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Theory and Practice of Cast-Iron Inoculation by Ultra - and Nanodispersed Materials

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Theoretical and practical basis of effective production and application of ultra- and nanodispersed materials that enable to reduce metal consumption of metallurgical casting processes and to raise its quality are developed.

Keywords: ULTRA- AND NANODISPERSED MATERIALS, INOCULATED CAST-IRON, CRYSTALLIZATION, ROLLS, STEEL MOLDS, EFFICIENCY

Introduction

Widespread use of traditional inoculation in foundry practice is prevented by instability of achieved effect caused by sensitivity to smelting and pouring conditions as well as processes of coagulation, dissolution and inoculant distribution in the volume of molten iron.

Creation and application of complex ultra- and nanodispersed materials will enable to avoid specified disadvantages which will provide reduction of inoculant charge at raise of its effect efficiency on the processes of crystallization and recrystallization.

The task of present research is to work out scientific grounds of theory and practice of ultra- and nanodispersed materials application when producing heavy castings.

Methodology

White, molten and grey hypoeutectic and eutectic irons of cupola, blast-furnace, open-hearth and electric-furnace melting applied for casting of rolls, steel molds, grinding spheres, dredging pump details are research material. Iron templates were cut out to investigate structure and mechanical properties.

Authors investigated effect of inoculants on structure formation of high-carbon ferroalloys, theoretical estimation of inoculating ability of elements on the basis of their thermodynamic criteria and mechanisms of effect of inoculants on crystallization processes in cast-iron. The process of inoculation is considered in view of interaction of inoculating additives with the melt. All used additives (elements and their compounds) are divided in three groups: soluble, high-melting and decomposable. Soluble additives are known inoculants of graphitizing and spheroidizing action and powders and granules of metals and alloys that have inoculating effect on the melt. High-melting partially soluble inoculants are powders of high-melting compounds with high melting point (TiC, TiN, TiCN, VC, ZrC, TaC, etc.) that have inoculating effect on the melt. Inoculants decomposed in the melt are: SiC, Sa_2S, Si_3N_4, A1N of graphitizing action and Mg_2Si, Mg_3N_2, MgC_2 of spheroidizing action. SiC is the most widespread inoculant from this group.

Hypoeutectic cast irons are subjected to graphitizing inoculation; inoculation efficiency decreases in eutectic and hypereutectic cast irons. Effect of inoculants is various at the different stages of crystallization: at nucleation and growth of dendrites (grains) of primary austenite, at eutectic crystallization and formation of metal matrix in solid condition. Forecasting of inoculating efficiency of chosen elements or compounds by means of comparative estimation enables to control necessary properties of the casting.

There are various approaches to estimation of inoculating activity of soluble additives: by value of graphitization factor, from position of donor-acceptor chemical interaction of elements, etc. The current estimation of inoculating activity of element in the melt by any parameter does not allow complete estimation of inoculant efficiency at all stages of iron crystallization.

The complex criteria estimation of efficiency of known inoculants during cast-iron treatment taking into account their activity at three stages of iron crystallization is developed [1]. Quantitative assessment of inoculating activity effect of element (factor K_a) on dispersity of primary austenite was carried out according to difference relation of ionic melt potentials (U_{ef}^{Me}) and inoculant (U_{ef}^{inoc}) to solubility of inoculant in the melt *(C_{inoc}):*

$$K_a = (U_{ef}^{Me} - U_{ef}^{inoc}) / C_{inoc} \qquad \text{(Eq. 1)}$$

Graphitization extent was estimated by factor K_g. Dispersity and purity of boundary lines of grains (colonies) of metal matrix were estimated by value of surface activity of element at intracrystalline competitive adsorption on grain boundaries (factor K_3).

Bar diagrams of inoculating activity of elements at iron crystallization are shown in **Figure 1**. The strongest inoculants by all three parameters are Sr, Ba, Ca. Widely applied Si, Al, C have good graphitizing properties however promote coarsening of primary austenite and have a weak influence on dispersity and purity of grain boundaries at eutectoid transformation.

The criteria estimation of efficiency of high-melting compounds at inoculation has the features. High-melting particles added to hot metal will be crisallization centers if primary phase crystals nucleate on their surface depending on sizes and properties of particles and their interaction with the melt. The basic criteria of estimation of inoculating efficiency of high-melting compounds are: melting temperature, change of enthalpy of formation, conductivity type and solubility in the melt. The higher thermodynamic stability of compound, the more difference of melting temperatures of compound and melt, the less solubility and electron affinity of inoculant and melt, the more its efficiency. The comparative analysis of thermodynamic parameters of high-melting partially soluble compounds enabled to range them in the following inoculating efficiency:

$$TiCN \rightarrow ZrN \rightarrow TiN \rightarrow BN \rightarrow TaN \rightarrow TiC \rightarrow$$
$$\rightarrow ZrC \rightarrow TaC \rightarrow NbC \rightarrow VC \rightarrow WC \rightarrow W_2C.$$

Compound of titanium with carbon and nitrogen - titanium carbonitride (TiCN) - completely satisfies the requirements to high-melting inoculants.

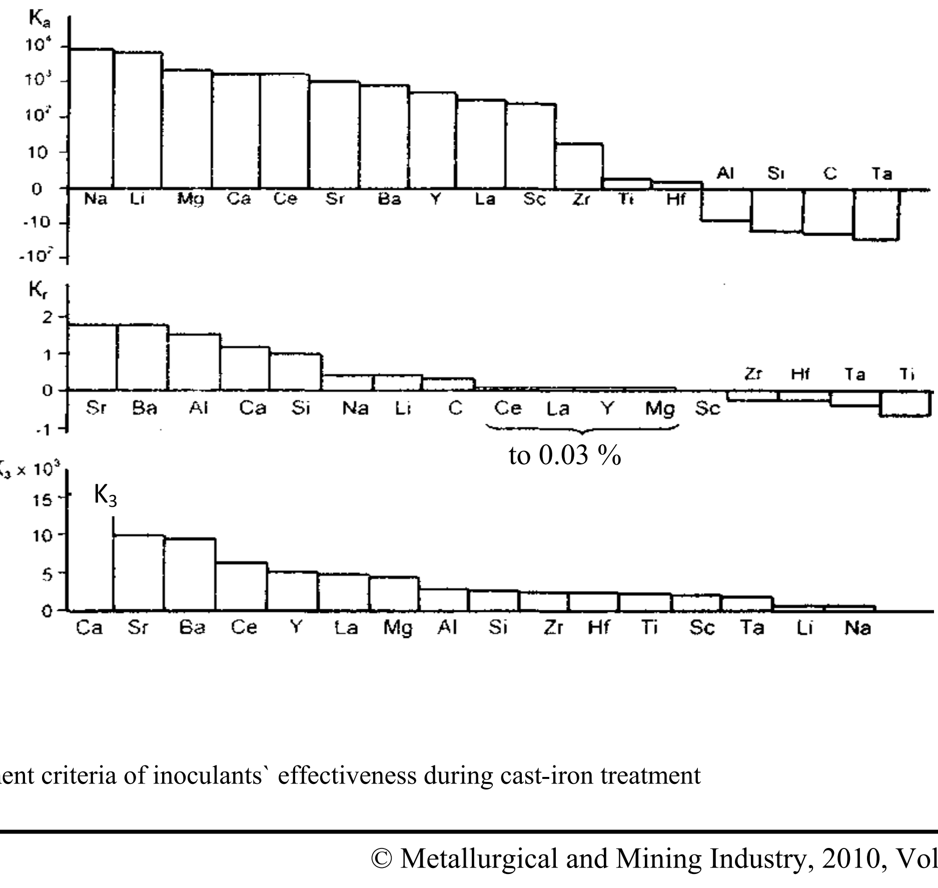

Figure 1. Assessment criteria of inoculants` effectiveness during cast-iron treatment

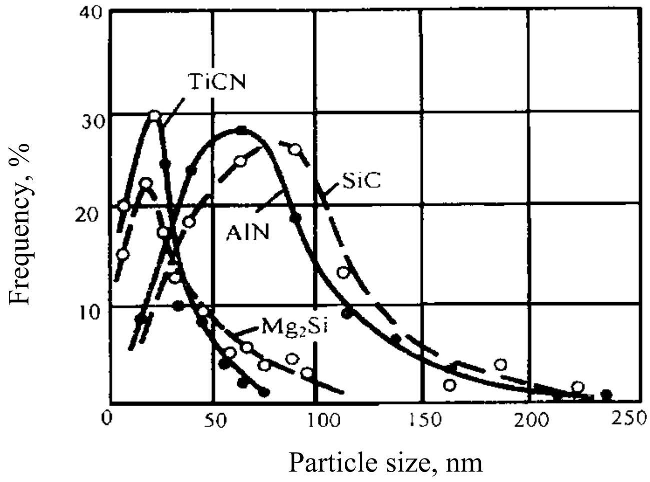

Figure 2. Generelized bar chart of fractional makeup distribution of ultra- and nanodispersed materials (TiCN, AlN, SiC, Mg_2Si)

Analysis of thermodynamic processes in heterogeneous melts inoculated by high-melting compounds allowed the following conclusions:

- gravitational forces weakly control kinetics of system "metal-particle" with reduction of particle size less than 1000 nanometers (ultradispersed condition), the particles have Brownian motion and factor of their diffusive mobility increases;
- coagulation of particles at melt agitation depends on specific surface energy on the boundary "metal-particle";
- particles with size less than 100 nanometers are commensurable with sizes of crisallization centres;
- with reduction of particle size less than 250-300 nanometers (ultra- and nanodispersed condition) their thermodynamic stability grows due to chemical and physical interaction between particle and absorption metal microcover formed on its surface protecting the particle against the contact with the melt;
- it is necessary to isolate particles by means of their sheathing in order to prevent aggregation of particles in the melt and improve wettability;
- application of nanopowders as high-melting inoculants is the most perspective for hot metal treatment in view of kinetic behavior features of particles in the melt;

Automated high-frequency plasma-chemical plant is created in cooperation with JSC "Neomat" (Latvia) and production of ultra- and nanodispersed inoculants of developed compositions is mastered to produce ultra- and nanodispersed powder [2, 3]. The distinctive feature of plasma-chemical synthesis process is application of powdered waste of ferroalloy, titanium-magnesium and silicon-polymeric production as initial raw materials.

The target product is formed at addition of initial materials into plasma-chemical reactor with temperature 5500-7000 °C. The size of particles of obtained high-dispersed powders can vary from 10 to 250 nanometers depending on requirements of specifications. The pattern of particle size distribution is asymmetrical (**Figure 3**). These compounds are referred to ultra- and nanodisperesd powders.

The role of oxidizing processes in adsorption activity of particles is considered. Particle sheathing method by means of coating of microlayer of solid hydrocarbons on the surface is developed for protection against oxidation [4]. The particles of plated inoculant keep a clean active surface within 7-9 months.

Effect of thermo-physical and dimensional-crystallographic parameters of nanocompound particles on their behavior in Fe-C-melts is studied. Dispersity of inoculant particles defines properties of ultradisperse system inoculant-melt and is quantitatively characterized by linear dimensions and specific surface of particles. Hyperbolic dependence of specific surface and specific surface energy on particle size (**Figure 3**) is indicative of considerable role for ultra- and nanodispersed systems of adsorption and superficial phenomena while behavior of macrodisperse systems is defined by volume properties.

Sharp increase of surface energy at transition of particles in ultradisperse state leads to abnormal physical phenomena, displacement of phase transformation temperatures and enhancement of oxidizing processes on the surface of particles.

It is shown by analytical method that intensive drop of specific surface energy starts at particle size less than 10-15 nanometers. Therefore in the area of ultra - nanodispersed range the specific surface energy is maximum, particles have high adsorbability, and nucleation of primary phase crystals on their surface is more probable. If the particle does not have properties of high-melting inoculant, there is no solid phase shell. Compound "particle-solid phase-melt" will be resistant only in case if free energy of system drops (**Figure 4**). Nucleation of primary phase on nanoparticles is simplified and goes with reduction of total free energy due to change of relationship of volume and surface constituents of free energy while nucleus formation in not inoculated melt requires energy consumption, and only after

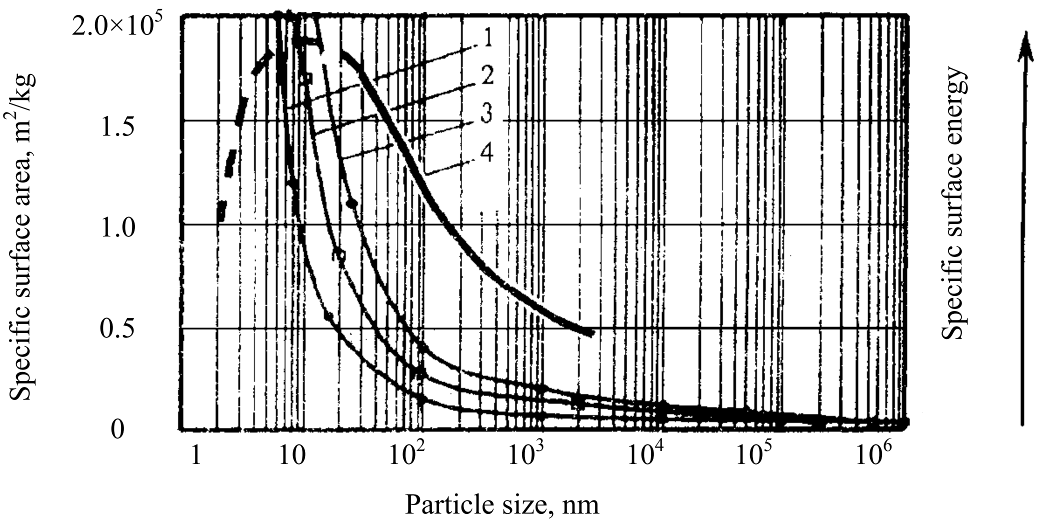

Figure 3. Effect of particle size on specific surface area (*1* - TiCN; *2* - SiC; *3* - Mg_2Si) and average surface energy (*4*)

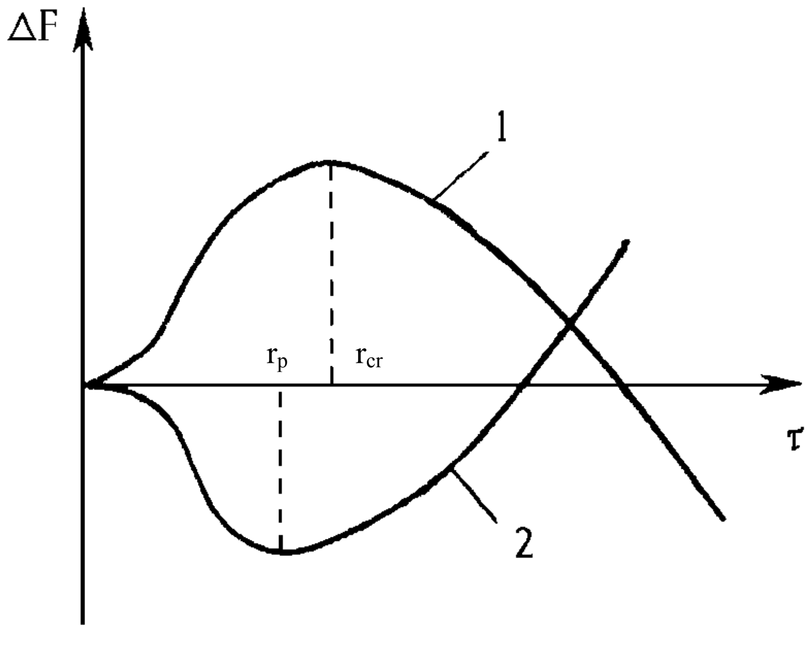

Figure 4. Change of ΔF depending on nucleus radius (*1*) and formation of solid phase on the surface of ultradispersed and nanoparticles (*2*)

achievement of critical size (**Figure 4**, curve 1) solid phase growth becomes energetically favorable. Large specific surface of particles makes the process of solid phase nucleation thermodynamically favorable: it goes with energy generation (hidden heat of crystallization). Graph of function ΔF under these conditions can be presented as curve 2 in **Figure 4**. The solid phase formed in the melt on the surface of particle is in energetically favorable condition, and there are no conditions for decomposition of such compounds.

We used cast-iron of the following chemical composition, %: 3.2 C; 1.5 Si; 0.8 Mn; 0.05 S; 0.15 P; 0.10 Cr for calculation of quantitative parameters of crystallization. Results of calculations (**Table 1**) showed that size of critical nucleus of austenite (r_{cr}^{A}) at supercooling of hot metal by 10-40 °C was 12-45 nanometers, and graphite (r_{cr}^{C}) - 55-305 nanometers.

The role of ultra- and nanodispersed additives is related to creation of additional artificial crisallization centers in the melt under condition of their proportionality with critical nucleus and maintenance of their sufficient quantity in order to receive finely dispersed structure in the cast. Experiments confirm that for refining of primary austenite in the industrial casts (inoculation), the particle size should be 10-50 nanometers and 50-200 nanometers for elimination of chill and refining of graphitic phase (graphitizing inoculation).

The other factor is achievement of crystallographic conformity of particles with crystallized inoculated phase. Electron microscope investigation and analysis of microdiffraction patterns have shown that ultra- and nanodispersed particles belonged to solid crystalline substances without amorphous phases. SiC particles are formed as hexahedral or trigonal prisms and refer to hexagonal crystallographic system with parameters: a = 0.308 nanometers, c = 1.004 nanometers. TiCN particles have a cubic lattice with parameters a = 0.425 nanometers and formed in the form of cube or tetragon. Mg_2Si particles are in the form of spheroids and have a lattice with parameter a = 0.634 nanometers.

Depending on crystal lattice type and shape of inoculant particles it is necessary to apply the following types of ladle inoculation:

1. SiC, A1N (hexagonal system and shape) - graphitizing inoculation for reduction of chill and refining of graphitic phase with hexagonal lattice;
2. TiC, TiN, TiCN (isometric system and shape) - inoculation for refining of structure and hardness increase. Austenite is crystallizing phase with cubic lattice;
3. Mg_2Si, Mg_3N_2 (spheroidal isometric system and shape) - spheroidizing inoculation to get spheroidal graphite in the structure.

Experimental-industrial check and implementation of technology of molten iron inoculation by complex nanomaterials in pressed or powdered condition (SiC, TiCN) were carried out at casting of roll, steel molds and dredging pump elements [4-6]. The charge of nanoinoculants is 0.05-0.25 kg per ton of hot metal, expenses for treatment do not exceed 10-12 % from the melt cost.

Computation and experimental data showed that nanoinoculants had high enough kinematic stability being evenly distributed in the melt. At consumption of TiCN 0.20-0.25 mass. %, deviation in titanium content in 10-ton teeming ladle does not exceed 0.02 %. Distribution of inoculated melt during soaking in the ladle is defined by result of action of two opposite directed processes: subsidence and diffusion of particles under effect of Brownian motion. The presence of microshell round a particle reduces concretion and raises aggregate stability of the system.

Operational tests of rolls with developed compositions (ЛПХНДМФд-74, ЛПХНМВд-74, ЛПХНДМд-73, ЛПХНДГд-71) at OJSC “Ilyich Iron and Steel Works of Mariupol” (mill 1700), Magnitogorsk Iron and Steel Works (mill 1450), Karaganda Iron and Steel Works (mill 1700) and Cherepovets Iron and Steel Works (mill 2000) showed that their durability was higher by 14.7-38.7 % than that of mass-produced rolls (ЛПХНд-71).

Operational tests of experimental and industrial batches of inoculated cast iron

Table 1. Dependence of critical sizes of austenite and graphite nucleus on extent of melt supercooling

ΔT, °C	5	10	15	20	30	40	50	60	70	80	90	100
r^{A}_{cr}, nm	83	40	28	22	15	10	7.3	5.8	4.5	4.1	3.5	3.2
r_{cr}, nm	595	305	205	165	85	55	48	42	33	30	26	23

molds in open-hearth plant of OJSC "Nizhnedneprovsk Pipe Rolling Plant" and converter plant of JSC "Dneprovsky Integrated Iron & Steel Works named after F. Dzerzhinsky" showed that their durability exceeded durability of usual molds in 1.22-1.45 times.

Dependence of operational durability of inoculated cast iron molds on relationship of components of ultra- and nanodispersed materials obtained with application of software program showed (**Figure 5**) that the maximum durability of molds was achieved at cast-iron treatment (50-60 % SiC and 40-50 % TiCN). Inoculation by ultra-dispersed materials reduces effect of cast iron eutectic extent on durability of molds (**Figure 6**). Technological processes of iron melt inoculation by ultra- and nanodispersed materials are introduced at the plants of Ukraine and Russia which enabled to raise technical-and-economic indices of casting for metallurgical equipment.

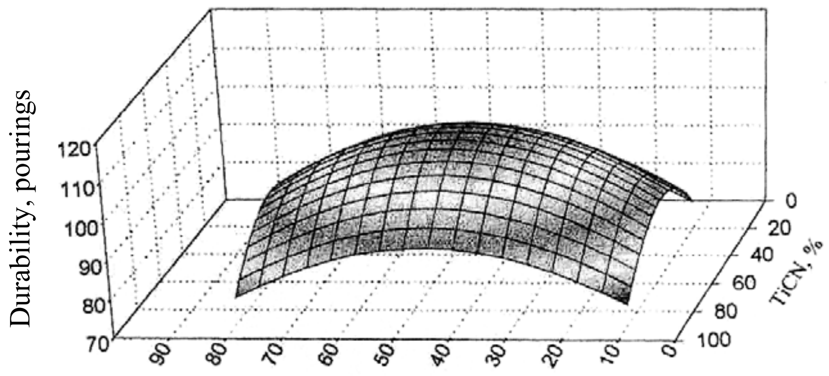

Figure 5. Effect of ratio SiC and TiCN on durability of inoculated cast iron molds

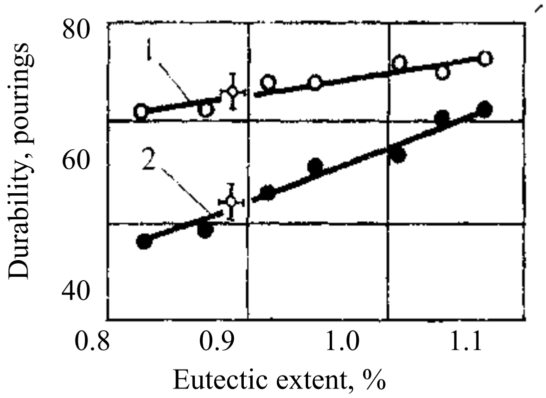

Figure 6. Effect of cast-iron eutectic extent on durability of inoculated cast-iron (*1*) and customary cast-iron molds (*2*)

Conclusions

1. High-effective ultra- and nanodisperesd inoculants and technological processes of metallurgical and machine-building equipment casting with increased operating characteristics at operation in the conditions of high deterioration, thermocyclic and mechanical loadings are developed.

2. The criteria estimation of efficiency of known soluble inoculants in the melt (Sr, Al, Si, etc.) is worked out taking into account their activity at all stages of crystallization of cast-iron: at nucleation and growth of primary austenite, at eutectic solidification, at matrix formation in solid state. It is shown that inoculating activity of high-melting compounds (TiCN, ZrN, BN, etc.) depends on melting temperature, enthalpy of formation, solubility and electron affinity of inoculants and melt.

3. The method of particles protection against oxidation by means of coating is developed which provided particles with size of 10-250 nanometers high adsorption activity to creation of artificial crystallization centers in the melt. Oxygen content in the plated powder is 8.0-8.5 times lower than

in not plated.

4. It is shown that inoculant particle sizes should be commensurable with sizes of crystallization centers: for refining of primary austenite dendrites in the industrial casts (inoculation) the size of TiCN particles should be 10-50 nanometers, and for elimination of chill and refining of graphitic phase (graphitizing inoculation SiC) 50-200 nanometers.

5. Operational tests of rolls ЛПХНДМФд-74, ЛПХНМВд-74, ЛПХНДМд-73, ЛПХНДГд-71 on sheet rolling mills 1450, 1700 and 2000 at integrated iron & steel works of Ukraine and Russia showed that their durability was higher by 14.7-38.7 % than durability of mass-produced rolls. Operational tests of inoculated cast iron molds showed raise of their durability in 1.22-1.45 times, the maximum durability of molds was achieved at treatment of cast-iron 50-60 % SiC and 40-50 % TiCN.

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Теория и практика модифицирования чугуна ультра- и нанодисперсными материалами

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Разработаны теоретические и практические основы эффективной технологии производства и применения ультра- и нанодисперсных материалов, позволяющих снизить металлоёмкость технологических процессов производства металлургического литья и повысить его качество.