Variational theory of crystal growth and its application for analysis of forming processes for metastable phases in overcooled metallic melts with eutectic composition

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The new crystallization theory for overcooled metastable melt is developed; it is based on variational mechanical principles and takes into account regularities of forming and diffusion growth of equilibrium crystals as well as diffusion-free growth of metastable crystals. Calculations for the melt $Fe_{83}B_{17}$ were conducted on the model; they displayed that simultaneous nucleation and growth of Fe and Fe_2B with metastable phase Fe_3B are observed in overcooled melt, and growth speed of near-critical dimensional crystals of Fe_3B exceeds crystal growth speed of Fe and Fe_2B. The effect of diffusion-free growth is observed for Fe_3B crystals, when quickly growing Fe_3B crystal surface catches boron atoms.

Quasi-equilibrium phase diagram for overcooled Fe-B melt was built on the base of the developed theory; it takes into account both equilibrium crystal growth and metastable phase growth. The obtained diagram allows to predict the values of components concentration near the surface of growing crystals both for Fe and Fe_2B crystals meeting the requirements of local equi-librium condition on their surface and for Fe_3B metastable crystals which are characterized by diffusion-free growth stipulated by high motion speed of crystal surface.

Key words: variation growth theory, crystal growth, metastable phase, diffusion-free growth, amorphous metals, nanocrystal metals Fe-B.
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Introduction

Forming of metastable phases in strongly overcooled eutectic systems of multi-component metallic melts arises increased interest in connection with development and putting into practice the commercial production of amorphous and nano-crystal metals, i. e. at Ashinsky metallurgical plant, the largest Russian producer of such metals [1–3]. These metals are characterized by the unique mechanical and physical properties, first of all — magnetic properties.

Conventional theoretical models uses assumption about local equilibrium near the growing crystal surface in description of crystallization processes in such systems [4]. However, this assumption is valid only in the case when crystal growth is limited by diffusion transfer of the components from initial melt. In this case phase equilibrium diagrams characterizing the examined macro-system are used for determination of regularities of micro-processes passing on the boundary "melt – crystal".

Growth of the new phase during crystallization of strongly overcooled multi-component metallic melts occurs in any cases with such high speed that crystallization front catches the atoms of melt components [3]. Thereby speeds of diffusion flows in this case don't determine regularities of a phase boundary transition. The arising effects don't correspond to the usual understanding of crystals growth regularities. In particular, deviation from the local equilibrium conditions on the boundary "melt – crystal" is observed [2, 4–7]. At the same time, these deviations have non-linear feature, and the methods of linear non-equilibrium thermodynamics become not valid for description of this system. In this connection, the new methods for description of such systems were developed last time [2]. The phase field theory [2, 8–12] can be noted as one of directions for such investigations. This theory describes a transition layer near growing nucleus via variational methods and allows to take into account non-linear effects connected with impurity trapping. Calculation allows predicting crystal growth regularities as well as determining the form of growing crystal dynamically.

The authors previously developed the new variational approach for description of crystal growth [13, 14]. The advantages of this approach conclude in complex description of mutually connected thermal and diffusion processes in the system "growing crystal – melt", taking into account the influence of non-linear effects on the phase boundary. The developed theory is used in this work for analysis of crystallization of dual-component eutectic melt in the conditions of deep overcooling. The developed mathematical model was applied for examination of Fe-B eutectic alloy having serious importance for many industries. The process of mutual influence of growth of crystals nuclei for several phases (i. e. metastable phases) is analyzed. The metastable analogue of

Fe-B system phase equilibrium diagram was built; it allows to predict growth regularities for overcooled melt. Choosing Fe-B system for investigations was stipulated by the problems of optimization of casting conditions for amorphized Fe-based melts during fabrication of amorphous ribbon in production conditions.

Regularities of eutectic melt crystallization

Let's consider a model case of dual-component eutectic system crystallization with the components *A* and *B* for description of crystals growth from overcooled melt. At first we shall suggest that the condition of local equilibrium is valid during crystals growth. We also think that in our system crystals extraction of the pure component A and chemical compound $A_{n_A}B_{n_B}$ (where n_A and n_B — corresponding stoichiometric coefficients), further noting as Z^E, is possible. The symbol *E* will manifest on maintenance of local equilibrium during growth of crystals $A_{n_A}B_{n_B}$. Growth of such crystals is limited by diffusion transfer of components, and the conditions close to equilibrium are established on the surface of crystals. Transition of the components through the boundary of phases separation can be considered as a chemical reaction with the speed describing by the following equation [16]:

$$I_k = L_k A_k (T) / T \qquad (1)$$

where I_k — molar speed of product *k* forming on the square unit of phases separation surface "crystal — melt"; A_k — chemical affinity of the process of component *k* transition through the phase boundary; L_k — phenomenological coefficient.

The growth process for crystals *A* and Z^E during melt overcooling can be demonstrated on the base of the phase equilibrium diagram of the considered eutectic system. The area of eutectic diagram with the eutectic point *O* is presented on the **Fig. 1**. The lines A_LO and Z_LO correspond to equilibrium between the melt and the components *A* and Z^E respectively. Let's consider the case of immediate overcooling of the melt with eutectic composition to the temperature T_1 as an example. The nuclei with composition *A* and Z^E can be formed in the melt as a result of overcooling. During a nucleus growth process, e. g. nucleus *A*, consumption of the component *A* from neighbor melt volumes takes place; content of the component *A* in these volumes decreases and, respectively, the part of the second component *B* increases. As soon as the condition of local equilibrium in the system is valid, some concentration c_2 of the component *B*, close to equilibrium concentration, is established near the nucleus surface. Thereby the equilibrium lines can be approximated in the low temperatures area. The examples of building of such lines were considered in several researches, e. g. [4, 16]. In our case, the lines OZ_S^E and OA_S continue the lines Z_LO и A_LO and correspond to the values of components concentrations which are established near nuclei surface for local equilibrium. In the meantime, in several cases the a. m. growth mechanism was not kept, as it was mentioned before. For a group of alloys, in the case of their quick overcooling, metastable nuclei *Z* can be created; they are more rich with the component *A* and, respectively, more poor with the component *B* in comparison with the nuclei Z^E. Impossibility of forming of these nuclei in usual conditions relating to slow cooling is their feature. Additionally, such nuclei can be unstable during secondary heating. Forming of metastable nuclei Fe_3B at the same time with the nuclei of stable phases Fe_2B and Fe in quickly overcooled eutectic melt Fe-B can be mentioned as an example of such nuclei [17, 18].

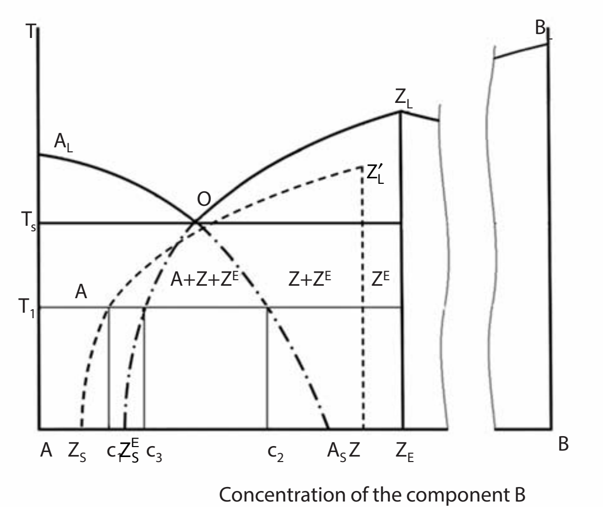


Fig. 1. Model phase equilibrium diagram. Lines OZ_S^E and OA_S are built with the condition of local equilibrium between the melt and phases Z^E and *A* respectively. $Z'_L Z_S$ line corresponds to variation of components concentrations on the surface of metasTable nuclei *Z* depending on temperature T. The symbols *L* and *S* display on liquid and solid states. Concentrations c_1, c_2, c_3 correspond to concentrations of the component *B* at the temperature T_1 for corresponding continuations of the equilibrium lines

Let's explain the mechanism of creation of metastable nuclei on the base of hypothetic phase equilibrium diagram with eutectics (see Fig. 1). We suggest that strong melt overcooling led to creation of metastable nuclei *Z* which are more rich with the component *A*, not usual nuclei Z^E. If growth of such nuclei on the surface was accompanied with observation of the local equilibrium condition, then excessive concentration of the component *B* would form on their surface, in correspondence with the "equilibrium" line OZ_S^E . Then the layer of atoms *B*, limiting diffusion of the component *A* to the nucleus surface, would be created near this surface. As a result, such nucleus could not grow [4], what occurs at usual cooling conditions of eutectic melts.

Growth of metastable nucleus of the phase *Z* is possible in the case when concentration of the component *B* in this nucleus deviates from equilibrium values which correspond to the line $Z'_L Z_S$ (Fig. 1). Such deviation can occur during strong melt overcooling owing to high nucleus growth speed, when crystallization front catches the initial phase and concentration of the component *B* on crystal surface lowers. A nucleus with composition *Z* is created as a result of impurity trapping, and the melt composition near its surface corresponds to concentration of impurity *B* in the point c_1[4]. Thereby, simultaneous growth of "equilibrium" nuclei of *A* and Z^E phases as well as metastable nuclei of *Z* phase, occur during cooling of the melt with eutectic composition, i.e. phase transformation takes place:

$$\text{Initial melt} \rightarrow A + Z + Z^E$$

It is important to note that in the case of nuclei *Z* forming the local equilibrium condition is not executed, thereby use of the equations (1) and Onsager principle is not correct. In this connection, the variational theory was proposed in our previous works [13, 14]; use of this theory for physical-chemical description of the system "nucleus — phase boundary — initial melt" allows to obtain the equation for nucleus growth speed in the case of deviation from equilibrium. The obtained equations can be easily transformed for the case of nucleus growth in eutectic overcooled melt.

The expression for molar speed of product forming on the surface square unit was obtained for the phase *Z* [13, 14] in the following way:

$$I_Z = -\left(\frac{J_A^\Psi}{M_A x_A^\Psi} - \frac{J_B^\Psi}{M_B x_B^\Psi}\right)\frac{\partial x_A^\Psi}{\partial r} \Bigg/ \left(\frac{n_A}{x_A^\Psi} - \frac{n_B}{x_B^\Psi}\right)\frac{\partial x_A^\Psi}{\partial r} + \frac{\rho^\Phi}{M_Z}\frac{dx_A^\Psi}{dt} \Bigg/ \frac{\partial x_A^\Psi}{\partial r} \qquad (2)$$

where for the components *A* and *B*: J^Ψ — flow of the component on nucleus surface; x^Ψ — molar fraction of the component near nucleus surface; *M* — molecular mass of melt and nucleus components; *r* — distance from nucleus center.

When formulating the equation (2), the allowance about spherical symmetry of the system "nucleus (Φ) — melt (Ψ)" was used. The second additive component in the denominator reflects the input of non-linear effects, connected with deviation from local equilibrium near the surface of growing nucleus [13]. If the conditions near nucleus surface are getting close to local equilibrium, the second additive component tends to zero. Respectively, the expression (2) for such conditions will be formulated as follows:

$$I_Z^E = -\left(\frac{J_A^\Psi}{M_A x_A^\Psi} - \frac{J_B^\Psi}{M_B x_B^\Psi}\right)\frac{\partial x_A^\Psi}{\partial r} \Bigg/ \left(\frac{n_A}{x_A^\Psi} - \frac{n_B}{x_B^\Psi}\right)\frac{\partial x_A^\Psi}{\partial r} \qquad (3)$$

where I_Z^E — molar speed of product *Z* forming under the conditions close to equilibrium ones on crystal surface.

Calculation of the metastable phase equilibrium diagram for Fe-B melt

The presented description of crystals growth regularities in eutectic system allows to execute calculations of analogues of the equilibrium lines OA_S, OZ_S^E, $Z'_L Z_S$ in the area of low temperatures [16, 17].

Let's choose the diagram of Fe-B eutectic system, which is the base for production of several amorphous Fe-based alloys, as an example. This system is examined rather well at present time [17, 18]. Calculations were conducted on the base of phase equilibrium diagram presented in the work [1] (**Fig. 2**). Usual cooling of melt with eutectic composition is accompanied by forming of Fe and Fe_2B phases. In the case of accelerated cooling below the temperature 1387 K, metastable crystals Fe_3B are formed together with these phases.

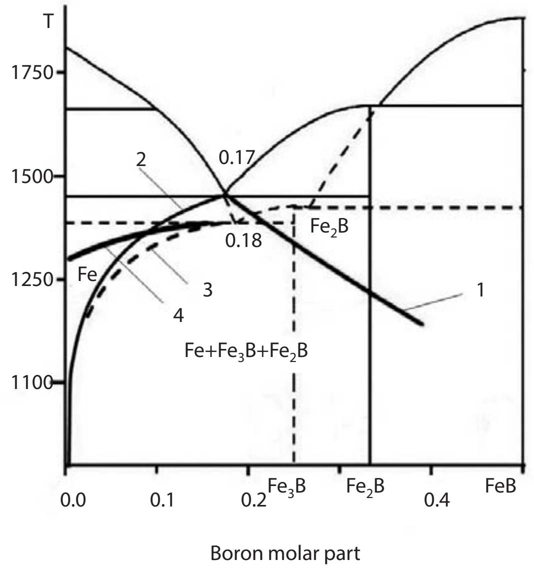


Fig. 2. Model phase equilibrium diagram of Fe-B system, taking into account deviation from local equilibrium on the surface of growing nucleus. Continuation of equilibrium lines in the area of low temperatures: *1* — line of Fe-melt local equilibrium; *2* — line of Fe_2B-melt local equilibrium; *3* — line of Fe_3B-melt local equilibrium; *4* — line, taking into account deviation from equilibrium for Fe_3B nuclei

To assess regularities of the processes in the examined system, a simplified method was used. The results of calculation can be clarified with details later, e.g. using the CALPHAD approach [19] with attracting of additional experimental data. Let's accept that variation of standard specific entropy Δs^0 and enthalpy Δh^0 during crystal forming does not depend on temperature for each of the crystal phases Fe, Fe_2B and Fe_3B. Then we can use the well-known expression for calculation of the equilibrium constant for each of these phases [20].

$$\Delta g^0 = \Delta h^0 - T\Delta s^0 = RT\ln K \qquad (4)$$

where *K* — equilibrium constant, Δg^0 — variation of standard specific free Gibbs energy.

Knowing the value of the equilibrium constant $K(T_e)_{EU}$ in the eutectic point at the temperature T_e, we can find out variation of specific entropy $\Delta s^0 = \Delta h^0 / T_e - R\ln\left(K\left(T_e\right)\right)$. If we shall apply the obtained expression to the equation (4), we shall get

$$K = K\left(T_e\right)_{EU} \exp\left(\frac{\Delta h^0}{R}\frac{T_e - T}{TT_e}\right) \qquad (5)$$

The required values of parameters for calculation according to the formula (5) are presented in the following table.

It was noted earlier that it is possible to accept the conditions of local equilibrium for Fe and Fe_2B nuclei. It means that the value of component concentration near nucleus surface can be considered as equal to corresponding concentration at the phase equilibrium diagram on the base of the formula (5). The results of calculations are presented on the diagram Fe-B. Calculated line 1 (Fe) and line 2 (Fe_2B) continue the corresponding equilibrium lines in the area of low temperatures on the basic phase equilibrium diagram. The diagram displays that the line 1 is not quite smooth continuation of the equilibrium line, what is stipulated by the simplified method (5). In the meantime, such simplification has slight effect on the results. The line 1 characterizes severe displacement of the equilibrium line in the boron-rich area, what is confirmed by consequent calculation and known experiments.

The corresponding "metastable" line for Fe_3B nuclei on the phase equilibrium diagram was built, whereas this line takes into account deviations from the equilibrium state. The previously developed technique [14] is used for it. Consideration of crystallization of metastable alloys showed, based on calculations, slight deviation from equilibrium state. Respectively, boron molar real concentration of X_B state differs slightly from the equilibrium concentration of X_B^E state. As soon as these concentrations correspond to concentrations near nucleus surface, we can expand the molar speed of product I_Z forming for Fe_3B nuclei near equilibrium as the component concentration function corresponding to the phase equilibrium diagram. Let's restrict our equation with the first order members:

$$I_{Fe_3B}\left(X_B\right) = I_{Fe_3B}^E + \left(X_B - X_B^E\right)\frac{\partial I_{Fe_3B}^E}{\partial X_B}. \tag{6}$$

To transform the obtained expression, we need to have into account that it is possible to use the equation of linear non-equilibrium thermodynamics (1) for the condition of local equilibrium on separation boundary of phases. Substituting the equation (10) in the equation (6), we shall get

$$I_{Fe_3B}\left(X_B\right) = I_{Fe_3B}^E + \left(X_B - X_B^E\right)\frac{L_k}{T}\frac{\partial A_{Fe_3B}}{\partial X_B}. \tag{7}$$

Then we shall consider the transition process for the components from melt to a nucleus as a chemical reaction to get consequent conclusions. In general we shall talk about transition m of initial melt components in a nucleus with constant composition (product of chemical reaction). Affinity of such chemical reaction can be presented as

$$A = \sum_{i=1}^{m} n_i \mu_i^{\Psi} - \mu^{\Phi}, \tag{8}$$

where μ — chemical potentials of corresponding components, n_i — stoichiometric coefficient of i-th component in reaction.

Then let's apply the theory of ideal solutions, taking into account the influence of surface effects on the value of nucleus chemical potential. Consequently, it can be expressed as follows [14]:

$$A = R_G T \ln \varepsilon_M - \nu\left(P^{\Phi} - P^{\Psi}\right), \tag{9}$$

where $\varepsilon_M = \prod_{i=1}^{m}\left(x_{iM}^{\Psi}\right)^{n_i} \Big/ K$ — average solution oversaturation by product of reaction, x_{iM}^{Ψ} — average part of i-th component in solution, ν — nucleus partial molecular volume.

Now let's consider the case of equilibrium growth, when local equilibrium is established near surface of a growing nucleus. Respectively, based on the equation (9), we can conclude that $RT\ln\varepsilon - \nu\left(P^{\Phi} - P^{\Psi}\right) = 0,$ where ε — solution oversaturation near nucleus surface in the condition of equilibrium. Using this relationship in the equation (9), we shall get the expression for the condition of equilibrium growth:

$$A = RT\left(\ln\varepsilon_M - \ln\varepsilon\right) = RT\ln\left(\prod_{i=1}^{m}\left(\left(x_{iM}^{\Psi}\right)^{n_i} \Big/ \left(x_i^{\Psi}\right)^{n_i}\right)\right). \tag{10}$$

Let's rewrite the obtained expression for the case of Fe_3B nuclei growth. As soon as difference $c_i^{\Psi} - c_{iM}^{\Psi}$ for each component is a small value, we shall obtain the equation

$$\frac{A}{RT} \approx \left(x_{BM}^{\Psi} - x_B^{\Psi}\right)\left(\frac{1}{x_{BM}^{\Psi}} - \frac{3}{1 - x_{BM}^{\Psi}}\right). \tag{11}$$

For local equilibrium $x_B^{\Psi} = X_B^E$, the equation (7) can be rewritten, taking into account the equations (1) and (11), as follows:

$$\frac{I_{Fe_3B}}{I_{Fe_3B}^E} = 1 - \frac{X_B^E - X_B}{X_B^E - x_{BM}^{\Psi}}. \tag{12}$$

Then let's apply the value of molar speed I_{Fe_3B} for real growth of metastable nucleus Fe_3B (2) and the expression of molar speed $I_{Fe_3B}^E$ for "equilibrium" growth. Substituting the equations (2) and (3) in the equation (12) as well as using the Fick equation and stationary expression for concentration gradient [14], it is possible to provide the final expression:

$$\frac{X_B^E - X_B}{X_B^E - x_{BM}^{\Psi}} = 2\frac{\nu^{\Psi} M_B}{M_{\aleph}}\rho^{\Phi}\frac{n_{Fe}X_B - n_B X_{Fe}}{M_B X_B + M_{Fe}X_{Fe}}\frac{1}{x_{FeM}^{\Psi} - X_{Fe}}. \tag{13}$$

Thermodynamic system parameters in the eutectic point

Phase	Molar boron part in a melt	Melt temperature, K	Δh_{Fe}^0, kJ/mol	Source
Fe	0.17	1452	–12,350	[21]
Fe_2B	0.17	1452	–54,470	[22]
Fe_3B	0.18	1387	–67,900	[21]

The obtained expression allowed to calculate continuation of the equilibrium line to the area of low temperatures for the case of deviation from equilibrium. Calculations of continuation of Fe_3B equilibrium line for the condition of deviation from local equilibrium were conducted via Newton's method based on the equation (5).

It can be seen from the graph that "non-equilibrium" line *4* Fe_3B (see Fig. 2) deviates essentially from the "equilibrium" one. Deviation effect of Fe_3B line from equilibrium values is determined by increased speed of crystals growth. Growth of Fe_3B nuclei needs Fe more by 1.5 times than growth of Fe_2B nuclei, and large boron amount is not required. Boron concentration in the initial eutectic melt $Fe_{83}B_{17}$ is rather smaller than boron concentration in a Fe_2B nucleus. Thereby Fe_2B crystal growth is limited by boron diffusion to a nucleus surface.

Quite different growth mechanism is observed evidently for Fe_3B atoms. Boron concentration in a nucleus differs from its melt concentration not so essentially comparing with the previous case. Additionally, growth of Fe and Fe_2B crystals occurs simultaneously with growth of Fe_3B nuclei, what promotes increase of boron concentration in the melt. As a result, the areas are forming in the melt, where boron molar fraction reaches the part in a Fe_3B nucleus. Forming of such areas promotes nucleus growth with the speed exceeding diffusion transfer of components from the melt in correspondence with the effect of diffusion-free growth. Crystallization front catches boron atoms.

Such understanding of the growth mechanism of Fe_3B nuclei is confirmed by experimental researches displaying that the areas of metastable Fe_3B crystals are presented by impregnations of Fe and Fe_2B crystals in the forming eutectic crystals [23].

Simulation of crystallization of Fe-B system overcooled melt

The developed metastable diagram allowed to conduct simulation of crystallization of Fe-B system overcooled melt. To build the model, the previously developed technique was used [4]. The generalized model assessed possibility of nucleation of Fe, Fe_2B and Fe_3B crystals. Taking into account the equation (20 and the equilibrium diagram (Fig. 2), crystals growth speeds were calculated for all their sizes. Distribution of crystals with different sizes was calculated on-line for the conducted processes. Thereby a macro-model of melt crystallization process in its volume was realized. At the same time the model allowed to reveal growth regularities for each separate crystal.

The obtained mathematical model includes the following main equations:

- equations of Fe, Fe_2B and Fe_3B nuclei forming intensity [4]:

$$J_i = N_0\, p_i\left(q_{KPi}\right)\sqrt{\frac{G_{2i}}{2\pi}}\exp\left(-\frac{\Delta Gi\left(q_{KPi}\right)}{kT}\right), \tag{14}$$

where q_{KP} — number of molecules in a critical nucleus, k — Bolzmann constant, T — temperature, $\Delta G(q)$ — variation of Gibbs energy during nucleus creation from q of molecules, G_2 — second derivative of $\Delta G(q)$ for a critical nucleus, p — possibility of particle joining to a critical nucleus surface, N_0 — initial number of molecules in solution.

- equations of particles distribution for each kind of Fe, Fe_2B and Fe_3B nuclei [4]:

$$\frac{\partial N}{\partial t} + \frac{\partial\left(Nb\right)}{\partial q} = 0, \tag{15}$$

$$b_{Fe}\left(t,q\right) = 4\pi RN_A\frac{D_{Fe}}{\nu^{\Psi}}\left(x^{\Psi}_{FeM} - x^{\Psi}_{Fe}\right), \tag{16}$$

$$\begin{gathered} b_{Fe_2B}\left(t,q\right) = 4\pi RN_A\frac{D_{Fe}}{M_B\nu^{\Psi}}\frac{M_Bx^{\Psi}_B + M_{Fe}x^{\Psi}_{Fe}}{n^E_{Fe}x^{\Psi}_B - n^E_Bx^{\Psi}_{Fe}}\times \\ \times\left(x^{\Psi}_{FeM} - x^{\Psi}_{Fe}\right), \end{gathered} \tag{17}$$

$$\begin{gathered} 4\pi RN_A\frac{D_{Fe}}{M_B\nu^{\Psi}}\frac{\left(M_Bx^{\Psi}_B + M_{Fe}x^{\Psi}_{Fe}\right)}{n_{Fe}x^{\Psi}_B - n_Bx^{\Psi}_{Fe}}\left(x^{\Psi}_{FeM} - x^{\Psi}_{Fe}\right) + \\ +8\pi RN_A\frac{\rho^{\Phi}D_{Fe}}{M_{\aleph}}, \end{gathered} \tag{18}$$

where $N(t,q)$ — density of nuclei distribution by sizes, ν — specific nucleus volume, D — diffusion coefficient, N_A — Avogadro's number, x^{Ψ}_M — average component fraction in solution, ε — solution oversaturation by corresponding component, b — growth speed of a particle (expressions b_{Fe} and b_{Fe_2B} were obtained in the work [5], growth speed b_{Fe_3B} of metastable particle was obtained in the works [13, 14]).

- balance equation of system components [5]:

$$\begin{gathered} N^l_{Fe}\left(t\right) = N_{init}\left(1 - c^0\right) - \int\limits_{q\Gamma Fe}^{\infty} N_{Fe}\left(t,q\right)qdq - \\ - n^E_{Fe}\int\limits_{q\Gamma Fe_2B}^{\infty} N_{Fe_2B}\left(t,q\right)qdq - n_{Fe}\int\limits_{q\Gamma Fe_3B}^{\infty} N_{Fe_3B}\left(t,q\right)qdq, \end{gathered} \tag{19}$$

$$\begin{gathered} N^l_B\left(t\right) = N_{init}c^0 - n^E_B\int\limits_{q\Gamma Fe_2B}^{\infty} N_{Fe_2B}\left(t,q\right)qdq - n_B\times \\ \times\int\limits_{q\Gamma Fe_3B}^{\infty} N_{Fe_3B}\left(t,q\right)qdq. \end{gathered} \tag{20}$$

where T_{init} — initial number of molecules, N^l_{Fe} и N^l_B — remaining number of molecules.

Calculations were conducted for the melt with eutectic composition $Fe_{83}B_{17}$. Equations of the mathematical model were solved using finite difference method. The software complex based on C++ language was developed for solving the equations. The following initial data were used during calculations [4]: boron diffusion activation energy in Fe-B melt — 80,000 J/mol, interfacial tension (for Fe nuclei in Fe-B melt) — 0.204 J/m², interfacial tension (for Fe_2B and Fe_3B nuclei in Fe-B melt) — 0.3 J/m².

Variations of critical size and intensity of nucleation were calculated at the first stage. The calculation displayed that intensity of Fe_3B phase nucleation is rather low during cooling within the temperature range 1100—1200 K (**Fig. 3*a***). Nucleation and growth of Fe and Fe_2B phases nuclei dominates within this temperature range, what is confirmed by the experimental results [23]. This effect is caused evidently from the built metastable phase equilibrium diagram (see Fig. 2). Slight overcooling below the eutectic point 1387 K finalizes in insufficiency of boron atoms required for growth of Fe_3B nuclei. Consequent overcooling leads to severe deviation of the “metastable” line (line 4) to the side of decreasing boron concentration, what promotes intensity rise of Fe_3B nucleation.

During further melt overcooling within the temperature range 1000—1100 K, nucleation intensity of Fe_3B crystals quickly increases. During more deep overcooling, nucleation intensity of Fe_3B phase is getting close to nucleation intensity of Fe and Fe_2B phase. Active growth of all three phases is observed at this stage. In the meantime, the growth speed of Fe_3B nuclei is substantially higher than the growth speed of Fe_2B nuclei, despite the fact that nucleation intensity of Fe_3B phase is less than nucleation intensity of Fe_2B phase. It confirms the above-mentioned proposal on the special growth mechanism of Fe_3B nuclei. For example, additional calculation during immediate melt overcooling to the temperature 1000 K showed that increase of the number of molecules in a nucleus per second makes for near-critical nucleus: $b_{Fe} = 1.07 \cdot 10^{10}$, $b_{Fe_2B} = 7.79 \cdot 10^{10}$, $b_{Fe_3B} = 4.01 \cdot 10^{11}$.

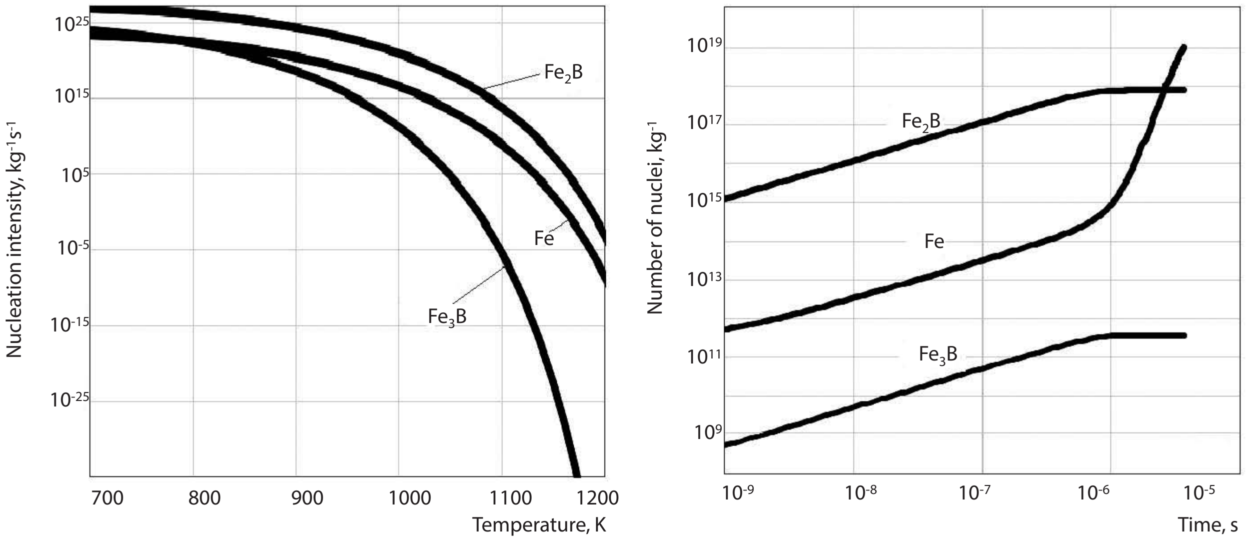
Calculation of variation of nuclei number depending on the temperature 900 K was conducted at the second stage. This calculation displayed that active growth of all nuclei is observed for this overcooling independently to their composition, what also corresponds to the experimental results [23]. At the last crystallization stages, solution is depleted by boron, what leads to more active growth of Fe crystals.

Conclusions

1. The new variational crystallization theory for overcooled eutectic alloys is developed. The theory allows to predict crystallization regularities of overcooled eutectic alloys for different conditions, providing save of expenditures for expensive experimental researches.

2. Metastable phase equilibrium diagram was built for Fe-B system. Influence of metastable effects on crystals growth is examined. The relationships of dependence between components concentration near crystals surface and temperature we obtained both for stable Fe and Fe_2B crystals (characterized by observation of local equilibrium conditions near surface of a growing nucleus) as well as for Fe_3B metastable crystals (whose growth is stipulated by the effect of impurity trapping).

3. Mathematical simulation of crystals nucleation and growth in the overcooled eutectic melt $Fe_{83}B_{17}$ is conducted. It is shown that simultaneous nucleation and growth of stable phases Fe and Fe_2B with metastable phase Fe_3B is observed in the overcooled melt. Regularities of nucleation and growth of metastable phase Fe_3B are studied. It is displayed that the growth mechanism of Fe_3B nuclei principally differs from growth of nuclei Fe and Fe_2B. It is explained by diffusion-free trapping of boron atoms by growing surface of Fe_3B crys-



a *b*

Fig. 3. Variation of nuclei creation intensity depending on the temperature (*a*); variation of nuclei number in 1 kg of melt depending on the time of process conduction st the temperature 900 K (*b*)

tals, while diffusion-free growth speed of near-crystal nuclei of Fe_3B phase exceeds the Fe and Fe_2B nuclei growth rate.

4. Calculated metastable phase equilibrium diagram Fe-B allows to predict solidification and crystallization regularities in overcooled melts during production of amorphous metals on the base of this system.

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