the heat transfer equations was carried out by the iterative method of block sequential upper relaxation [16]. Calculations continued until the melt solidified completely.

Figure 2 shows the dynamics of temperature, undercooling of the melt, and the solid phase fraction in the melt in the center of the emerging casting \( (r = 0) \) and in the point of contact with the mold’s wall \( (r = R) \) at a distance equal to half height of the casting, \( z = h_b + H/2 \) (points ‘3’ in figure 1).
As follows from the simulation results, at the point of contact of the melt with the side wall (curves 1), overheating is removed in a time equal to 5 seconds (figure 2, a), and then the undercooling of the melt in a short period of time (about 0.2 s) reaches a value of 0.96 K (figure 2, b). This period of time can be considered as the stage of the melt staying in a metastable state, when the fraction of the crystalline phase in it is negligible. Then, the stage of intensive growth of the solid phase comes, in which the undercooling decreases rapidly to values less than 0.01 K due to the release of latent heat of crystallization. Crystallization of the α-phase near the wall lasts about 125 seconds, the fraction of the solid phase by the end of this period reaches \( f_{\alpha} = 0.985 \), and then \( f_{s} \) increases to 1 abruptly due to eutectic crystallization of the alloy (figure 2, c).

In the centre of the casting, where heat exchange with the surrounding material is limited, the initial overheating is removed much later compared to the wall area: at \( t = 23 \) s (curves 2). The process of formation of nuclei of crystals of the α-phase with a noticeable rate begins at \( t > 28 \) s, when the undercooling of the melt reaches the value of 0.8 K. This indicates a significant increase in the period of the metastable state of the crystal phase up to 20 seconds, when both the nucleation rate and the growth rate are very small.

In contrast to crystallization near the mold walls, in the central zone of the mold there is a gradual equalization of the rate of release of latent heat of crystallization and the rate of heat removal to the surrounding melt. As a result, the undercooling of the melt for quite a long time up to the time moment \( t = 90 \) s is maintained at approximately a constant level of about 0.8 K. Intensive α-phase solidification in the centre of the casting occurs in the time interval \( 48 \leq t \leq 90 \) s. Then, undercooling \( \Delta T \) monotonically decreases due to the gradual enrichment of the melt by carbon, which leads, respectively, to a decrease in the growth rate of the solid phase. The fraction of the solid α-phase at
this stage of crystallization increases to $f_{\alpha}=0.9$ at $t=120$ s until the melt temperature drops to the value near eutectic point $T_E$. Further, crystallization process occurs at a very low rate: solidification of the alloy is completed at $t=198$ s (figure 2, c).

Solidification time, magnitudes of undercooling and crystallization rate vary significantly with the distance from the wall of the mold. Obviously, the conditions of nucleation in the melt also differ. Figure 3 illustrates the changes in the concentration $N$ of nuclei and of effective size of grains as a function of the distance from the central axis of the mold in its middle section ($z=H/2+h_b$).

![Figure 3. Radial distribution of the nucleus concentration (a) and grain size (b) in the cross section of the casting.](image)

As follows from the calculations, the values of the volume concentration of nuclei in the central region and at the boundary with the wall differ by more than five orders of magnitude: $N=8 \times 10^7$ at $r=0$, whereas at $r=R$, $N=10^{13}$ m$^{-3}$. The estimation of the size of the grain structure of the metal in the casting, calculated by formula $d_0=(2^{1/2}/N)^{1/3}$ [17], derived for spherical packing of maximum density, is shown in figure 3, b. As one can see, according to the simulation results, it is possible to distinguish a central zone with radius equal to about a third of the mold radius, where the effective diameter of the grains is maximal and reaches 3 mm. Area with the smallest metal structure ($d_0\sim100$ nm) is located near the side wall of the mold, which qualitatively coincides with the available experimental data [7]. It is interesting to note that the estimate of the grain structure size near the mold wall practically coincides with the size of the edge of the cubic nanoparticles $l_p=80$ nm, which was taken into account in these calculations. This result may suggest that the greatest efficiency of modification of the melt by nanoparticles is achieved in the near-wall region of the mold.

4. Conclusion

A mathematical model of non-equilibrium crystallization of a binary alloy (Fe-C) with modifying refractory nanoscale particles is proposed. The numerical simulation of melt solidification in a cylindrical mold is carried out and the features of crystallization are considered. The kinetics of heterogeneous nucleation and crystallization in the melt cooling process is described.

It is determined that the conditions of nucleation and solidification differ significantly within the casting. It is established that as the melt cools, the volume-sequential solidification of the metal takes place. The calculated temperature regimes of crystallization of the alloy and the size of the structure of the hardened metal are qualitatively consistent with the known experimental data.

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