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# On crystallization of a metal inoculated with nanoparticles

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**Abstract**. A mathematical model of the crystallization of a binary metal alloy inoculated with exogenous refractory nanoparticles has been developed. The process of cooling and solidification of an aluminum alloy with a phase diagram of the eutectic type is considered. Equations describing the growth of the solid phase with the continuous cooling of the alloy to the eutectic temperature and subsequent crystallization of the eutectic are given. Verification of the proposed model was carried out by comparing the results of numerical calculation of the crystallization process of the binary Al+Si system with the corresponding data of the physical experiment.

## 1. Introduction

One of the main tasks in the casting of metals and their alloys is to obtain a fine and uniform grain structure in order to reduce defects and improve the properties of the castings. For this purpose, it is possible to use nanoparticles-nucleants, which are specially introduced into the melt or, in other words, performed its inoculation. On such substrate particles, heterogeneous nucleation will occur, the course of which depends on the shape of the substrate, its wettability, dimensions, and conjugation of atomic lattices of the substrate and the nucleus material [1-3]. The basic principles of the technology of processing metals and alloys with nanoscale refractory chemical compounds in the foundry and welding industries are described in detail in monographs [4-6]. It was found that the modifying effect (the effect of grain refinement), depending on the composition, number, and wettability of nanoparticles introduced into the melt.

A significant number of works devoted to the experimental and theoretical investigation of the formation of the grain structure of cast metals and alloys [7-16] does not exhaust all the necessary aspects of this complex, complex issue. It is necessary to develop analytical and numerical models for describing heterogeneous nucleation on nanoseeds and further growth of crystalline grains in inoculated alloys. Improving the mathematical model of the nucleation and growth of the solid phase in the nanomodified alloy with the eutectic-type diagram of states, proposed earlier in [16], in the present paper we supplemented it with the kinetic equation for describing the crystallization of the alloy when the eutectic temperature is reached and below it.

## 2. Problem statement

Let us consider the volume solidification of an aluminum alloy Al+Si inoculated with refractory nanoparticles in a cylindrical form. We assume that the casting height is much greater than its radius $r_0$, and the internal thermal resistance is much smaller than the outer one $r_0/\lambda \ll 1/\alpha$, where $\lambda$ is the thermal conductivity coefficient of the casting material, $\alpha$ is coefficient of the heat transfer from its surface to the form. In order to simplify the numerical analysis, the thermophysical characteristics of the alloy for the liquid and solid phases are assumed to be identical and equal to their average values in the temperature range under consideration. Since the mass content of nanoparticles in the melt is small, the effect of inclusions on the thermophysical parameters of the melt and the fraction of the liquid phase can be neglected. Then the heat transfer equation averaged over the cross-section of the ingot, provided that the temperature is unchanged along its axis will have the form [16]:

$$c\rho \frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{2}{r_0}\alpha(T - T_\mathrm{f}) + \rho\kappa\frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}t}, \tag{1}$$

where $T$ is the temperature, $t$ is the time, $c$ and $\rho$ are the heat capacity and density of the alloy, respectively, $\kappa$ is the heat of crystallization, $T_\mathrm{f}$ is the average temperature of the form, $f_\mathrm{s}$ is the section of the solid phase. The total section of the solid phase formed in the melt upon its continuous cooling is defined similarly [17]:

$$f_s(t) = \int_{t_c}^{t} I_\mathrm{eff}(\tau)\big(1 - f_s(\tau)\big)V_s(t - \tau)\mathrm{d}\tau, \tag{2}$$

where $t_c$ is the time of the onset of crystallization, $I_\mathrm{eff}$ is the effective nucleation rate of α-crystal, and $V_s$ is the volume of solid phase formed on the nanoseed by the time $\tau$.

The melt in question contains highly activated wettable refractory nanoparticles. As follows from the results of [10], 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 seeds, therefore homogeneous nucleation is not taken into account here. To determine the rate of the heterogeneous nucleation, we assume that the nanoseed has the shape of a cube, whose faces are characterized by the wetting angle $0^0 < \theta < 90^0$. In order to simplify the model, the size dependence of the wetting angle is neglected and heterogeneous nucleus is considered as spherical cap. From geometric considerations it follows that the nucleus forming on the facet of the cubic nanoparticle should have a diameter of the contact spot no greater than the length $l_\mathrm{p}$ of its edge [1]: $2R_c\sin\theta \le l_\mathrm{p}$, where $R_c = R_0(1 - \delta/R_0)$ is the critical radius of the nucleus [16], $\delta$ is the Tolman parameter [18], $R_0 = 2\sigma_{12}^{\infty}T_{l0}/(\kappa\rho\Delta T_{l0})$, $\sigma_{12}^{\infty}$ is the free energy of the liquid – nucleus interface without allowance for curvature, $T_{l0}$ is the initial temperature of the liquidus, $\Delta T_{l0} = T_{l0} - T$. As a result, we obtain the minimum supercooling for the nucleus formation on the nanoparticle flat face: $\Delta T_\mathrm{m} = \big(4\sigma_{12}^{\infty}T_{l0}\sin\theta/\kappa\rho l_\mathrm{p}\big)$. The nucleation rate is determined in accordance with the formula [16]:

$$I = n_\mathrm{p}\frac{12\pi D_0}{l_\mathrm{a}^4}\left(\frac{l_\mathrm{p}}{l_\mathrm{c}}\right)^2 R_c^2(1 - \cos\theta)\exp\left[\frac{-(E + \Delta G^*)}{k_\mathrm{B}T}\right],$$

where $n_\mathrm{p} = m_\mathrm{p}\rho/(100\rho_\mathrm{p}l_\mathrm{p}^3)$ is the volume density of nanoseeds in the melt, $m_\mathrm{p}$,% is the mass fraction of the nanoseeds in the melt, $\rho_\mathrm{p}$ is the density of the nanoparticle matter, $l_\mathrm{c}$ is the lattice constant of the seed material, $l_\mathrm{a}$ is the atomic diameter of the melt, $k_\mathrm{B}$ is the Boltzmann constant, $D_0$ is the pre-exponential factor in the Arrhenius law, $E$ is the activation energy of the diffusion process in the melt, $\Delta G^*$ is the Gibbs energy of the critical nucleus:

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

The effective nucleation rate of α-crystals is determined by the relation $I_{\text{eff}} = BI$, where parameter $B$ connects the number of critical nuclei formed per unit time on a cubic seed with the number of effective spherical nuclei of the solid phase growing on these particles in a continuously cooled melt. To estimate this value, we take into account that the maximum number of critical nuclei of radius $R_c$, which can be placed per unit time on the faces of the seed, $n_z = 6l_p^2 / \pi R_c^2 \sin^2\theta$. Then the coefficient $B$ is defined as $B = b_0/n_z$, where $b_0 \sim 1$ is the correction factor. With above expressions for $n_p$, $R_c$, $R_0$ and $I$ the effective formation rate of spherical crystallization centers $I_{\text{eff}} = (b_0/n_z)I$ will take the form

$$I_{\text{eff}} = \frac{b_0 m_p \rho}{100\rho_p l_p^3}\frac{2\pi^2 D_0}{l_a^4 l_c^2}R_c^4\sin^2\theta(1-\cos\theta)\exp\left[\frac{-(E+\Delta G^*)}{k_B T}\right], \Delta T_{l0}\geq\Delta T_m\tag{4}$$

To determine $V_s$, following [3], we replace the cubic nanoparticle with an equivalent sphere with the same surface area, then its effective radius will be equal to $R_{e0} = (3/2\pi)^{1/2}l_p \approx 0{,}69l_p$. We consider that the rate of growth of the new crystalline phase formed on the surface of the seeds is described by a power law on supercooling [9] $\dot{R}_e = K_v(T_l - T)^m$, where $K_v$, $m$ are physical constants (for a normal growth mechanism $m=1$, for a dislocation mechanism, $m=2$), dot means the time derivative. Taking $m=1$ further, we get:

$$V_s(t,\tau) = (4\pi/3)\left\{\left[R_{e0}+K_v\int_\tau^t\Delta T d\xi\right]^3 - R_{e0}^3\right\}, t_c \leq \tau < t,\tag{5}$$

where supercooling $\Delta T = T_l - T$ has the form

$$\Delta T = T_A - \beta C_0 f_l^{k-1} - T.\tag{6}$$

Here the liquidus temperature $T_l$ is approximated by a linear dependence on the composition $C$, $T_A$ is the melting point of pure metal-solvent, $\beta$ is the modulus of slope of the liquidus line in the phase diagram. The composition of the alloying component is determined from the equation of the nonequilibrium lever [9] $C = C_0 f_l^{k-1}$, where $C_0$ is the initial concentration of the dissolved component, $f_l = 1 - f_s$, $k$ is the distribution coefficient of the alloying component.

To estimate the kinetic constant $K_v$, we used the formula [16, 19]:

$$K_v = (D\Delta H_a)/(l_a k_B T_A^2),\tag{7}$$

where $\Delta H_a$ is the enthalpy of melting per atom, the diffusion coefficient in the liquid $D$ is determined by the Arrhenius equation: $D=D_0\exp(-E/k_B T)$.

The number of α-crystals formed during the cooling time $t_e$ of the ingot to the eutectic temperature is determined by the formula:

$$N(t) = \int_{t_c}^{t_e} I_{\text{eff}}(\tau)f_l(\tau)d\tau,$$

and the characteristic grain size $d$ is estimated from the relation $d = 2(3/4\pi N)^{1/3}$.

Thus, the problem reduces to the solving system of integral-differential equations (1) and (2) taking into account relations (3)-(7) and the initial conditions:

$$T(t=0) = T_0, \qquad f_l(0\leq t\leq t_c) = 1.\tag{8}$$

In the second condition (8), it is taken into account that the volume content of seeds in the melt is small, therefore their parts in the liquid phase can be neglected.

Equation (2) is valid up to the eutectic transformation temperature in the corresponding phase diagram of the binary alloy. Assuming the eutectic crystallization as a self-consistent process accompanied by a single supercooling $\Delta T_E = T_E - T$, where $T_E$ is the equilibrium eutectic temperature, we will describe its growth by a kinetic equation of the form

$$\frac{d\psi_s}{dt} = K_E(1 - \psi_s)(T_E - T), \tag{9}$$

where $\psi_s$ is the total fraction of the solidifying eutectic, $K_E = K_\alpha + K_\beta$, $K_\alpha$, $K_\beta$ are the kinetic growth constants of the α and β phases. Because of the small mutual solubility $K_\alpha = K_{Al}$, $K_\beta = K_{Si}$ where $K_{Al}$ and $K_{Si}$ are the kinetic growth constants of aluminum and silicon, respectively. The change in temperature is determined by equation (1), in which the right-hand side instead of the term $\rho\kappa df_s/dt$ should be

$$\frac{K_{Al}}{K_E}\left(\rho\kappa + \rho_{Si}\kappa_{Si}\frac{K_{Si}}{K_{Al}}\right)\frac{d\psi_s}{dt}.$$

Here, $\rho_{Si}$ and $\kappa_{Si}$ are the density and heat of crystallization of silicon respectively. Equation (9) is solved under the condition $\psi_s = f_{sE}$, where $f_{sE} = f_s$ at $T = T_E$.

## 3. Results and discussion

Numerical calculations were carried out for an Al + 6.5% Si aluminum alloy modified with titanium nitride in the form of crystals close to cubic. The thermophysical characteristics of the alloy [20, 21] and the initial data are taken as follows: $T_A = 933$ K, $T_{l0} = 886.85$ K, $T_E = 850$ K, $\beta = 7.1$ K/%, $C_0 = 6.5$ % wt., $k = 0.14$, $\rho = 2600$ kg/m$^3$, $\rho_{Si} = 2330$ kg/m$^3$, $c = 885$ J/(kg×K), $\kappa = 4.02\times10^5$ J/kg, $\kappa_{Si} = 1.8\times10^6$ J/kg, $D_0 = 10^{-7}$ m$^2$/s, $\Delta H_a = 1.75\times10^{-20}$ J, $E = 4.2\times10^{-20}$ J, $\sigma_{12}^\infty = 0.093$ J/m$^2$, $l_a = 2.86\times10^{-10}$ m, $l_c = 4.235\times10^{-10}$ m, $\rho_p = 5440$ kg/m$^3$, $T_f = 658$ K, $r_0 = 0.02$ m, $\alpha = 250$-$350$ W/(m×K), $l_p = (5$–$10)\times10^{-8}$ m, $m_p = 0.03$-$0.3$ % wt., $\theta = 5^0$-$15^0$.

A preliminary estimate of the value of the kinetic constant was performed using (7) for pure aluminum, according to which $K_v \sim 0.015$ m/(K×s). For the binary alloy in question, this value varied in the range: $K_v = 0.001$-$0.01$ m/(K×s).

As follows from the calculations, an increase in the mass fraction $m_p$, and hence the number of seeds $n_p$ by an order of magnitude, leads only to an insignificant (less than 2%) decrease in the characteristic grain size $d$ (figure 1). The decrease in the size of the cubic nanosubstrate at a fixed mass fraction of the substrate material in the melt (here $m_p = 0.3\%$ wt.) also leads to a small decrease in the grain size (figure 2). The most significant effect on the grain size is exerted by the contact angle $\theta$ of the wetting (see figures 1 and 2). Therefore, the activation of nanoparticles by their cladding with metals will significantly affect the structure and properties of the alloy.

To verify the mathematical model an experimental study of the crystallization process of an aluminum alloy in a cylindrical form with an internal diameter of 40 mm was carried out. During the crystallization of the sample, its temperature was recorded. For this purpose, a high-speed thermocouple was located in its center. The signal from the thermocouple entered the memory of the computer through the digital thermometer TMD90, RS232 and the software package TM-SW of the company "Meterman". A comparison of the calculated and experimental thermograms of an ingot obtained by continuous cooling of an AlSi7 alloy modified with TiN nanopowder at m$_p$=0.3% is shown in figure 3. The numerical calculation was performed at $K_v = 0.001$ m/(K×s), $\theta = 5^0$, $l_p = 7\times10^{-8}$ m, the calculated maximum supercooling was $\Delta T \sim 0.5$K. During the eutectic solidification the values were $K_{Al} = 2.3\times10^{-3}$ K$^{-1}$c$^{-1}$, $K_{Si} = 0.23\times10^{-3}$ K$^{-1}$c$^{-1}$, $\alpha_E = 325$ W/(m×K). The experimental and calculated values in figure 3 coincide with a sufficiently high degree of accuracy, the error is about 1%. In accordance with the experimental data, the grain size amounts to hundredths of a millimeter which agrees satisfactorily with the presented calculations at $\theta = 5°$ (see figures 1 and 2). This indicates that

the proposed model satisfactorily describes the actual physical process of crystallization of the modified alloy with the adopted values of the kinetic growth constants and the wetting angle.
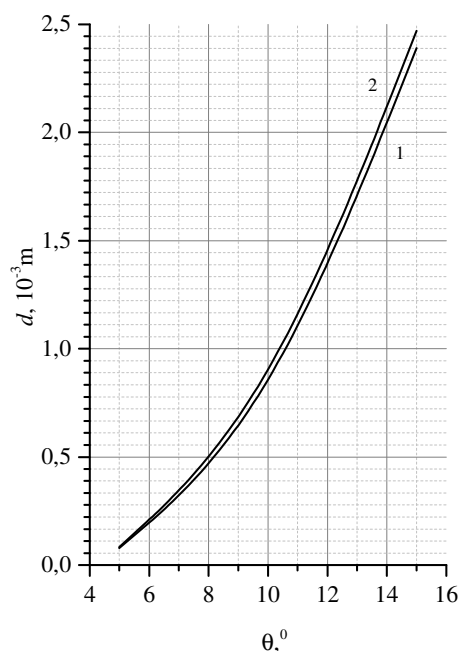


**Figure 1.** Dependence of the crystal grain size on the wetting angle at $n_p = 2\times10^{19}$ m$^{-3}$ ($m_p = 0.3\%$ wt.) – *1*, $n_p = 2\times10^{18}$ m$^{-3}$ ($m_p = 0.03\%$ wt.) – *2*.
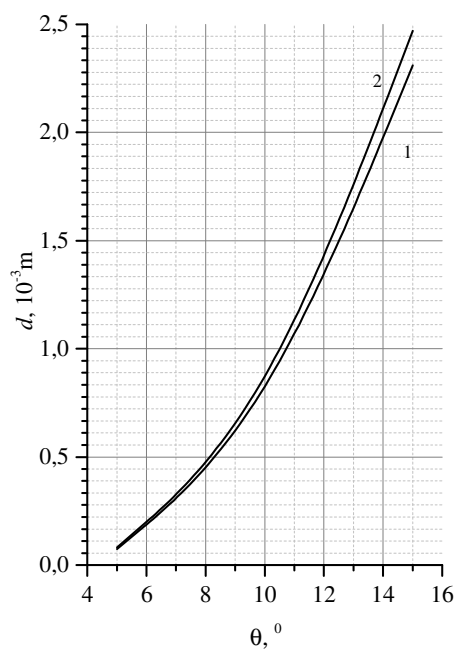
**Figure 2.** Dependence of the crystal grain size on the wetting angle at $l_p = 7\times10^{-8}$ m – *1*, $l_p = 10^{-7}$ m – *2*.
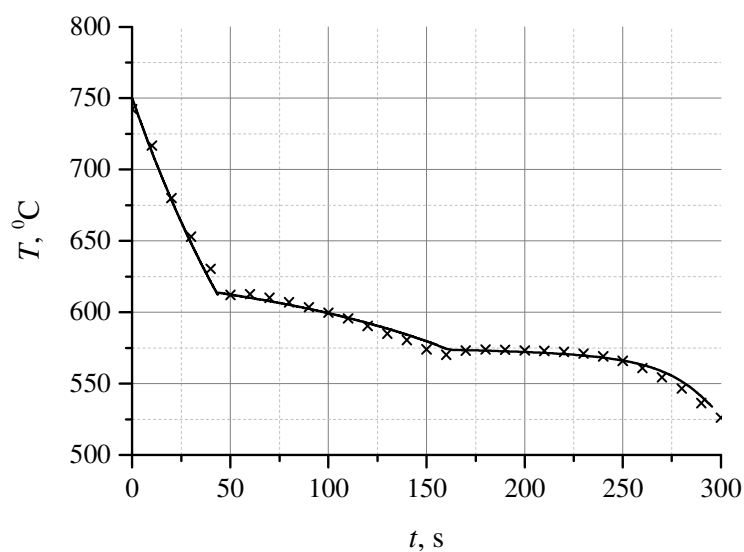


**Figure 3.** Thermograms of cooling and crystallization of aluminum alloy Al+6.5%Si. The points correspond to the experiment, the solid line correspond to the calculation.

## 4. Conclusion

A mathematical model of the crystallization of a binary metal alloy inoculated with highly activated wettable nanoseeds is proposed. Equations for describing the macroscopic growth of the primary phase during the continuous cooling of a binary alloy to the eutectic temperature and the growth of the fraction of the solidified eutectic with further cooling of the alloy are given. The presented model makes it possible to quantify the dynamics of temperature changes, supercooling, as well as the rate of nucleation, the fraction (section) of the solid phase, the number of crystallization centers, and the characteristic size of the crystal grain. Numerical experiments were carried out for an Al+6.5% Si alloy modified with titanium nitride nanoparticles. The results of calculations show that the wettability of the substrate surface has the greatest effect on cooling and crystallization of an alloy inoculated with refractory nanoparticles. This causes the need to clad their surfaces with metals in order to obtain the grain refinement of the casting. The results of numerical calculations correlate well with the data of the physical experiment (error within 1%), which indicates the adequacy of the mathematical model.

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## References

[1]   Turnbull D 1953 *Acta Metall.* **1** 8
[2]   Fletcher N H 1958 *J. Chem. Phys.* **29** 572
[3]   Maxwell I and Hellawell A 1975 *Acta Metall.* **23** 229
[4]   Zhukov M F, Chersky I N, Cherepanov A N, Konovalov N A, Saburov V P, Pavlenko N A, Galevsky G V, Andrianova O A and Krushenko G G 1999 *Hardening of Metallic, Polymeric and Elastomeric Materials by Ultradispersed Powders of Plasma-Chemical Synthesis* (Novosibirsk: Nauka) 307 p [in Russian]
[5]   Saburov V P, Eremin E N, Cherepanov A N and Minnehanov G N 2002 *Modification of Steels and Alloys by Dispersed Inoculators* (Omsk: publishing house of Omsk State Technical University) 212 p [in Russian]
[6]   Moskvichev V V, Krushenko G G, Burov A E, Uskov I V and Fedorova E N 2013 *Nanopowder Technologies in Mechanical Engineering* (Krasnoyarsk: publishing center of SFU) p 186 [in Russian]
[7]   Balandin G F 1979 *Basics of the Theory of Casting* (Moscow: Mashinostroenie) 335 p [in Russian]
[8]   Chalmers B 1964 *Principles of Solidification* (New York: Wiley) 288 p
[9]   Flemings M C 1974 *Solidification Processing* (New York: McGraw-Hill) 424 p
[10]  Cherepanov A N, Popov V N and Solonenko O P 2006 *J. Appl. Mech. and Tech. Phys.* **47** 29
[11]  Qian M 2007 *Acta Materialia* **55** 943
[12]  Greer A L 2016 *J. Chem. Phys.* **145** 211704
[13]  Wang K, Jiang H, Wang Q, Ye B and Ding W 2016 *Metallurgical and Materials Transactions A* **47** 4788
[14]  Xu Y, Casari D, Du Q, Mathiesen R H, Arnberg L and Li Y 2017 *Acta Materialia* **140** 224
[15]  Liu Z 2017 *Metallurgical and Materials Transactions A* **48** 4755
[16]  Cherepanov A, Cherepanova V and Manolov V 2017 *AIP Conf. Proc.* **1893** 030114
[17]  Lezhnin S I and Chernov A A 2007 *J. Appl. Mech. and Tech. Phys.* **48** 208
[18]  Tolman R C 1949 *J. Chem. Phys.* **17** 333
[19]  Christian J W 1981 *The Theory of Transformations in Metals and Alloys* (Oxford: Pergamon Press) 586 p
[20]  Chirkin V S 1968 *Thermophysical Properties of Nuclear Engineering Materials* (Moscow: Atomizdat) 485 p [in Russian]

[21]    Beletsky V M and Krivov G A 2005 *Aluminum Alloys. Composition, Properties, Technology, Application* (Kiev: COMINTEH) 365 p [in Russian]