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Influence of modification of the cast metal structure by solid phase particles on the nucleation of crystallization centers and their stability

The inoculation method has wide possibilities for improving the mechanical and operational properties of cast metal, which makes it possible to create artificial centers of crystallization due to the direct introduction of dispersed refractory particles into the melt. The efficiency of such particles serving as crystallization centers is due to the presence of an activated transition layer on their surface. In this regard, it is promising to use complex modification, in which activating additives are introduced into the melt together with dispersed refractory particles, which form a transition layer with the desired properties on the particles. At the same time, the features of the interaction of particles with activating additives have not been sufficiently studied. A theoretical assessment of the influence of dispersed particles on the nucleation of crystallization centers and their stability was carried out on the basis of a study of the phenomena of wetting, adsorption, and dissolution using the relationship between the critical size of additional nuclei, their wetting angle, and supercooling of the melt. It is shown that if between the particle and the cladding layer the difference in chemical potentials of the contacting phases will exist throughout the entire process, and on the surface of the complex it will have a low value of surface tension, then such a particle will be stable, which takes place during adsorption of a surface-active component from a melt. Therefore, the efficiency of melt heterogenization and modification of the cast metal structure is determined by the thermodynamic activity of the substance of the transition layer to the material of the solid phase particle. The obtained conclusions make it possible to select the composition of complex modifiers that allow controlling the structure of castings in the process of their crystallization.

Key words: cast metal, suspension, modification, particles, crystallization, adsorption, wetting, interfacial energy, structure

Introduction

Of considerable interest for improving the quality of cast metal is the use of the modification method by creating artificial crystallization centers due to the direct introduction of refractory inoculant particles into the melt [1–9]. The efficiency of such particles as crystallization centers is characterized by the presence of an activated transition layer on their surface. Therefore, it is advisable to use complex modification, in which certain elements are introduced into the melt together with inoculator particles as activating additives (protectors), with the help of which it is possible to form a transition layer with the desired properties on the particles [10, 11]. However, the features of the interaction between the inoculant particle and the protector metal have not been sufficiently studied. This work is devoted to this problem.

Analysis of the processes of nucleation of crystallization centers and their stability during the complex modification of foundry metal with particles of dispersed powders

To assess the effect of complex modification of dispersed powder particles on the nucleation of crystallization centers and their stability, the concepts presented by B. Chalmers [12] were used, based on the relationship between the critical size r^* of prenuclei, their wetting angle θ and supercooling of the melt ΔT , shown in the diagram (Figure 1), from which it follows that with a decrease in θ , ΔT decreases. This provision can be taken as a working hypothesis when solving the issue of increasing the efficiency of modifying the structure of steels and alloys using natural and artificial solid-phase substrates (inoculator) activated by surface-active elements (protector) or intermetallic compounds and heterogenizing the melt as a result of selective adsorption of chemical elements from the alloy.

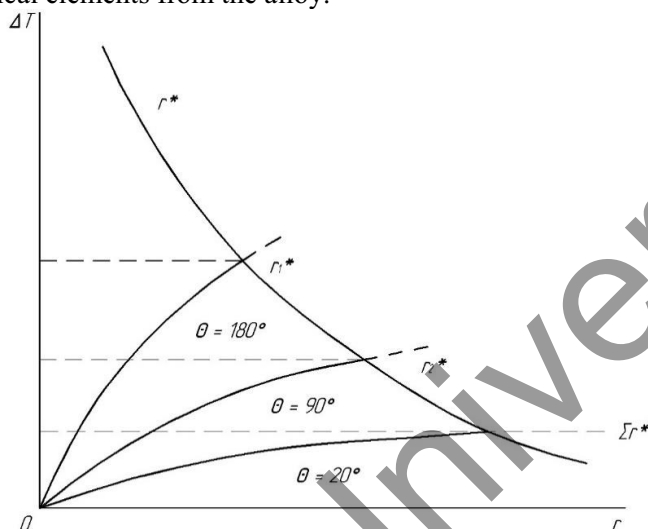


Figure 1. Conditions for heterogeneous nucleation of crystallization centers with radius r at different contact angles θ

The study of the phenomena of wetting, adsorption, dissolution, and nucleating activity of solid phase particles was carried out on the model of the structure of a suspension with particles in a metal melt, shown in Figure 2.

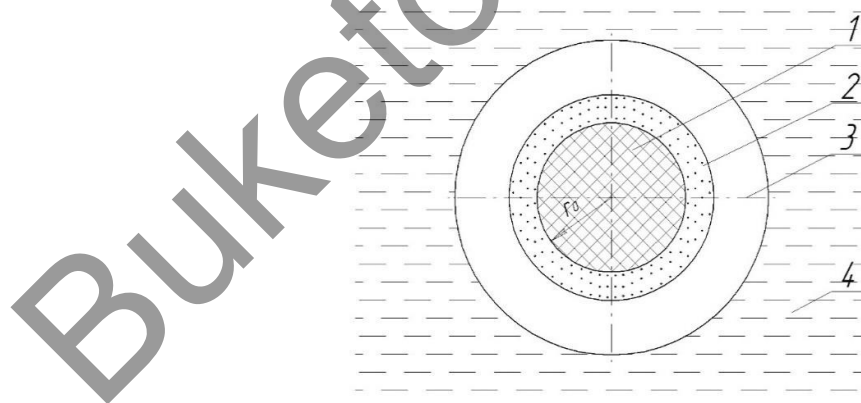


Figure 2. Model of the structure of a particle of a complex modifier in a metal melt: 1 — particle core; 2 — transition layer; 3 — adsorbed layer; 4 — metal melt

The core of such a complex is a refractory particle of the solid phase 1 with radius $r_0 < r^*$, the surface of which is clad with a layer of substance 2 formed by the product of the interaction of the protector metal with the material of the particle and chemical elements adsorbed from some volume 3 of the melt 4. The boundary between 3 and 4. However, in volume 3, which is depleted in the content of chemical elements that have reacted with the material of the cladding layer, adhesion forces can act on the surface of the particle, forming a concentration fluctuation [13].

Wettability in the system solid (s) — liquid (l) — gas (g) is usually considered by the example of the contact of a flat substrate with a melt drop [14]. If a flat substrate is rolled into a sphere of radius r , then the wetting conditions — the values of the wetting angle (θ) and the values of surface tension (σ_{sl}) will change, σ_{sl} will decrease, and the work of adhesion between the solid and liquid phases W_A will increase, since from the Dupre equation follows:

$$\sigma_{sl} = \sigma_{lg} + \sigma_{sg} - W_A, \quad (1)$$

$$W_A = W_A^e + W_A^{\text{none.}}, \quad (2)$$

where W_A^e and $W_A^{\text{none.}}$ are the equilibrium and nonequilibrium parts of W_A : $W_A^e = W_A^x + W_A^{\text{VDW}}$. Here W_A^x is the energy of cohesion of the liquid and solid phases at a steady state equilibrium of chemical bonds; W_A^{VDW} is the energy of the Van der Waals interaction. As r decreases, the contribution of W_A^{VDW} to W_A^e increases. Therefore, in equilibrium systems, the interfacial energy σ_{sl} is the smaller, the smaller the difference in the structure of the contacting phases.

If there is a chemical interaction between the S and L phases, then σ_{sl} will change with time and can be extremely low [15].

It follows from Dupre's equation (1) that the more intensively the phases interact, the less σ_{sl} . When the system approaches equilibrium, when the chemical potentials of the phases are equalized ($\mu_i^s \approx \mu_i^l$), σ_{sl} can increase due to the action of the transition layer (the effect of A.A. Zhukhovitsky) [16].

This property of the interacting phases ensures the stability of the solid phase in the melt in the case of the formation of a refractory transition layer with a low diffusion mobility of atoms, which is characteristic of metallides or intermetallides.

Change σ_{sl} depends on the difference in chemical potentials of the contacting phases $\Delta\mu$ and is found by the formula

$$\Delta\sigma_{sl} = M \cdot \Delta\mu, \quad (3)$$

where M is a constant.

The stability of suspension particles with a transition layer between a solid core and a melt can be estimated by a criterion obtained from formal thermodynamic relations [17]:

$$K = \sigma_{sg} - \sigma_{sl} - 0,5\sigma_{lg}. \quad (4)$$

The system is considered stable if $K > 0$, i.e. $\sigma_{sg} > \sigma_{sl} - 0,5\sigma_{lg}$. This condition is satisfied when σ_{sl} is sufficiently small. If a chemical potential difference $\Delta\mu$ exists between the particle and the cladding layer throughout the entire process, then, according to formula (3), $\Delta\sigma_{sl}$ is sufficiently large, and a low value $\mu_i^l \approx \mu_i^s$ will occur on the surface of the complex at σ_{sl} , and such a particle will be stable. This is noted during the adsorption of some surface-active component from the melt, the transition of one of the components through the phase boundary, or during partial dissolution of the solid phase. According to the Neumann equation $K = \sigma_{lg}(\cos\theta - 0,5)$, and considering adhesion to a solid $K = W_A - (3/2)\sigma_{sl}$. The boundary between $K > 0$ and $K < 0$ is at $\theta \approx 60^\circ$, and the evaluation criterion acquires a positive sign, which is a sign of suspension stability.

Based on the studies of the mechanism of homogeneous nucleation during steel deoxidation, carried out by S.I. Popel and M.P. Dokhov [18, 19], and the possibility of using the Gibbs equation instead of the Helmholtz function for small volume changes during the formation of a spherical nucleus with a critical size r^* , can be written:

$$r^* = 2\sigma \cdot V_0 / \Delta G, \quad (5)$$

where σ is the interfacial energy; V_0 — molar volume of the embryo; ΔG is the total change in the free energy of the system. With a small change in volume, the change in stresses in the old phase can be neglected, then ΔG can be represented by the sum:

$$\Delta G = \Delta G_V + \Delta G_S. \quad (6)$$

$\Delta G_V = -4LAT\pi r^3/(3T_e)$ is the change in volumetric and surface free energy, where T_e is the equilibrium melting temperature; ΔT is the difference in melting and crystallization temperatures (supercooling); L is the volumetric heat of transformation. Then the critical radius of the equilibrium embryo is determined:

$$r_e^* = 2\sigma V_0 T_e / (L\Delta T). \quad (7)$$

The calculation of r_p^* according to expression (7), performed by Yu.Z. Babaskin [20], showed that at $\Delta T = 320$ °C for pure iron $r_e^* = 1.3$ nm. If a surfactant is introduced into the melt, then the value of σ can decrease, for example, to 10^{-5} J/cm². Then the nucleus will reach the critical size at supercooling $\Delta T \approx 160$ °C.

A change in the chemical composition of the liquid metal will certainly affect the value of the interfacial energy σ_{sl} , but for transition metal alloys, the general pattern of formation of metal-like compounds should be preserved due to the similarity in the electronic structure and high values of the adhesion work WA. Calculations show that the probability of heterogeneous nucleation crystallization centers by carbide phases in iron-carbon alloys, in accordance with the change in the free energy of formation of compounds, 33 decreases in the following series of chemical elements: Zr → Ti → Ta → Nb → Cr → V → Si → Fe [18, 19].

If ready-made nucleation centers are introduced into the melt, for example, particles of ultrafine powders (UDP) TiC, TiN, TiCN, strong carbide-, nitride- and oxide-forming elements Ti, Cr, Mo, V, Y, Zr, Ta, and the melt will contain C, N, and O, then the scheme of suspension formation may look like that shown in Figure 3.

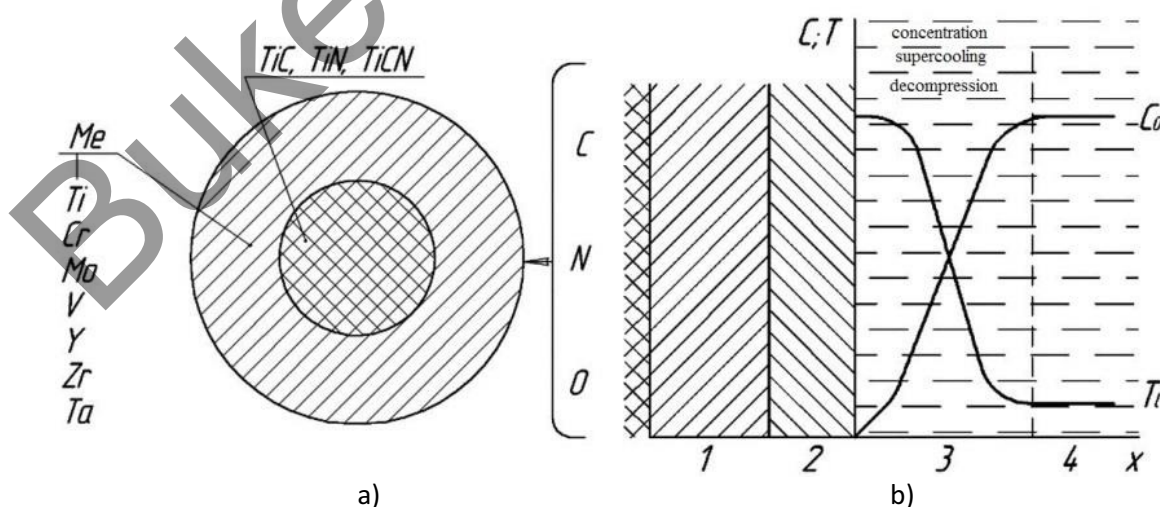


Figure 3. Schemes of the formation of a suspension with an ultrafine particle (a) and transition layers (1-2) on UDP (b) and a change in the concentration of the adsorbed element C_0 and the melting temperature T_l in the adsorbed layer (3) and the volume of the melt (4)

In this case, the equilibrium constant K_e of the reaction of a metal cladding a particle with a non-metal — carbon C ($Me + C = MeC$) will be inversely proportional to the product of the activity of the components:

$$K_e = 1/(a_{Me} \cdot a_C). \quad (8)$$

Then, near the interfacial surface, the carbon activity will be close to zero; therefore, the melting temperature of the alloy T_l (Fig. 3b) in melt layer 3 will approach the melting temperature of pure metal T_{Me} . In this case, concentration supercooling can form in layer 3, which slows down the destruction of the complex.

Studies of the crystallization of alloys in the concentration and temperature fields are given in [21]. Using the results of these studies, the heterogenization of a metal-carbon-alloying element alloy belonging to a pseudobinary system can be represented considering local concentration fluctuations in heterophase complexes. The composition of alloy 4 in subsequent sources (Fig. 3b) will be depleted in the outcome (component).

Crystallization of an ordinary alloy under non-equilibrium conditions will begin according to a metastable diagram in the temperature range T_L-T_S with supercooling ΔT relative to the equilibrium diagram. Crystallization of the heterogenized melt will begin according to the metastable diagram with a larger metastability range than that of the original alloy. At a content of 107 particles in 1 cm^3 of the melt, the spheres of action of adsorption forces can overlap, and to start crystallization, an atom needs to overcome the sum of the adsorption forces G_r and the activation energy of the transition to the solid phase G_b .

But G_r and G_b have opposite signs, so G_b compensates G_r if $|G_r| > |G_m|$, G_m is the change in free energy during the formation of a solid phase. Then $G_r - G_m = G_z$, and the atom needs to overcome the energy barrier G_z (potential well) in order to occupy a position in the crystal lattice of the solid phase with a higher level of free energy. Therefore, the crystallization of such an alloy will begin with a metastability interval exceeding this value for the original alloy, and may be accompanied by a decrease in density (decompression). If the impurity concentration C_0 in the transition layer is close to zero (Fig. 3b), then the cooling curve should show a plateau due to the precipitation of pure metal, and crystallization will be completed earlier than in the initial alloy, since clustering and adsorption forces change integral free energy of the system, and the duration of crystallization of the treated melt will be less than that of the original.

The kinetic law of continuous growth [22] is expressed by the formula

$$V_P = -D_L \cdot \Delta H_m \cdot \Delta T_K / (a \cdot k_{id} \cdot T^2), \quad (9)$$

where V_P is the growth rate; D_L — diffusion coefficient in the liquid phase; ΔH_m — molecular (atomic) heat of fusion; ΔT_K — kinetic supercooling; a — interplanar distance, which determines the position of the interfacial boundary. As can be seen, the rate of advancement of the interfacial boundary linearly depends on supercooling. An increase in kinetic supercooling during melt heterogenization increases the growth rate. The integral characteristic of the crystallization of a heterogenized eutectic alloy, in accordance with the hypothesis put forward, can be expressed by the course of the process in the temperature range with an inflection of the curve within the crystallization range. The low stability of the crystallization front during directional solidification of a conventional alloy is due to the value of the equilibrium impurity distribution coefficient $k_{id} < 1$, which causes the growth of columnar crystals at high crystallization overcooling (Figure 4a). In a heterogenized alloy, because of modification, concentration supercooling at the crystallization front may be absent, and kinetic supercooling may increase significantly. The growth of a dendrite in a metal suspension is hampered by a barrier of particles at the crystallization front, which causes splitting of the stem and separation of the axes. Excess phases are formed on the substrates in the early stages of solidification and can grow into the dendrite shaft, being in the metal in the volume of grains, and then the alloy will have a fine-grained structure (Figure 4b).

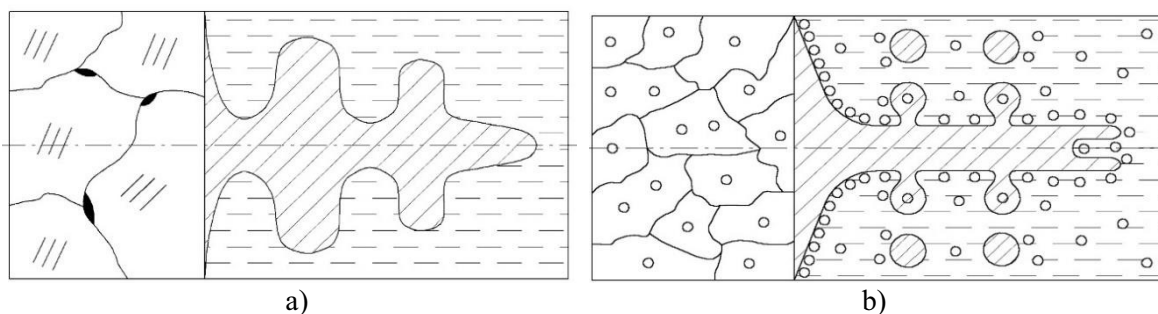


Figure 4. Scheme of crystallization of suspensions: *a* — ordinary alloy; *b* — modified alloy

The criterion of concentration supercooling, originally obtained by B. Chalmers [12], in the absence of convective mixing, characterizes the stability of a flat crystallization front:

$$\frac{T_L}{V_p} \geq -\frac{m_i \cdot C_0 (1 - \omega)}{\omega \cdot D_L}, \quad (10)$$

where T_L is the temperature gradient; m_i is the slope of the liquidus line; C_0 is the impurity concentration in the melt.

Impurity adsorption on heterophase complexes reduces the concentration of C_0 in the bulk of the melt, and the growth rate of V_p with a flat crystallization front, other things being equal, can be increased. In addition, an increase in the stability of a dispersed thermodynamic system will make it possible to increase the temperature gradient ahead of the crystallization front without the danger of the nucleation and growth of crystallization centers in the melt volume remote from the growing solid phase.

Thus, the efficiency of melt heterogenization and modification of the cast metal structure is determined by the thermodynamic activity of the substance of the transition layer to the material of a solid phase particle, to an impurity, or to one of the chemical elements that make up the alloy. Since all real metal melts are suspensions to one degree or another, the interaction of solid phase particles with thermodynamically active additives of modifiers will inevitably have a positive effect on the kinetics of the nucleation of crystallization centers.

The performed analysis makes it possible to select the composition of complex modifiers for their successful practical use [23].

Conclusion

On the basis of the foregoing, it is possible to formulate the basic principles of the crystallization activity of solid phase particles and the stability of metal suspensions during modification: the particle size of the solid phase must be commensurate with the critical size of the nucleus of the crystallizing phase; the surface of the particles of the suspension must be activated by the adsorbed substance, in which the thermodynamic potential of the interaction of the particle with the non-metal (O, N, C, B, etc.) must be higher than that of the metal of the solid phase; between the substance of the solid phase and the adsorbed layer, there must be a chemical interaction with the release of excess energy; the adsorbed layer should heterogenize the melt due to the increased chemical affinity for one of the chemical elements from the composition of the alloy that forms the eutectic.

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Е.Н. Еремин

Қатты фазалы бөлшектермен толтырылған металл құрылымының модификациясының кристалдану орталықтарының қалыптасуына және олардың тұрақтылығына әсері

Құйылған металдың механикалық және пайдалану қасиеттерін арттырудың кең мүмкіндіктері дисперсті отқа төзімді бөлшектерді балқымаға тікелей енгізу арқылы жасанды кристалдану орталықтарының құруға мүмкіндік беретін модификация әдісіне ие. Кристалдану орталықтары ретінде қызмет ететін мұндай бөлшектердің тиімділігі олардың бетінде белсендірілген өтпелі қабаттың болуына байланысты. Дисперсті отқа төзімді бөлшектер қосылған ерітіндіге бөлшектерде қажетті қасиеттерге ие өтпелі қабат түзетін белсендірілген қоспалар қосылады, бұл жағдайда кешенді түрлендіруді қолдану перспективті болып табылады. Сонымен қатар, бөлшектердің белсендіруші қоспалармен әрекеттесу ерекшеліктері толық зерттелмеген. Кристалдану орталықтарының пайда болуына және олардың орнықтылығына дисперсті бөлшектердің әсерін теориялық бағалау сулау, өскіннің критикалық өлшеміне дейінгі сіңіру мен еруі арасындағы тәуелділікті қолдану, оларды сулау бұрышы және балқудың суытылуы құбылысын зерттеу негізінде жүргізілді. Егер бөлшек пен қаптама қабаты арасындағы бай-

ланьсатын фазалардың химиялық потенциалдарының айырмашылығы толық процесс барысында бар болса, ал кешеннің бетінде—беттік керілу аз мәнге ие болса онда бұндай бөлшек орнықты болады, ол беттік—белсенді компонентінің балқымадан адсорбция барысында орынға ие болады. Сондықтан балкудың гетерогенизациясы және құйылған металдың құрылымын түрлендіру қатты фаза бөлшегі материалына заттың өтпелі қабатының термодинамикалық белсенділігі арқылы анықталады. Алынған қорытындылар құйманың құрылымы мен кристалдану процестерін басқаруға жүзеге асыратын кешенді модификаторлардың құрамын таңдауға мүмкіндік береді.

Кілт сөздер: құйылған металл, суспензия, түрлену, бөлшектер, кристалдану, сіңіру, сулау, фаза аралық қуат көзі, құрылым.

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Влияние модифицирования структуры литого металла частицами твердой фазы на зарождение центров кристаллизации и их устойчивость

Широкими возможностями повышения механических и эксплуатационных свойств литого металла обладает метод модифицирования, позволяющий создавать искусственные центры кристаллизации за счет прямого введения в расплав дисперсных тугоплавких частиц. Эффективность таких частиц, служащих центрами кристаллизации, обусловлена наличием на их поверхности активированного переходного слоя. В этом отношении перспективно использовать комплексное модифицирование, при котором в расплав совместно с дисперсными тугоплавкими частицами вводятся активирующие добавки, формирующие на частицах переходный слой с нужными свойствами. В то же время особенности взаимодействия частиц с активирующими добавками изучены недостаточно. Теоретическая оценка влияния дисперсных частиц на зарождение центров кристаллизации и их устойчивость проведена на основании изучения явлений смачивания, адсорбции и растворения с использованием зависимости между критическим размером дозародышей, углом их смачивания и переохлаждением расплава. Показано, что если между частицей и плакирующим слоем разность химических потенциалов контактирующих фаз будет существовать на протяжении всего процесса, а на поверхности комплекса будет иметь низкое значение поверхностного натяжения, то такая частица будет устойчивой, что имеет место при адсорбции из расплава поверхностно-активного компонента. Поэтому эффективность гетерогенизации расплава и модифицирования структуры литого металла определяется термодинамической активностью вещества переходного слоя к материалу частицы твердой фазы. Полученные выводы позволяют осуществлять выбор состава комплексных модификаторов, позволяющих управлять структурой отливок в процессе их кристаллизации.

Ключевые слова: литой металл, суспензия, модифицирование, частицы, кристаллизация, адсорбция, смачивание, межфазная энергия, структура.

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