The basics of choosing the composition of complex modifiers

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Abstract. Based on the analysis of the thermodynamic conditions of stability of the process of heterogeneous nucleation of phases in the melt, it is shown that the growth of the solid phase on the substrate is determined by the properties of the transition layer, which should provide the maximum increment in the chemical potential that changes the dielectric constant and density of the component. On the basis of the analysis, the criteria for the selection of complex modifiers, consisting of exogenous refractory particles - inoculators and activating additives - inoculators and activating additives - protectors. To intensify heterogeneous nucleation in the melt, inoculators should be selected based on the conditions of resistance to dissolution and the highest electrical conductivity, while catalytic activating additives - from the condition of their affinity for particles of inoculators, contributing to the completion of their crystal lattices and the ability to ensure the formation of a transition layer of a stable hardly soluble or weakly dissociating chemical compound having a density close to that of the melt, which reduces the density differences between the particle and the melt at their interface.

Keywords: metal melt, chemical potential, electrical conductivity, the dielectric constant, density.

1. Introduction

High-alloy steels and alloys, widely used for the manufacture of the most critical parts of various machines and plants, tend to have a coarse crystalline structure and have a large structural heterogeneity. The increased requirements for the reliability and durability of cast machine parts necessitate a significant improvement in the structure of cast metal in the direction of reducing its chemical heterogeneity, improving the morphology of excess phases and nonmetallic inclusions, reducing the size of macrograins and achieving uniformity of properties in sections of castings with different wall thickness. The possibility of a significant increase in the properties of these materials by improving the composition of alloying elements has obviously reached the limit, so a further increase in properties can be achieved mainly by improving the structure of the cast metal [1].

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The use of traditional methods of modification and microalloying does not solve this problem as a whole. In recent years, there has been progress in the field of obtaining specified metal structures by modification with inoculators. One such example is the modification of alloys with small additions of poorly soluble particles of refractory compounds that initiate crystallization. Such inoculators can be introduced into the melt in the form, for example, of a powder [2] (exogenous particles), or synthesized in a melt of a metal or ligature due to chemical reactions between its components (endogenous particles) [3].

Exogenous inoculators are the most promising for the modification of many alloys, since the process of making powders now allows widely varying their chemical composition and particle size and makes it possible to obtain ultrafine powders with nanoparticles (from 0.01 to 0.5 microns) [4].

2. Setting work tasks

The effectiveness of nanoparticles as crystallization centers is characterized by the presence of an activated transition layer on their surfaces [5]. The latter should provide good wettability with the
melt, protect against coagulation and oxidation, and also contribute to the nucleation of the crystalline phase at low supercooling. The chemical composition of the transition layer determines the activity of the inoculant particle towards various phases of the alloy during its crystallization. By changing the chemical composition of the particle and the transition layer, it is possible to purposefully initiate the crystallization of various phases of the alloys.

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A deep understanding of the processes occurring in liquid and crystallized melts under the influence of modification is necessary for the development of technological processes for obtaining high quality cast billets.

Currently, there is no single point of view on the choice of the chemical composition of particles required to initiate crystallization of a particular phase of the alloy. At the same time, in order to select the type of particles required to initiate the crystallization of a particular phase, it is necessary to have a set of data that allows one to form theoretical ideas about the principles of such a choice. The available information is extremely contradictory. Therefore, the substantiation of the criteria for choosing the composition of modifier particles is of great scientific and applied importance.

3. **Formulation of criteria for choosing the composition of modifier particles**

Analysis of the thermodynamic conditions for the stability of the process of heterogeneous nucleation and growth of phases made it possible to outline a real way of intensifying the process of heterogeneous nucleation - complex modification [6-8]. With this method of modification, along with refractory additives that form a dispersed suspension of particles with crystallization activity, that is, the ability to serve as crystallization centers - inoculators, it is necessary to introduce into the melt soluble additives that reduce the free surface energy at the phase boundary.

Since soluble impurities are adsorbed on the crystal faces of the parent phase [1], it is necessary that the added additives are chemically related to the crystallizing substance. Then the substances of the additive will enter the crystal lattice of the growing crystal of the basic substance with a slight violation of its structure and will inhibit their growth. Moreover, a decrease in the rate of crystal growth will lead to an increase in the number of crystallization centers and an increase in the dispersity of the cast metal structure. At the same time, it should be noted that the chemical nature of the substrate plays a greater role than the difference in lattices in determining its catalytic activity.

Due to the lack of values of the free surface energy of various substrates in real alloys and the complexity of its experimental determination, it is difficult to use the value of the free surface energy as a criterion for choosing activating additives. To reveal the chemical properties of the transition layer, which ensures the stability of the crystallization process on the substrate, one can use the equation [9]:

$$\sigma \cdot A < \sum \Delta \mu_i \cdot m_i + \Delta T S$$  \hspace{1cm} (1)

Thus, the maximum value of the free surface energy at which the growth of a solid phase on a given substrate is possible is determined by the chemical properties of the transition layer and, in order for the process to be as stable as possible, the transition layer must provide the maximum increment in the chemical potential.
In the transition layer, the density and dielectric constant of a substance change smoothly from values characterizing one phase to values corresponding to another phase. Moreover, during a phase transition, atoms are displaced from one phase to another through the transition layer. The displacement of atoms caused by their transition from liquid to solid phase will lead to a change in density $\rho$ by $\Delta \rho$ and dielectric permittivity $\varepsilon$ by $\Delta \varepsilon$ in accordance with the equation [10]:

$$\Delta \varepsilon = \frac{\partial \varepsilon}{\partial \rho} \Delta \rho.$$  (2)

In turn, $\Delta \mu$ and $\Delta \rho$ are linked by the relationship [10]

$$\Delta \mu = \frac{m \cdot T}{4 \cdot \pi} \sum_{S=0}^{\infty} D_{ll}^{E}(e_{S}^{E}, \tau) \frac{\partial \varepsilon}{\partial \rho},$$  (3)

- where $m$ – is the mass of the atom, $T$ – is the temperature, $D_{ll}^{E}$ – is the Green’s function for a photon in the medium, $e_{S}^{E}$ – is the imaginary frequency of the electromagnetic wave, $\tau$ – is the radius vector that determines the location of the atom, $S = 1, 2, 3 \ldots \infty$, $\varepsilon_{S}^{E}$ – is the change in the dielectric constant, $\partial \rho$ – is the change density. The Green's function characterizes the passage of electromagnetic radiation through a given medium, and, according to [10], its change is a second-order small quantity during crystallization.

Taking into account that $\mu_{\alpha} - \mu_{\beta} = \Delta \mu$, where ($\mu_{\alpha}$ is the chemical potential of the transition layer), with a small assumption, we can write:

$$\Delta \mu = kT \Delta \varepsilon \Delta \rho,$$  (4)

- where $\Delta \varepsilon$ and $\Delta \rho$ – are the increments of the dielectric constant and density of the component when its chemical potential changes from $\mu_{\alpha}$ to $\mu_{\beta}$, i.e., $\Delta \varepsilon = \varepsilon_{\alpha} - \varepsilon_{\beta}$, $\Delta \rho = \rho_{\alpha} - \rho_{\beta}$; $k$ – coefficient of proportionality.

Due to the lack of values of the dielectric constant of refractory compounds, we use the relation [11]

$$\varepsilon = \frac{4\pi}{\omega} \sigma_{s},$$  (5)

- where $\omega$ – is the frequency of the electromagnetic field; $\sigma_{s}$ – electrical conductivity.

Then

$$\Delta \mu = kT \cdot \Pi \frac{\sigma_{s}}{\beta},$$  (6)

- where $\Pi = \frac{\sigma_{s}}{\beta}$ – is the parameter of the nucleus forming ability of the $\alpha$ phase to the $\beta$ phase.

Thus, the displacement of atoms in the transition layer during the phase transition and the resulting changes in the dielectric conductivity of the medium and its density lead to a change in the value of $\Delta \mu$ and a deviation of the melt – solid system from the equilibrium state.

When the melt-solid system leaves equilibrium, $\Delta \mu$ will increase sharply, which, in accordance with the Le Chatelier-Brown principle [11], will lead either to crystallization (or adsorption) of the melt layer adjacent to the solid, or to the melting (or dissolution) of a part solid.

Therefore, the nucleating activity of the substrates (inoculators) will be determined by a value of $\Delta \mu$, i.e., the difference in the chemical potentials of atoms in the melt and on the substrate. In turn, to ensure high values of $\Delta \mu$, it is necessary, first, that the substrate differs as little as possible in density from the metal being modified, i.e., that the density change in the transition layer is small. Secondly, (which is apparently the most important), it is necessary that the electrical conductivity of the substrate be as high as possible so that its change over the thickness of the transition layer $\frac{\Delta \varepsilon}{\Delta \rho}$ is sufficiently large. In practice, it is very difficult to select substrates (inoculators) that fully
meet these requirements, as well as possess the necessary stability in the melt. This also confirms the need to use complex additives for modification - inoculants and activating impurities.

Thus, the selection criteria for modifying complexes can be formulated as follows. The choice of additives should be carried out in such a way that each of them meets one of the requirements imposed by equation (4).

In this case, the inoculators must be selected from the condition of ensuring the highest possible $\frac{\Delta \varepsilon}{\Delta h}$ values (in the first approximation, the inoculators should have the highest possible electrical conductivity), since the radius of perturbation (orienting effect) exerted by the inoculator particle on the melt in this case is large, since the $h$, in which a change in electrical conductivity occurs, is almost four orders of magnitude greater than the thickness of the transition layer $h_p$, in which a change in density occurs [5]. This ratio can be expressed as follows: $h_e \approx c \cdot 10^4 h_p$, where $c$ – is the coupling parameter, which determines $h_e$ when deviating from equilibrium, and under equilibrium conditions $c \approx 1$.

The change in the $\varepsilon$ величины value is determined by the electromagnetic field, and its transition layer must be commensurate with the $\lambda$ wavelength of this field, that is, $h_e \approx \lambda$. Under equilibrium conditions, according to Wien's law ($\lambda = \frac{2.89 \times 10^{-3} \mu}{T}$), the thickness of the transition layer, in which $\varepsilon$ changes, will be $\approx 10^{-6}$ m. Therefore, the influence exerted by the inoculant particle on the melt extends over thousands of atomic layers and more, while under equilibrium conditions the transition layer, in which the density change occurs, occupies a volume of approximately several atomic layers. Activating impurities, however, must be selected from the condition of the formation of a "primary" transition layer on the particles of inoculants with as small a value of $\frac{\Delta \rho}{\Delta h_p}$ as possible. Since the increment in the chemical potential is directly proportional to the adsorption energy of the impurity on the substrate or the work of adhesion of the substrate to the melt containing impurities, the activation of the substrate should be provided by such impurities that, under these conditions, will most strongly adsorb on the substrate and increase the work of its adhesion to the melt. Along with this, it is also necessary that the "primary" layer formed on the substrate consisting of adsorbed impurity and melt atoms crystallizes at a temperature higher than that of the melt, since it is obvious that only in this case can the inoculating properties of the substrate manifest. That is, impurity atoms interacting with the melt and substrate should not form low-melting phases. As a first approximation, the choice of activating impurities can be carried out on the basis of the Fayans-Paneth adsorption rule [12]. According to this rule, an ion is most strongly adsorbed on a charged crystal surface when it is isomorphic to the crystal, i.e., is capable of completing the crystal lattice of the adsorbent, and forms a hardly soluble or weakly dissociating compound with the opposite crystal ion.

4. Conclusion

Criteria for the selection of complex modifiers, consisting of exogenous refractory particles - inoculators and activating additives - protectors, are formulated. To intensify heterogeneous nucleation in the melt, inoculators should be selected based on the conditions of resistance to dissolution and the highest electrical conductivity, and catalytic activating additives should be selected from the condition of their affinity for inoculant particles, which contributes to the completion of their crystal lattices and the ability to provide the formation of a transition layer of a stable hardly soluble or weakly dissociating chemical compound, having a density close to the density of the melt, reducing the density difference between the particle and the melt at the interface.
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