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Application of Nanopowders in Casting Production

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Abstract

The review presents the results of experimental and pilot industrial studies on the use of nanosized powders of refractory compounds in metallurgical and foundry industries. The main attention is paid to the presentation of the results of studying the effect of nanodispersions on the formation of the structure and mechanical properties in cast products from alloys based on iron, aluminum, and nickel. Using metallographic studies, it was found that small additions of nanomodifying powder compositions in an amount not exceeding 0.1% by weight significantly refine the structural components of the cast metal and increase its mechanical and operational characteristics. Thus, the nanomodification of heat resistant nickel based alloys makes it possible to increase the long term strength, plasticity, and thermoscyclic characteristics of prototypes (by a factor of 1.5–3). During nanomodification of aluminum alloys, a refinement of crystalline grains, including segregations of primary Si, and a decrease in porosity (up to 60%) are observed. Nanomodification has a significant effect on the structure and properties of the metal in the continuously cast steel ingot. The central porosity decreases (by 25%–36.7%), as well as the general chemical heterogeneity (by 39.8–75%), liquation, and general fracturing (by 34%–100%). The zone of equiaxed crystals and the mechanical properties of the cast metal increase.

Keywords: Nanopowders • Casting production • Aluminum alloys

Introduction

In the last 20 years, due to the increased requirements for the physical and mechanical properties of products made of steel and alloys used in modern operating conditions, growing attention has been paid to a new class of materials: nanosized powders of chemical compounds, which are crystalline or amorphous particles with a characteristic size not exceeding 100 nm. The interest in these materials is explained by the fact that they have unique physicochemical and mechanical properties that differ significantly from the properties of materials of the same chemical composition in a bulk state [1-6]. These properties can, to a certain extent, be transferred to materials obtained from them or with their participation, modifying their structure, physicochemical and mechanical properties [7-9].

One of the most important areas of application of nanosized materials is their use as modifying additives in the foundry production of articles made of ferrous and non-ferrous metals (ingots, castings, etc.). The purpose of this modification is to radically improve the mechanical and operational properties of products for various purposes. To achieve this goal, specially prepared nanopowders of refractory compounds are used. They have unique properties due to their small size, highly distorted crystal lattice which affects the activation energy of particle melt interaction processes, and high specific surface area. Introduced into the melt, they heterogenize it throughout the entire volume and become active centers for the nucleation of a new phase. Due to this, it becomes possible to control the processes of structure and phase formation in the solidifying melt: to cause refinement of the matrix grains and excess phases as a result of an artificial increase in the number of crystallization centers and changes in the structurally sensitive properties of the liquid metal, to significantly change the morphology of the crystal grain, carbide and intermetallic phases. Consequently, it is possible to directly influence the formation of mechanical and physicochemical properties of the cast metal.

Work in this direction has been carried out since the end of the 80's of the last centuries. Since then, a large number of articles and monographs have been published devoted to the problem of strengthening metals and alloys using nanopowder modifiers [9-19]. In the past 15 years, the number of publications on the results of experimental and pilot industrial work in the field of application of nanotechnology in mechanical engineering has been steadily growing [20-48]. Scientific and technological principles of the use of nanopowders in welding, surfacing of hardening coatings and electrochemical coatings are being actively developed [49-60].

This review mainly presents the results of experimental and pilot industrial work on the use of nanosized refractory powders in continuous casting of steel in a continuous casting machine, in the production of castings from manganese steel, gray cast iron, high temperature alloys, and alloys based on aluminum. With the help of metallographic and mechanical studies using electron microscopy, XRF, TEM, and tensile testing machines, it was found that small (≤ 0.05% by weight) additives of specially prepared refractory compounds (TiN, TiCN, AlN, etc.) introduced into an overheated melt, essentially influence the structure and physico mechanical properties of the cast metal.

The research results presented in this review were carried out mainly at the Khristianovich Institute of Theoretical and Applied Mechanics SB RAS and the Institute of Metal Science, Equipment, and Technologies with the Center for Hydro and Aerodynamics "Acad. A. Balevski" BAS within the framework of scientific and technical cooperation.

Preparation of Nanopowders for Modifying Metals and Alloys

The original ceramic nanoparticles are poorly wetted by the melts, as a

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result of which they are poorly absorbed by them and cannot be effective centers of crystallization. Therefore, their surface must be clad with metals. Cladding of nanoparticles can be carried out in various ways: mechanically in centrifugal planetary mills, by extrusion through a die in a metal shell in the form of a rod, by ultrasonic treatment in molten salts, using SHS methods (self-propagating high temperature synthesis), by plasma chemical treatment, by rolling in the form of flux-cored tape [14,43,61-66]. In all these methods, a cladding metal powder or a mixture of powders (nickel, iron, chromium, etc.) is added to the ceramic powder. The SEM image in Figure 1 shows a nanocomposition based on SiC nanoparticles clad with micro Al and Cu particles. A planetary mill was used [34].

Figure 1. A mixture of SiC nanoparticles and Al and Cu microparticles in 4:1:12 ratio after mechanochemical treatment in a planetary mill

Modification of Aluminum Alloys

The effect of nanopowder modifiers on the properties of aluminum based alloys has been investigated in a large number of works [12-14, 25-38]. The high efficiency of the use of refractory compound nanopowders to improve the mechanical and operational properties of aluminum alloys is shown. Below are the results of a study of the nanomodicators (NM) influence on the structure and properties of pilot industrial castings of the "Boat" type made of AlSi7Mg alloy (Figure 2a) and the "Piston" made of AlSi12Cu2MgNi alloy (Figure 2b), the composition of which is given in Table 1 [32,33].

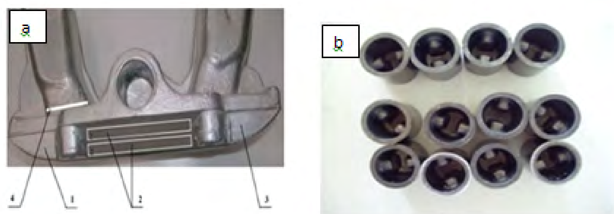

Figure 2. Photos of the "Boat" (a) and "Piston" (b) castings

Table 1. Chemical composition of alloys, wt. % (the rest is Al)

Alloy	Si	Mg	Ti	Fe	Cu	Mn	Zn	Pb	Sn	Ni
AlSi7Mg	7.50	0.39	0.02	0.39	0.05	0.03	0.10	0.08	0.05	-
AlSi12Cu2MgNi	12.20	0.80	-	0.57	1.84	0.40	0.24	-	-	0.82

The "Boat" casting weighing 0.470 kg was made by chill casting at the metal pouring temperature of 720–730°C and the mold temperature of 150–160°C. It is designed for installation in electrically transportable networks. Two castings were obtained without NM and four with two types of NM: AlN with concentration of 0.05% by weight, clad in a centrifugal planetary mill with a mixture of Al+Cu (0.05:1.0); and SiC with concentration of 0.1% and electrochemical cladding of Cu (0.1:1.0). The average nanoparticle size was 50 ± 5 nm. Heat treatment was carried out according to the T6 regime: heating for quenching at 535 ± 3°C for 6 h; quenching in water (25°C -40°C); aging at 160 ± 3°C for 6 hours. Hardness, density, and porosity were determined in the casting zones with different sections and cooling rates (Figure 2): 1 – 6.6 cm^2 from the side of the head (4); 2 – 12.1 cm^2 ; 3 – 6.6 cm^2 from the feeder side.

Metallographic analysis was performed with Reichert MeF2 and PolyvarMet microscopes and with an Olympus MicroImage automated system. The distance between the axes of the dendrites (DAS) and the size of Si particles in the eutectic were determined. Tensile strength σ_B, yield strength $\sigma_{0.2}$, elongation and hardness HB (10/1000/30) were determined according to EN 10002-1. For a comprehensive assessment of strength and ductility, the quality index Q was calculated according to the dependence:

$$Q=\sigma_B+150\log\delta,\ \text{MPa}$$

The density ρ was determined by the gravimetric method. The theoretical density ρ_0 was calculated additively, and the porosity P, % was determined by formula

$$P = \frac{\rho_0 - \rho_m}{\rho_0} 100\%$$

The results of the study of the "Boat" casting made of AlSi7Mg alloy are presented in Tables 2 and 3 and in Figure 3.

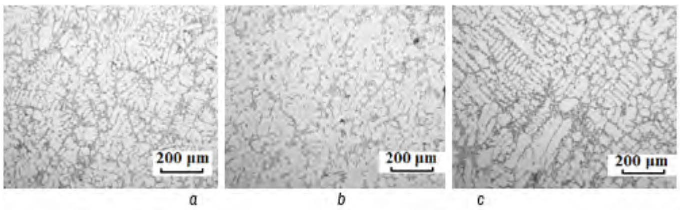

Figure 3. The microstructure of the "Boat" castings made of AlSi7Mg alloy without and with NM: (a) without a modifier, b) with 0.05 % AlN+Al+Cu, c) with 0.1 % SiC+Cu

Table 2. Hardness HB, density, and porosity of the "Boat" castings (ρ_0=2.7050 g/sm^3)

Modifier type and concentration	Zone N	HBmean		ρmean, g/sm	P, %	Δ P, %
		Zone N	Mean value,			
	1	104	101	2.6768	1.04	-
without modifier	2	98		2.6783	0.99	-
	3	102		2.6763	1.06	-
	1	105	105	2.6967	0.31	-70.2
0.05% AlN+Al+Cu	2	105.5		2.6956	0.35	-64.6
	3	105		2.6940	0.41	-61.3

	1	101		2.6951	0.37	-64.4
0.1% SiC+Cu	2	104.5	101	2.6950	0.37	-62.6
	3	97.2		2.6926	0.46	-56.6

Table 3. Microstructural and physical-mechanical characteristics of the "Boat" castings

Modifier type and concentration	DAS, μm	The size Si - particle, μm	$\sigma_{0,2}$, MPa	σ_{B}, MPa	δ,%	Q, MPa	ρ, g/cm3 (zone 2)	P, % (zone 2)
without a modifier	23.90	3.52	240	296	4.0	386	2.678	0.99
0.05 % AlN+Al+Cu	17.69	2.94	253	318	4.3	413	2.696	0.35
Changes, %	-26.0	-16.5	5.4	7.4	7.5	7.0	0.70	-64.6
0.1 % SiC+Cu	17.66	2.59	238	317	6.4	438	2.695	0.37
Changes, %	-26.0	-26.4	-0.8	7.1	60.0	13.5	0.62	-62.6

The fact is confirmed that the higher the crystallization rate and the finer the grain, the lower the microporosity [35]. In zone 3, where cooling conditions are unfavorable, P is higher than in the other zones. The refinement of the structure and a decrease in porosity leads to an increase in σ_B by more than 7%, and δ by 7.5%-60% (Table 3). The value of $\sigma_{0.2}$ changes to a lesser extent and with a modifying addition of 0.1% SiC+Cu decreases slightly, which is also noted by the authors [36]. For AlSi7Mg alloy, it was found that the fatigue strength σ equal to 70 MPa-80 MPa on the basis of 107 cycles, which is usually required for dynamically loaded parts, is achieved at Q=300 MPa-400 MPa. With the addition of NM, the value of Q increases by 7%-14% and exceeds 400 MPa. This indicates an increase in the reliability of castings and is associated with the effect of NM on the formation of a more dispersed and denser structure, which is illustrated in Table 3 and Figure 3.

SEM showed how the casting grains were refined as a result of modification with 0.1% SiC+Cu. The results of the microstructure analysis using EBSD are shown in Figure 4 [37]. A significant refinement of the grains after modification is visible. The resulting database was used to determine the grain size for the samples (equivalent grain diameters). The results are shown in Figure 5.

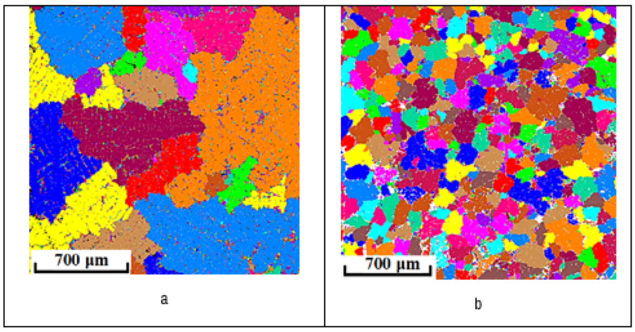

Figure 4. Unique EBSD maps of the grain color for unmodified (a) and modified (b) (with 0.1 wt.% SiC+Cu) samples of A356 alloy

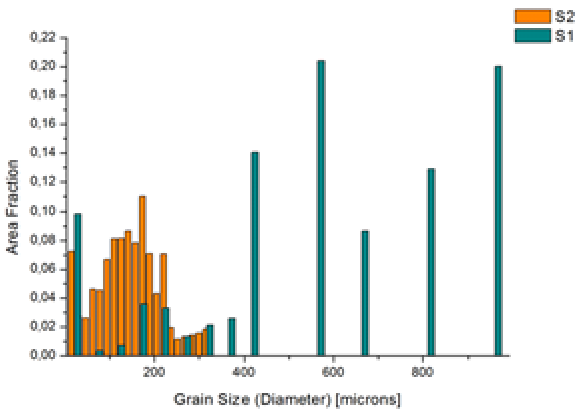

Figure 5. Sizes (diameters) of unmodified S1 and modified S2 grains and the area fraction

The grain diameter varies from 28.53 μm to 967.47 μm for S1 (unmodified sample) and from 14.58 μm to 316.15 μm for S2 after modification. The more favorable effect of the 0.1% SiC+Cu additive can be explained by a greater refinement of Si particles and an increase in AlN+Al+Cu compared to the 0.05% additive. Transmission electron microscopy analysis was performed on thin foils obtained by electrolytic double jet thinning of a 0.1% Sic+Cu sample modified by NM [37]. Figure 6 shows the image obtained by scanning transmission (STEM).

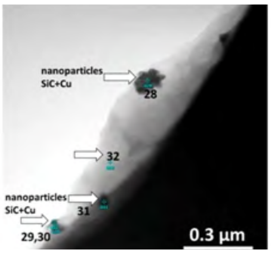

Figure 6. STEM image of modified A356 alloy with an indication of the points at which the EDX analysis was performed

Figure 6 shows that in the inner part of the grain there are nanoparticles coagulated into separate clusters. This indicates that modifying nanoparticles act as crystallization centers even in the case of their coagulation. The results of EDX point analyses are shown in Table 4.

Here, for comparison, the content of the main alloy for the same chemical elements is added (in at.%). The numbers in the first column on the left correspond to the point in Figure 6. Note that the results for the C and O contents are semi-quantitative, i.e., they only show that these elements are present, but they cannot be considered as a measure of their content.

Investigation of the "Piston" casting made of AlSi12Cu2MgNi alloy showed that NM additions lead to the refinement of the structure (Figure 7) with a decrease in the DAS to 25%, at that, a mixture of 0.1% SiC and 0.03% AlN demonstrates a stronger effect (Table 5). A refinement of primary Si segregations in the structure is observed.

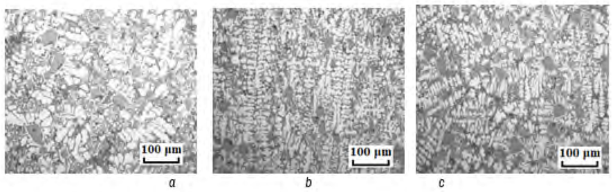

Figure 7. The microstructure of the "Piston" castings made of AlSi12Cu2MgNi alloy; without NM (a) and with NM: 0.1% ND+Ag (b), 0.1% SiC+Cu+0.03% AlN+Al (c)

Table 4. Results of EDX point analysis for the modified sample and the base alloy, in at.%. (STEM)

Point number	C	O	Mg	Al	Si	Fe	Cu	Total (at.%)
28	1.33	6.87	0.18	11.04	1.31	0.37	78.9	100
29	2.0	3.71	0.0	12.87	1.45	0.48	79.49	100
30	2.37	11.89	0.23	12.85	1.68	0.49	70.49	100
31	1.41	12.25	0.42	56.91	1.73	0.28	26.98	100
32	0.0	7.6	0.15	88.85	1.6	0.24	1.56	100
Base alloy			0.3336	92.187	7.2417	0.1899	0.0214	99.97

Table 5. Microstructural and physico-mechanical characteristics of the "Piston" casting made of AlSi12Cu2MgNi alloy without and after heat treatment

Modifier type and concentration	DAS, μm	ρ_{Mean}, g/cm^3	$\sigma_{0.2}^*$, MPa	σ_B*, MPa	δ*, [%]	HB*
Without modifier	10.56	2.7685	243/367	266/388	0.4/0.5	114/154
0.1% ND+Ag	8.67	2.7686	233/369	273/393	0.7/0.6	118/154
Changes, %	-17.9	-	-4.1/0.5	2.6/1.3	75/20	3.5/0
0.1% SiC+Cu	9.64	2.7694	238/373	283/402	0.7/0.7	117/154
Changes, %	-8.7	-	-2.1/1.6	6.4/3.6	75/40	2.6/0
0.1% SiC+Cu + 0.03% AlN+Al (UZD)	7.92	2.7698	245/371	281/406	0.7/0.8	115/152
Changes, %	-25.0	-	0.8/1.1	5.6/4.1	75/60	0.9/-1.3

* the values in the numerator are for the cast state, in the denominator - after heat treatment.

A similar effect of Al2O3 NM additives on primary Si crystals is also reported in [38].

In conclusion, we can say that the established influence of modifying nanoscale additives on the formation of the structure and properties of the shaped castings under consideration indicates the possibilities of their use to improve the quality, reliability, and durability of complex loaded parts made of heat treated pre-eutectic and eutectic piston silumins.

Nanomodification of Continuously Cast Steel Ingot

Modification of a continuous ingot of carbon steel was carried out with TiN, Y_2O_3 nanopowders or their mixtures 15–40 nm in size, clad with metal (chromium) in an AGO-3 planetary mill. The powder composition NM in the amount of 0.03–0.05% by weight calculated for the refractory component, previously rolled into a steel strip, was introduced into a tundish using a tribe apparatus [65,66]. The analysis of the structure of the prototypes carried out using electron microscopy showed a significant change in the morphology and dispersion of crystal grains. Instead of a coarse dendritic structure (Figure 8a), a globular dispersed crystal structure was formed (Figures 8b and 8c).

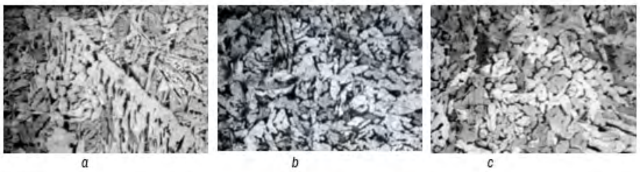

Figure 8. Crystal structure in the axial region of the ingot cross-section with magnification ×100: (a) without NM, (b) 0.035 %TiN + Cr, (c) 0.035% (TiN $+Y_2O_3$) + Cr

The physical and mechanical characteristics of the metal have changed significantly. The central porosity decreased by 25–36.7%, the general chemical heterogeneity – by 39.8–75%, liquation and general fracturing – by 34–100%, the zone of equiaxed crystals increased by 26.5–35%, the mechanical characteristics of the metal (ultimate strength and yield strength, relative elongation and contraction) increased by 5.5–19%.

Nanomodification of Castings Made of Manganese and Carbon Steel

For the study, castings in the form of a rod and a sleeve were obtained, which were cast into sand molds at atmospheric pressure with and without the use of NM [46,47]. Chemical composition of steel: 1.1%–1.3% C, 11.5–13.5% Mn, up to 0.5% Si, and up to 0.06% P, % by weight. To modify the rods, a TiN+Cr composition was used with an average size of TiN nanoparticles equal to 30 nm in the ratio TiN:Cr=1:2. The sleeve was modified with a powder composition of $TiCN+Y_2O_3$ +Cr+Fe in the ratios of $TiCN:Y_2O_3$: Cr:Fe=2:1:1:6. The macrostructure of the rod without NM and with NM is shown in Figure 9.

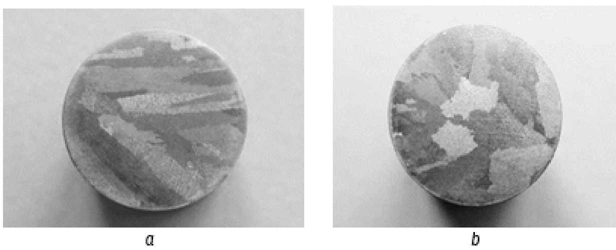

Figure 9. Macrostructure of GX120Mn13 steel samples: (a) without NM; (b) with NM 0.025wt%TiN. The diameter of the samples is 20 mm

Changes in the morphology and refinement of crystallites in the sample with a nanomodifier are clearly visible. Instead of columnar, they have acquired a globular shape. Figure 10 shows the results of testing samples for wear resistance (average values over three tests).

It can be seen that the nanomodified samples have a lower mass loss Δm compared to samples without NM at the same number of cycles N (Figure 10a). Figure 10b shows the dependence of wear ΔM on time, the values of which are also lower for samples obtained with a nanomodifying additive. Figure 11 illustrates the microstructure of unmodified and modified samples of the "sleeve" type casting.

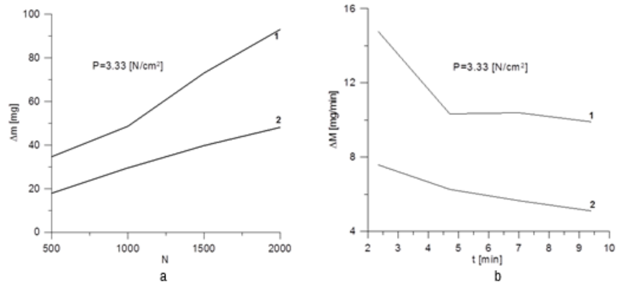

Figure 10. Dependences of mass loss rates Δm on the number of cycles N (a) and wear dynamics ΔM on time t (b) for samples made of manganese steel. 1 – without nanomodifier, 2 – with a nanomodifying additive TiN 0.025%

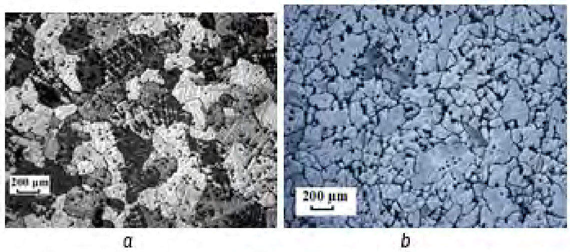

Figure 11. The microstructure of GX120Mn13 steel casting with magnification×32: (a) without NM; (b) with NM ($TiCN + Y_2O_3$ + Cr + Fe)

The average equivalent diameter for all grains in the sample with NM is 104 μm, and for the unmodified one – 128 μm. Consequently, the grain refinement is 18.7%. The study of the mechanical properties of castings with and without NM showed an increase in yield strength by 16.3%, tensile strength by 18%, elongation by 36%, and hardness (HB) by 8%. As a result of the modification, the wear resistance of the modified samples increased by 60%.

Studies of P265GH steel unmodified and modified with TiCN nanoparticles were carried out [24]. The nanoparticles were clad with Fe in a planetary mill. The results of the modification are shown in Figures 12 and 13. It can be seen that the microstructure of the modified sample is refined. The grain size distribuions of unmodified and modified steel were determined according to the EBSD data. The modification leads to a decrease in the average diameter of the ferite grain from 112 μm to 50 μm and to a more homogeneous grain size distribution (Figure 13).

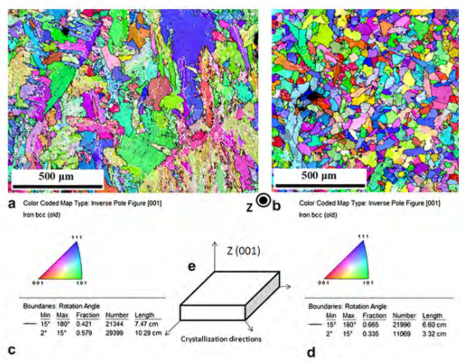

Figure 12. Color coded maps with inverse pole figure (IPF) in Z direction displaying the crystal orientation with respect to the vertical axis of the samples; (a) without modification, (b) after modification with 0.1wt%TiCN; (c) and (d) key for the IPF maps with fraction of the grain boundaries high angle (15–180°) and low angle (2–15°), and (d) schematic of sample orientation and solidification directions. P265GH cast steel

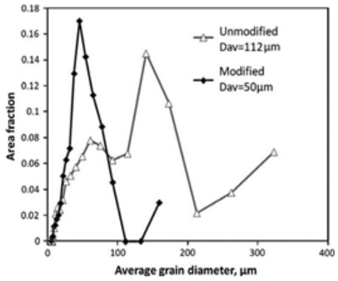

Figure 13. Grain size distribution (area fraction) for non-modified P265GH steel and after its modification with 0.1% TiCN

Nanomodification of Grey Cast Iron GG25

Cast iron GG25 was melted in an induction furnace. After modification with a standard modifier (Si6Ba), a TiCN+Y_2O_3+Ni+Fe nanomodifier was introduced into the melt in the composition: TiCN: Y_2O_3: Ni: Fe=2:1:1: 6 using a special device. Here, Ni and Fe are cladding metals. The "Brake disc" castings were cast with and without NM into sand molds [46,47]. Samples were cut from the castings for metallographic analysis and mechanical tests. The microstructure of the unmodified and modified samples from castings is shown in Figure 14.

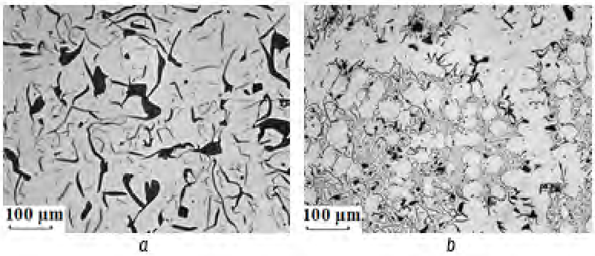

Figure 14. Microstructure of cast iron GG25 ingots without NM (a) and with NM 0.03wt% TiCN (b)

In the unmodified sample, the graphite phase has mainly the classical form of extended plates (Figure 14a). In the modified one, it forms a grid in the form of club shaped and rounded small inclusions (Figure 14b). It is established that the conditional average diameter of these inclusions for unmodified samples is 181 µm, and for modified samples it is 28 µm. Comparative studies of the mechanical characteristics of cast iron ingots show an increase in yield strength by 9%, tensile strength by 15%, elongation by 36% and wear resistance for castings with NM by 16%. In the features of structure formation in cast iron with spherical graphite when used as a tin based ligature modifier with additives of titanium carbide nanoparticles, yttrium oxide and multilayer carbon nanotubes were studied [66]. The spheroidizing treatment of the liquid metal was carried out by the bucket method due to the magnesium containing ligature FSMg7 (Si-Mg-Ca base). Secondary processing of high strength cast iron was carried out by adding a ligature modifier in an amount of 0.1% to the bottom of the filling bucket. Studies have shown that a pearlitic metal base and spherical graphite of improved shape are formed in the structure under the influence of yttrium oxide, titanium carbide, and carbon tubes. At the same time, the tendency of high strength cast iron to form carbides in the cast structure has decreased. According to the mechanical properties, the resulting cast iron corresponds to the GGG60 brand.

Modification of Heat Resistant Alloys

The influence of NM on the properties of heat resistant alloys of the grades ZhS 6K and Inconel 718 was studied. Melting was carried out in a vacuum induction furnace to a temperature of 1580°C-1650°C, and casting was carried out at a temperature of 1460°C-1550°C in ceramic molds, the walls of which were preheated to 900°C.

Alloy ZhS 6K

Chemical composition of the alloy in percent by weight: C 0.15, Sg 10.79, Co 5.22, W 5.06, Mo 4.10, Al 5.58, Ti 2.58, B 0.018, Zr 0.05, Ni 66.452. A nanomodifier of the composition TiN+Y_2O_3+Cr (in the ratio 1:1:3) with a concentration of the refractory component mp=(0.025–0.035) % by weight was used [67]. Figure 15 illustrates the macrostructure of samples cast without NM and using NM.

Figure 15. Macrostructure of the ZhS 6K alloy: 1 – without NM; 2 – 0.025% NM; 3 – 0.035% NM. The sample diameter is 20 mm

The measurements showed that without NM (m_p=0), the average grain size is (4.49-5.34) mm, and the grains are heterogeneous in size. At m_p=0.025%, the grain size is reduced to 2.25-1.89 mm, and at m_p=0.035%, the macro grain is refined to 1.59 mm-1.33 mm. Figure 16 shows the carbide structure

Table 6. Influence of the nanomodifier on the service properties of the ZhS 6K alloy

NM concentration, mp, % by weight	Long-term tensile strength (975°C, 195 MPa)			Cyclic fatigue at temperature 600°C
	τ, ч	δ_5, %	ψ, %	N_f, number of cycles
0.00	49.00	3.92	3.56	1659
0.025	54.35	7.20	10.67	3586
0.035	71.30	11.20	11.60	6165

of the ZhS 6K alloy.

After conventional melting (without NM), the morphology of the carbide phase has the form of Chinese characters (Figure 16a), the characteristic size of carbides is about 60 microns. When 0.025% NM is added, most of the carbide is formed as a club shaped structure with a grain size of ~20 microns, and a small number of them still exists as a structure of Chinese characters (Figure 16b). When 0.035% NM is added, the proportion of the carbide phase in the structure of the Chinese scenario becomes even smaller, and most of it exists in the form of granular carbides (Figure 16c). Table 6 shows the mechanical properties of the ZhS 6K alloy.

It can be seen that NM additives increase the service life of the alloy at temperature of 975°C and tensile load of 195 MPa by 11%–46%, elongation increases by 83.7%–185%, the service life at a cyclic load of the alloy at 600°C increased by 2.1-3.7 times.

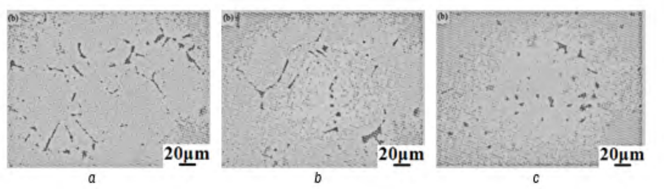

Figure 16. Micrographs of the carbide phase of the ZhS 6K alloy: a - mp=0; b - mp=0.025%; c - mp=0.035%

Table 7. Heat-resistant characteristics of the Inconel 718 alloy

Alloy type	Long-term tensile strength at temperature of 650°C under load of 195 MPa			Cyclic fatigue at temperature of 482°C
	τ, h	δ_S, %	ψ, %	N_f, number of cycles
ithout NM	*69.00*	*6.28*	*3.17*	*3360*
NiAl+TiN	*107.50*	*6.76*	*3.57*	*11531*
NiAl+(TiN+TiCN)	*144.40*	*4.84*	*2.20*	*11239*

Inconel 718 alloy

The chemical composition of the alloy in percent by weight: Ni 52.0, Cr 19.0, Cu<0.30, Nb 4.75, Mo 2.80, Ti 0.65, Al 0.50. Co<1.0, Mn<0.35, C<0.08, Si<0.35, Fe ≥ 18.19. To modify this alloy, various nanostructured powder compositions were used, containing nanodisperse particles of refractory compounds TiN, TiC0.5N0.5, clad with intermetallic NiAl: TiN+NiAl (1:6), (TiN+TiC0.5N0.5)+NiAl (6:1), (further, for the sake of simplicity, we will write TiCN instead of TiC0.5N0.5) [68]. Table 7 shows the experimental data obtained on the properties of the alloy at high test temperatures. Introduction to the melt of the heat resistant Inconel 718 alloy of composite powders (TiNC (0.04)+NiAl) or (TiCN (0.04)+Y_2O_3 (0.04)+Fe+Ti) in an amount of ~0.04% by weight leads to a more than 1.5–2 times increase of the time of the sample under load of 195 MPa at temperature of 650°C and a more than 3 times increase in the number of cycles at T=482°C.

From the analysis of the Inconel 718 alloy grain structure (Figure 17), it follows that this increase in the strength properties of the alloy when it is modified with composite powders is due to a decrease in the average grain size in the alloy by 1.5-2 times [69]. At the same time, the grains have a shape close to the equiaxial one and are more uniform in size. Transmission electron microscopy studies have shown that the alloy modified with TiN powder additives has a chaotic dislocation structure (Figure 18).

Figure 17. Macrostructure of Inconel 718 alloy:(a) without NM, (b) with TiN + NiAl, (c) with (TiN+TiCN) + NiAl. The sample diameter is 20 mm

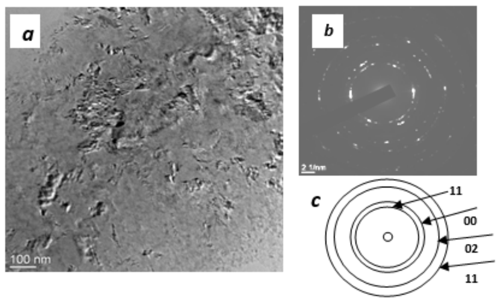

Figure 18. Dislocation substructure of the alloy grain volume; (a) light field; (b) microelectronogram; (c) microelectronogram decoding scheme

In the junctions of grain boundaries, regions with a submicrocrystalline (70...100 nm) structure containing TiN particles are detected (Figure 19). Along the grain boundaries, extended clusters of TiN nanoparticles (particle conglomerates) are detected that have not become crystallization centers and have been displaced to the inter boundary regions by growing crystals.

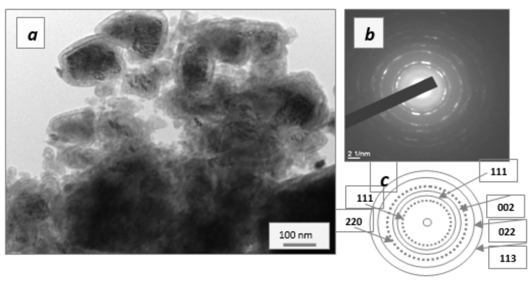

Figure 19. Layers along the grain boundaries of alloy with a submicrocrystalline structure containing particles of TiN composition; (a) a light field; (b) a microelectronogram; (c) a microelectronogram decoding scheme (solid rings indicate the alloy reflexes; dotted rings – TiN)

Paper presents the results of a study on the effect of nanomodifying additives of titanium carbonitride on the properties of turbine blades of aircraft engines made of heat resistant nickel alloy ZHS3DK (chemical composition in percent by weight: Ni 64. 4, Cr 11.5, Fe<2.0, C<0.1, Si<0.4, Mn<0.4, Co

9.5, Mo 4.5, Ti 2.8, Al 4.2) [70]. The Ti+TiCN modifier was introduced in the form of tablets in amount of 0.05% at a temperature of 1650 ± 10°C with an exposure time of 1.0 min-1.5 min. After the introduction of the modifier, the melt was poured at a temperature of 1550 ± 10°C into ceramic molds heated to temperature of 900°C. The values of the long term strength of ingots made of ZHS3DK-VI alloy with carbon content of 0.07% and 0.1% (both serial and modified) are ~31800 h in the original alloy and ~52030 h in the modified one. Primary carbides had a more favorable morphology, segregating as discrete globular particles.

Discussion

Castings of aluminum alloys

Aluminum alloys are used in many areas of the industry to cast various castings. It is very important that they have suitable mechanical properties for their application. In some cases, it is necessary to work to increase the mechanical properties. One of the methods for improving the properties is the introduction into the melt of nanoparticles of various chemical compounds with low mass concentrations (0.025-1.0 wt%) [12-14, 25-38]. The studies presented in this review establish the influence of AlN + Al + Cu, SiC + Cu, ND + Ag on the microstructure and mechanical properties of castings "Boat" and "Piston" of AlSi7Mg and AlSi12Cu2MgNi alloys, respectively [32,33]. These castings have important practical application and have been selected to prove the influence of nanomodifiers on their properties. The microstructure of the modified with nanoparticles castings of AlSi7Mg compared to that of the unmodified ones is significantly refined - DAS decreases by 26%, the size of silicon particles decreases by 16-26%. The porosity decreases significantly, by an average of 60%. SEM studies show that the grain size decreases significantly: unmodified alloy from 28.53 μm till 967.47 μm and modified one from 14.58 μm till 316.15 μm. Tensile strength increased by 7%, linear elongation by 60% (when modified with SiC). Similar results have been obtained by other authors [30]. Modification with TiCN nanoparticles increases the tensile strength and specific elongation of alloy A356 by 18% and 19%, respectively. It can be considered that the presence of nanoparticles or clusters of them leads to an increase in the centers of crystallization and structure refinement [37]. This also improves the mechanical properties.

Castings of iron-based alloys

P265GH steel castings modified with TiCN nanoparticles were studied. The grain size distribution determined by EBSD shows that the average size decreases almost twice as a result of the modification. The influence of nanoparticles is also shown in the mechanical properties: the relative elongation increases by 19% and the yield strength by 10.7% [24]. Nanocompositions containing TiN, TiCN and Y_2O_3 nanoparticles are introduced into the GX120Mn13 steel melt. As a result, the shape of the crystals changes, their average size decreases and, as a consequence, the dynamic friction wear significantly decreases [46,47]. The use of nanocompositions of TiN, Y_2O_3 for continuously cast carbon steel expands the two-phase zone, increases the number of active particles - nuclei of new crystals, refines the structure and changes the morphology of the crystal phase. This improves the physical and mechanical characteristics of the metal: strength, elongation, etc. Central porosity, chemical heterogeneity and liquation are reduced [65,66].

"Brake disc" castings of gray cast iron GG25 have been modified with a nanocomposition containing TiCN + Y_2O_3 . There is a significant effect on the shape and conditional average size of graphite inclusions - a decrease of about 6 times. An improvement in mechanical properties has been obtained [46,47].

Castings of cheat resistant alloy

It was studied the effect of the addition of nanoparticles on the properties of the cheat resistant alloy ZHS3DK-VI, which is close by a composition to the ZhS 6K alloy studied by us in [68,70]. It was used to modify the Ti (C, N) + Ti nanocomposition in the form of tablets. Dendritic structure refinement was found. Primary carbides acquire a more favorable morphology. They are discrete globular particles, which is consistent with the results obtained by us. The authors have found that the long-term strength of the castings of ZHS3DK-VI alloys with a carbon content of 0.07% and a test temperature of 850°C without a nanomodifier is about 318 hours, and after nanomodification about 520 hours (the increase is more than 1, 6 times). In our case for the alloy ZhS 6K when modified with nanocomposition TiN + Y_2O_3 + Cr and test temperature 975 oC these values are 49 hours and 71.3 hours, respectively. Here the increase is also more than 1.6 times, but the test temperature is significantly higher. The results for the influence of the modification with high-melting-point nanoparticles on the structure and properties of castings of cheat resistant alloy Inconel 718 are similar [69].It follows from the above mentioned that the modification with nanoparticles is applicable and effective for castings of alloys of different composition.

Conclusion

New scientific and technological principles have been developed to improve the quality of metals and alloys by modifying the melt with nanopowders of refractory compounds. Their essence lies in the purposeful effect on liquid metals and alloys at the stage of their crystallization. To do this, special additives are introduced into the melt, represented by highly activated nanodisperse powders of refractory compounds clad with metal. This causes the formation of a heterogeneous system in the melt in the form of a nanosuspension with the particles of size d ≤ 1 00 nm, evenly distributed over the volume of the melt, well wettable and serving as crystallization centers. As a result of continuous cooling, a finely dispersed globular structure is formed in the solidifying melt, which contributes to a significant increase in the physical, mechanical, and operational properties of cast products made of ferrous and nonferrous alloys.

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