The interaction of zirconium oxide nanoparticles with model binary and complex alloyed nickel alloys containing TiN

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Abstract. Interaction of exogenous nanoparticles of refractory compounds ZrO₂ with model binary and multicomponent nickel alloys containing surfactants - tin were investigated. Shown that the removal of surfactants in the metal after ZrO₂ nanoparticles introduction depends from the time of isothermal holding in the induction furnace and alloying elements composition. The complete chemical composition of the alloys has been studied using the method of atomic emission spectrometry with inductively coupled plasma. The contents of various forms of zirconium have been determined. The effect of alloying elements on the change in the ratio of forms have been showed.

Development of nanotechnologies in metallurgy opens the ways to improve metal properties using exogenous nanoscale particles of refractory phases (NPRP) as reagents refining melts from harmful surfactants, and inoculation in metal crystallization processes. Currently, there are a large number of publications devoted to the interaction of ultrafine particles with melts based on iron, nickel and aluminum exclusively in the process of crystallization of industrial metal products. The technological process for treating of nickel melt by the modifying complex on the base of Ti(C,N) with 50-100 nm refractory particles is described in [1]. Nickel alloy GS3DK-VI was used for study. During the crystallization of the casting, the nanoparticles of titanium carbonitride served as additional centers of crystallization and contributed to the formation of a smaller grain structure. A homogeneous structure with inclusions of intermetallic phases along the boundaries and inside the grains was obtained after modification. A significant of grinding of the macrostructure (grinding grain 6-10 times) led to improvement in the tensile strength (8-10%); yield strength (10-13%); elongation (1.1-1.3 times); toughness (40-44%), and the durability of the alloy (6-30%) depending on the stress test. The influence of SiC nanoparticles on the structural and mechanical properties of nodular cast iron was studied in [2]. It was noted that the effect of SiC nanoparticles on the formation of ferrite, decreases of perlite, and the content of carbide contributes to the improvement in toughness of the cast structure. Increase in toughness and decrease in hardness after heat treatment were also observed. Modification of high-strength cast iron by nanoscale particles was investigated in [3]. Cerium oxide nanoparticles with a size of 10 nm were added to the melt before casting. Concentration of nanoparticles in the metal was ranged from 0.03 to 0.09 wt.%. The authors found that after the introduction of cerium oxide, globular graphite and carbides were crushed. It was shown that the modification led to an improvement in hardness and strength, mainly due to changes in the volume fraction and size of
The abrasive wear resistance of the material increased with changes in hardness. It was noted that only small concentrations of nanoparticles were effective and with a high amount of cerium oxide in the metal, their advantages diminished. The alloying of 08Cr18Ni10T steel with nano- and microdispersed ZrO₂ particles during vacuum-arc remelting was described in [4]. Authors have shown that the nanosized ZrO₂ particles are more evenly distributed in the melt volume than micron sized ZrO₂ conglomerates. Values of strength and yield strength increase at concentrations of ZrO₂ particles up to 0.3 wt%, compared to the original steel, and decrease at concentrations above 0.4 wt%. Fatigue on alternating cantilever bending of steel in initial and modified states was investigated. In case of modification a significant (>30%) increase in fatigue strength of the low-cycle fatigue region, and slight (~10%) change in fatigue strength with a large number of loading cycles have been observed.

The presented review confirms relevance of application NPRP in melts during the crystallization process to improve service properties of products. But in these studies, the physicochemical regularities of the interaction nanoparticles with metal melt components are not fully considered. Results obtained differ significantly depending on the selected system NPRP-melt. The papers also do not consider the interaction between surface-active substances and NPRP in a liquid metal, and their possible effect on the redistribution of nanoparticles in the melt. Ultrafine particles of tungsten carbide, titanium nitride and carbonitride with microparticles of nickel and slag as protectors were used in [5]. Listed particles were introduced into powder, composite wires, agglomerated fluxes and coated electrodes for manual arc welding. Authors suggested that during the transition to the weld metal, on surface of the nanoparticles adsorb the surfactant – oxygen, sulfur, or other compounds. Under the influence of the circulation flow, the formed complexes of NPRP-surfactants are uniformly distributed in the peripheral area of the weld pool. On the cooled layer these complexes can form clusters that serve as additional crystallization centers, which contribute to the modified weld metal and its operational properties. Thus, the study of the physicochemical laws for the interaction of NPRP and surfactants in model binary and multicomponent nickel alloys could lead to more fully investigation of refractory nanoparticles on improving metal properties as a result of inoculation processes during metal crystallization and melt refining from harmful surfactants.

In [6] have been proposed and experimentally confirmed the hypothesis about the interaction of nanoparticles of refractory phases with metal melt surfactants. The mechanism was schematically presented as follows: introduction exogenous NPRP (disperse phase) into a liquid metal (dispersion system) leads to redistribution of surfactants on the boundary particle-melt (lyophilic or lyophobic) and their adsorption on the surface of the nanoparticles. Taking into account the quasichemical theory of the structure of melts, structural compounds are formed - ensembles Me + (NPRP-surfactants) as result of absorption. Due to the surfactant gradient, the processes of moving the ensembles in the melt, their possible merging or degradation, and further removal under the influence of adsorption nature forces on the Me-phase interface (ceramics, slag, gas) occur. As a result, one part of the ensemble is removed from the metal, i.e. the process of metal refining from harmful surfactants is implemented. Another part of the ensembles will further influence the crystallization processes and mechanical characteristics of the metal.

The purpose of this work is to study the interaction of ZrO₂ NPRP with binary and alloyed nickel alloys containing surfactants – impurity-tin, and to determine the forms of existence of zirconium in these alloys after entering ZrO₂. Surfactant impurity tin has been selected because of it is a typical non-ferrous metal impurity (NFMI) with surface-active properties [7]. The existing problem of NFMI removal [8] could also make possible to consider a new mechanism for removing NFMI by an adsorption mechanism from nickel alloys using NPRP. The choice of zirconium oxide is explained, firstly, to obtain new knowledge about the behavior of group IV metal oxides of the Periodic Table of Elements when interacting with liquid nickel and its impurities, taking into account the crystallography of materials. Secondly, in expanding the use of this oxide for practical purposes, for example, when producing ODS steels, cell material for measuring the EMF components of liquid alloys, etc.
Methods and materials of research.

ZrO₂ nanoparticles were obtained by a plasma-chemical method using a plasma generator of an electric arc plasma torch with a power of 25 kW, and the synthesis process took place during the interaction of the powder of zirconium chloride with an air plasma. The specific surface area 19.14 m²/g was analyzed by the BET method on a Micrometrics TriStar 3000 analyzer. The average particle size dₘₐₓ (BET) for ZrO₂ was 55 nm. X-ray phase analysis (Rigaku Ultima 4) showed the presence of 80% ZrO₂ (baddeleyite) and 20% - ZrO₂₁₈₈. The introduction of NPRP into a liquid melt was realized as a briquette of a composite material prepared from a mixture of NPRP powders ZrO₂ and Ni. The analysis of nickel powder showed the presence of 80% of particles with a size of 5–25 μm. Preparation of a mixture Ni powders (97.5 wt.%) + ZrO₂ (2.5 wt.%) [9] was carried out in a Fritsch Pulverisette 6 planetary mill in Ar atmosphere for 1 hour. Chemical analysis of the powder showed the presence 2.23 wt. % ZrO₂ in the resulting mixture.

To refine the powder from oxygen, reductive annealing was carried out in an atmosphere of hydrogen at 800°C for 1 hour with a consumption of hydrogen of 25 l/h. After treatment, the mixture of powders was subjected to uniaxial pressing at a pressure of 35 MPa degassing in an Ar atmosphere at 300°C and in vacuum at 300°C, followed by vacuum storage at 25°C.

To carry out elemental analysis of the samples both on the main components (Cr, Co, Al, Mo, Nb, Ta, W, Re, Ti, etc.) and on microalloyed additives and impurities (La, Y, Si, Sn, Fe, Ca, Mg, B, P, Zr) and to determine the content of the forms of zirconium existence, the method of atomic emission spectrometry with inductively coupled plasma (AES with ICP) was used. When determining zirconium and these elements of an AES with ICP, it has a number of advantages over other methods: higher sensitivity than atomic absorption, atomic fluorescence spectrometry and photometric method of analysis and a wide range of calibration graphs [10]. The studies were carried out on a sequential atomic emission plasma spectrometer of ULTIMA 2 firms "HORIBA JOBIN YVON" (France-Japan). The high optical resolution of the spectrometer (5pm) provides a better signal to background ratio, which leads to low detection limits of elements. The following optimal analytical parameters for the simultaneous AES with ICP determination of the chemical elements were chosen: discharge power - 1.2 kW; flow rate of cooling argon is 14 l/min; transporting 0.80 l/min; plasma-forming 0.5 l/min; observation height of 15 mm above the upper coil of the induction coil; sample flow rate is 1.0 ml/min. The analytical lines for each element were found as free from spectral overlays of the nickel matrix element. The influence of nickel on the analytical signals of metals has been studied. Increasing the Ni concentration to 200 ppm did not affect the analytical signals of impurity elements with their content exceeding 10 ppb. The method of interactive matrix matching [10] was used to eliminate matrix noise caused by changing nickel concentration. It has been found that the content of determined elements at the levels of 0.1 - 10 ppm mutual effects are not manifested. The concentration of the matrix element in the solution has been chosen, the stability of the burner - nebulizer system is not disturbed. For nickel favorable concentration is not more than 2000 ppm.

The method of AES with ICP requires conversion of analyzed samples into solution. Optimal schemes of sample dissolution have been found and the composition of acids has been selected to obtain stable solutions of easily hydrolysable determinable elements: Mo, Nb, Ta, Ti, W, Zr. To prevent the deposition of tungsten salts into the sediment, H₃PO₄ was added [11]. For acceleration of decomposition of samples modern systems were used: microwave mineralizer "Minotaur-2(Russia) and microwave system MARS 5(CEM Corporation, USA). Autoclave microwave dissolution using the MARS 5 module proved to be the most effective. The 100 mg samples were completely dissolved in 10 minutes in a mixture of HF + HNO₃ + HClO₄ at a temperature of 210°C. The method of "wet fusion" was used to determine silicon: heating of samples in the mixture H₂SO₄ and (NH₄)₂SO₄ [12]. All used reagents were of the high purity. We used twice distilled water. Standard solutions were prepared from metals of high purity [11] or applied standard multi-element solutions of Merk company. To determine the content of different forms of zirconium existence by AES with ICP, the difference in their solubility was used. Aqua regia: mixture of HCl conc. + HNO₃conc. (3:1) was applied for conversion into solution Zr dissolved in metal. Zirconium oxide (ZrO₂ - in the form of baddeleyite) is one of the most
difficult compounds to be open. Dissolution of ZrO₂ was carried out in the microwave sample preparation system MARS 5 under different modes (P, T) by different acid mixtures according to the previously developed method [13].

Three series of experiments with model binary and multicomponent alloys were conducted. During the first series of experiments the interaction of ZrO₂ with model binary systems Ni-Sn (0.0840 wt.%) and Ni-Sn (0.0460 wt.%). These alloys were smelted in a vacuum resistance furnace with a graphite heater in a corundite crucible (98% Al₂O₃) with a capacity of 46 ml at PHe=10% H₂=0.1 MPa. Nickel was introduced into the melt without breaking the tightness of the Sn grade VHF-000 with a 20-minute isothermal exposure and crystallization of the metal in the crucible. The second series of experiments included investigation model multicomponent nickel alloys (MNA). As known the melting of heat – resistant nickel alloys occurs in two periods: oxidative and reducing [14]. To study the efficiency of the input of exogenous refractory nanoparticles in different periods of melting, as a model MNA alloy was chosen, the composition of which corresponded to the oxidative period in the melting of heat-resistant alloys. These alloys were smelted in a resistance vacuum furnace with a graphite heater, where Sn of VHF-000 grade was also introduced into the melt to study the heterophase interaction NPRP of ZrO₂ with surfactant impurities. As two model systems, a multicomponent carbon alloy of composition (wt.%): Ni (basic) - Co (8.97) - Cr (4.93) - Mo (1.02) - W (8.54) - Re (3.96) - C (0.168) - Sn (0.0532) - S (0.0161) - O (0.0063) (hereinafter - MNA1) and a multicomponent carbon-free alloy of composition (wt.%): Ni (basic) - Co (9.04) - Cr (4.02) - Mo (1.18) - W (11.62) - Re (2.04) - C (0.005) - Sn (0.0487) - S (0.0146) - O (0.0029) (hereinafter - MNA2) were melted. During the third series of experiments, adsorption interactions in heat-resistant nickel industrial alloys were investigated. GS32 and GS36 were chosen as model alloys. The composition of these alloys (wt.%) was: GS32 - Ni (basic) - Cr (4.54) - Al (4.31) - Mo (1.10) - W (8.13) - Co (8.78) - Re (3.35) - Ta (4.21) - Nb (1.47) - C (0.222) - B (0.013) - Y (0.405) - Mg (0.0014) - Ca (0.0002) - S (0.0003) - O (0.0005) - N (0.0002) - Si (0.14) - P (0.0065); GS36 - Ni (basic) - Cr (3.81) - Al (5.47) - Mo (1.26) - W (11.42) - Co (8.27) - Re (2.01) - Nb (1.04) - Ti (1.13) - La (0.02) - Y (0.005) - Ca (0.005) - O (0.0016) - N (0.0004) - Si (0.061) - P (0.0017) - Fe (0.12). To study the heterophase interaction of ZrO₂ with tin, the tin content in the metal was increased to 0.0385 wt.% (GS 32) and up to 0.0428 wt.% (GS 36) when introduced into the melt of Sn brand VHF-000. Carbon content in all alloys was determined by oxidative melting using the analyzer of "LECO" model CS-400, and oxygen content – by reducing melting using the analyzer "LECO" model TS-436.

The study of the heterophase interaction of NPRP with surfactants was carried out in a vacuum induction furnace (VIF) with a special conical inductor, which provided a concentrated input of RF energy into the melt and intensive mixing of the metal with NPRP on the surface and inside the melt [15]. The experiments were carried out in an atmosphere He with 10% H₂ at a pressure of 0.2 MPa. Heating and melting of the metal were controlled by an optical pyrometer EOP-66, calibrated at the melting points of pure metals, with data processing using the Ecochrome software. After attaining equilibrium with the gaseous phase of the liquid metal injected preform of the composite material (Ni+NPRP ZrO₂) with subsequent isothermal aging from 120 to 1200 second depending of the experience. The average temperature of the experiments ranged from 1519-1653°C and depended from the series of experiments. The content of NPRP ZrO₂ in the melt after the introduction of the briquette was 0.10 wt.%.

**Results of experiments and their discussion.**

The changes in the tin content in the melt were studied, analyzing the redistribution of nanoparticles and ensembles in the melt under the influence of adsorption forces [16]. More than 80 experiments with the following 12 types of alloys were conducted: Ni-Sn(0.0460 wt.%); Ni-Sn(0.0460 wt.%) - ZrO₂(55 nm); Ni-Sn(0.0840 wt.%); Ni-Sn(0.0840 wt.%) - ZrO₂(55 nm); MNA1; (MNA1) - ZrO₂(55 nm); MNA2; (MNA2) - ZrO₂(55 nm); GS32; (GS32) - ZrO₂(55 nm); GS36 and (GS36) - ZrO₂(55 nm). The results are presented in the form of dependences [Sn]=f(τ). The change in the content of Sn was presented as the degree of removal α = ([Sn]initial-[Sn]ending)/[Sn]initial)·100.
The results of the first series of experiments with Ni-Sn binary systems (Figure 1) allow to draw the following conclusions: 1) The introduction of ZrO$_2$ NPRP provided a decrease in the content tin and the $\alpha_{Sn}$ values were 14-22 rel.%. 2) Value comparison of the content tin and the $\alpha_{Sn}$ with and without the introduction of ZrO$_2$, makes it possible to consider the existence of heterophase interaction of ZrO$_2$ NPRP with surfactant in the Ni-Sn melt and the removal of Ni+(ZrO$_2$-Sn) ensembles. 3) Data processing of time dependence by the least squares method when describing by polynomial function ($[\text{Sn}]=0.0811-3.42\cdot10^{-3}\tau+1.86\cdot10^{-3}\tau^2$ for the Ni-Sn system (0.0840 wt.%) and $0.0451-1.87\cdot10^{-5}\tau+1.06\cdot10^{-8}\tau^2$ for Ni-Sn(0.0460 wt.%) showed the presence of an extremum at 720-860 seconds, which can serve as a proof of possible reversible processes of tin adsorption/desorption at the boundaries of ZrO$_2$-Sn.

![Figure 1](image1.png)

**Figure 1.** Dependence of tin content on the duration of exposure in melts Ni-Sn (0.0460 wt.%) (a) and Ni-Sn (0.0840 wt.%) (b): 1 - without introducing NPRP; 2 - ZrO$_2$ (55 nm).

Concentrations of different forms of zirconium in this alloy have been determined. It was found that under experimental conditions in the model binary systems the ratio of Zr, which was in the melt in the form of a solution and in the form of NPRP ZrO$_2$ is 1:80 or about 99% exists in the form of ZrO$_2$.

The results of the second series of experiments with model multicomponent nickel alloys (Figure 2) showed that, first of all, the introduction of ZrO$_2$ low-frequency nickel alloys at an isothermal exposure time 240-1200 s. The content of tin decreased, the values of $\alpha_{Sn}$ were 16-27 rel.% (MNA1) and 15-28 rel.% (MNA2). It may indicate heterophase interaction of NPRP ZrO$_2$ with surfactants in the melt and their removal in the form of ensembles (Ni-Me)+(ZrO$_2$-surfactants), where Me is a component of a complex alloy. Secondly, data processing by the least squares method describing by polynomial function ($[\text{Sn}]=0.0502-2.90\cdot10^{-3}\tau+2.14\cdot10^{-3}\tau^2$ for MNA1 and $[\text{Sn}]=0.0476-2.31\cdot10^{-3}\tau+1.09\cdot10^{-8}\tau^2$ for MNA2) showed the presence of an extremum, which can serve as evidence of possible processes of surfactant desorption. When comparing the obtained data with the model binary systems, it was found that in the MNA the processes of tin removal in experiments without inputting NPRP are more intensive. The values of $\alpha_{Sn}$ in MNA 1 and MNA2 after 1200 s. were 4.3 and 5.1 rel.%, respectively. After the introduction of ZrO$_2$, the degree of tin removal in MNA1 had the highest values at the initial stages of melting, and in MNA 2 - at longer exposures of about 1000 seconds (Figure 2), that can be connected with different influence of alloying elements of the melt on the change of the structure of ensembles and tin desorption from their surface.
The content of various forms of existence zirconium was determined by the method of AES with ICP: in the form of “easily opening” and “hardly opening” compounds. An assumption was made that the “easy-opening” compounds were zirconium dissolved in the metal or in the form of non-oxide inclusions, “hardly opening” as ZrO₂. Analysis of the results showed that, firstly, with an initial Zr content in the metal of 0.074 wt.% (in the form of ZrO₂), the amount of zirconium removed from the metal to the interface phases, presumably in the form of ensembles, is on average in MNA1 - 55 rel.% and in MNA2 - 64 rel.%, while 45-36 % remain in the metal and influence the crystallization process. The highest degree (71%) of zirconium removal from metal is observed at an exposure of 1200 seconds in MNA2. Secondly, there is a significant change in the composition of the particles that have not been removed during long exposures of the metal. In the MNA1 at 240 seconds exposure, the ratio of zirconium in the form of “easily opening” and “hardly opening” compounds were 1:9, i.e. 90% of the particles are presumably in the form of ZrO₂. At 1200 seconds exposure the ratio was 1:1, i.e. only half of the particles remain as oxide. In the MNA2, in contrast to the MNA1, there was no significant change in the composition of the particles that have not been removed during long metal exposures. The amount of zirconium in the form of "easily opening" compounds after 1200 seconds exposure is about 7%. These results indicate the significant role of the elemental composition of the MNA1 in the formation and change of non-metallic inclusions.

The change in carbon content was studied during experiments with MNA1 without introducing NPRP and after entering ZrO₂. It was found that after introducing ZrO₂ NPRP a significant decrease in carbon content was observed. After 1200 seconds exposure in VIF the value [C] in experiments without introducing NPRP and after entering ZrO₂, was 0.123 and 0.078 wt.% respectively. In [17] it was noted, that zirconium has a high affinity not only for oxygen, but also for other implantation elements (nitrogen, carbon, sulfur) and forms with them strong compounds ZrN, ZrS₂, ZrC. The possibility of reducing zirconium oxide with carbon can also be judged by the deoxidizing ability of carbon and zirconium in nickel. It was shown [18, 19], that with a content of 0.168 wt.% C and 0.074 wt.% Zr in a nickel melt, carbon has a greater deoxidizing ability than zirconium. From a thermodynamic point of view, the reaction of formation of carbide can be represented as a total reaction:

$$\text{ZrO}_2(s) + 3[C] = \text{ZrC}(s) + 2\text{CO}(g) \quad \Delta G^0_{rT} = -609070 - 235,11 \cdot T \ [20,21]$$

Partial pressure $P_{CO}$ (excluding the influence of alloying elements) was estimated. The model system Ni-C(0.168 wt.%)-O(0.0063 wt.%)-$\text{ZrO}_2$(0.1 wt.%) was considered. Dependence of the equilibrium constant from the reaction on temperature [6] was used to determine the value 31.56 Pa of $P_{CO}$ at 1873 K what, taking into account the assumptions, may indicate the possible formation of
zirconium carbide after the introduction of nanoparticles, which will lead to a change in the adsorption mechanism of the interaction of NPRP with tin.

The results of the third series of experiments with heat-resistant nickel alloys (Figure 3) showed that, firstly, the introduction of ZrO₂ NPRP at isothermal exposure of 120-600 s. resulted in a decrease in [Sn]. Values of αSn in the GS32 and GS36 alloys were 11–18 and 12–18 rel.%, respectively, which may indicate heterophase interaction of the NPRP ZrO₂ with tin in the melt and their removal as ensembles. Secondly, data processing using the least squares method when describing by a polynomial function (GS32 - [Sn] = 0.0370·2.99·10⁻⁵τ + 4.49·10⁻⁸τ² and GS36 - [Sn] = 0.0417·3.91·10⁻⁵τ + 5.63·10⁻⁸τ²) showed the presence of an extremum, which can serve as evidence of possible processes for the desorption of surfactant tin. Comparing the obtained data, it can be seen that, first, a more intensive removal of tin was observed without introducing NPRP compared to binary alloys. Secondly, the degree of removal of tin has the highest values in the initial stages of smelting. This once again confirms the influence of alloying elements during long exposures on the change in the structure of ensembles and the desorption of tin from the surface of nanoparticles.

As before, the content of various forms of zirconium is determined: in the form of "easily opening" and "hardly opening" compounds. The analysis of the results showed that, firstly, at the initial 0.074 wt.% Zr content in the metal (in the form of ZrO₂), the amount of zirconium removed from the metal to the interface, presumably in the form of ensembles, in both alloys averages 50 rel.%. Secondly, the time of isothermal exposure in the VIF does not significantly affect the proportion of zirconium removed from the metal. Third, there is a significant change in the composition of the particles not removed. At the minimum exposure 120 seconds the ratio of zirconium in the form of "easily opening" and "hardly opening" compounds is 1:1 (GS32) and 1:1.5 (GS36). This indicates the effect of alloying elements of the alloy and changes in the composition of the oxide particles even at low exposures. During long exposures at 600 seconds the amount of the "easily opened" connections is 89 rel.% (GS32) and 84 rel.% (GS36), which confirms the possibility of reducing the zirconium oxide melt elements. All this once again indicates that nanoparticles with excess surface energy will interact with melt elements with changes in the composition of inclusions and desorption of tin from the surface of nanoparticles. Changes in the content of tin and zirconium show increasing concentration of tin with increasing exposure time but the proportion of removed zirconium remains unchanged. This suggests that the interaction of zirconium oxide with the melt elements may result in the formation of complex, spinel-like compounds which remain in the slag phase. The tin after desorption passes into the melt. Therefore, in order to achieve the greatest effect of nanoparticles, it is necessary to introduce them into the liquid metal at minimum holding times before crystallization.
Figure 4. REM micrographs of non-metallic inclusions MNA 1 after 240 s. (a, b, c, d) and 1200 seconds (e, f) exposure in VIF.

The analysis of the matrix, grain boundaries and non-metallic inclusions of MNA1 samples after experiments with different isothermal exposures on JEOL JSM-6700F and JSM-6480LV raster electron microscopes was carried out. Non-metallic 1-3 microns inclusions were fixed in the sample without input of nanoparticles. Elemental analysis was constant and characterized by the presence of Cr, O, Co and Ni. After the introduction of the ZrO$_2$ NPRP into samples, the following types of non-metallic inclusions were found - simple and complex inclusions containing oxygen and complex inclusions of spherical and trapezoidal shape containing sulfur. Simple inclusions containing oxygen are agglomerated zirconium oxide particles of micron-sized size (Figure 4a), complex ones have Zr, Co, Cr, Ni and O in their composition (Figure 4b). Inclusions containing sulfur (Figure 4c, 4d, 4e and 4f), consist of Zr and S with the presence of Cr, Co, Ni, W, Fe and Sn. The presence of iron peaks in elemental analysis can be related to the steel cup/balls napkin during the preparation of composite material in a planetary mill for the introduction of ZrO$_2$ NPRP into the liquid metal. It is worth noting that elemental analysis always detects 20-30% of carbon inclusions, but as a rule, it does not considered when analyzing by this method. Figure 4f shows the inclusion containing a small fraction of tin, which is probably related to the adsorption of tin as a surfactant admixture at the interface between the phases of nanoparticle - melt with the formation of ensembles with an excess tin content. Thus, it can be assumed that these inclusions could be formed from the Ni-C-Me+(ZrO$_2$-Sn) ensembles, where Me is a component of a complex alloy formed as a result of interaction of exogenous nanoparticles with melt components at long exposures. Comparing the data related to different forms of zirconium, it is clear that the proportion of "hardly opening" compounds at 240 seconds is 90%, and at 1200 seconds - 50%. Assuming that only ZrO$_2$ is the "hardly opening" compound, the absence of a large number of oxide inclusions may indicate that a significant proportion of ZrO$_2$ contains in the form of nanoscale particles.
Conclusions:
1. Heterophase interaction of exogenous ZrO₂ nanoparticles (55 nm) with tin surfactants in model binary and multicomponent nickel alloys has been studied for the first time. An assumption was made about the redistribution of nanoparticles in the melt under the influence of adsorption forces.
2. It was found that tin removal was probably the result of heterophase interaction between NPRP ZrO₂ and surfactant, with forming ensembles and their removal to the the following phase interfaces: metal-gas, metal-slag or metal-lining. It was shown that the degree of tin removal depends on the time of isothermal maturation in VIF and composition of alloying elements. The values of αSn were 14-22 rel.% for Ni-Sn binary systems, 15-28 rel.% for multicomponent nickel alloys and 11-18 rel.% for heat-resistant alloys.
3. Using the method of atomic emission spectrometry with inductively coupled plasma, the contents of various forms of zirconium were determined. The influence of holding time in the VI metal on the composition of alloying elements. The values of αSn were 14-22 rel.% for Ni-Sn binary systems, 15-28 rel.% for multicomponent nickel alloys and 11-18 rel.% for heat-resistant alloys.
4. The analysis of the matrix, grain boundaries and nonmetallic inclusions of MNA1 was carried out. Nonmetallic inclusions of the following several types were found – simple and complex inclusions containing oxygen and complex inclusions of spherical and trapezoidal shape containing sulfur. The influence of the holding time in the VIF on the composition and size of inclusions was shown.

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References
[1] Kalinina N E, Yukhimenko A E and Kalinin V T 2014 Complex modification of the complex alloyed heat-resistant alloys Vestnik engine-building 2 pp 181-185.
[2] Ruixiang Zhu, Yong S and Xinyu Qin 2017 Study on the Influence of Nano-SiC on the Structure and Properties of Nodular Cast Iron. IOP Conf. Series: Materials Science and Engineering V.250 pp 1-8 (012051).
[3] Sun Xiaoguang, Wang You, Li DYand Wang Guodong 2013 Modification of carbidic austempered ductile iron with nano ceria for improved mechanical properties and abrasive wear resistance. Wear V. 301 № 1–2 pp 116-121.
[4] Aksenova S I, Borts B V, Korotkov I M, Pakhomov A V and Sokolenko V I 2016 Problems of atomic science and technology V I Fatigue of austenitic steels, modified with oxides of zirconium and yttrium №1 (101) pp 160-166.
[5] Sokolov G N, Lysak V I, Zorin I V, Artemyev A A, Dubtsov Yu N, Antonov A A and Yelsukov S K 2016 the Mechanism of the effect of ultrafine refractory components contained in the welding material, on the structure of the deposited metal. News of Volgograd state technical University №9 (188) pp 116-120.
[6] Anuchkin S N, Burtsev V T and Samokhin A V 2010 The interaction of nanoparticles of refractory compounds with a surfactant in a nickel melt: I. Heterophase interaction. Russian metallurgy (physical metallurgy) №11 pp 1014-1020.
[7] Nogi K, Chung W B, McLean A and Miller WA 1991 Surface tension of liquid Fe-(Cu, Sn, Cr) and Ni-(Cu, Sn) binary alloys. Materials Transactions JIM V.32 №2 pp 164-168.
[8] Guzenkova A S, Ivanov S S, Isaev G A and Kudrin V A 2008 Production of steel, pure, nonferrous metals. (Moscow: MGVMII) 118 p.
[9] Anuchkin S N, Gvozdkov I A, Samokhin A V, Serov G V and Burtsev V T 2011 Properties of composite nanomaterial Al₂O₃/Ni, obtained by the method of Mechanochemistry. Physics and chemistry of materials processing №2 pp 71-78.
[10] Thompson M and Walsh D N 1988 Guide to inductively coupled plasma spectrometric analysis
[11] Lazarev A I, Kharlamov I P and Yakovlev P Ya 1976 Handbook of chemist-analyst. M.: metallurgy 184 p.
[12] Bock R 1984 Decomposition methods in analytical chemistry (Moscow:Chemistry) 432 p.
[13] Andreeva N A, Anuchkin S N, Volchenkova V A, Kazenas E K, Penkina T N and Fomina A A 2018 Development of phase analysis methods of impurity elements in alloys based on iron and nickel. IOP Conf. Series: Materials Science and Engineering V.347 pp 1-9 (012003).
[14] Sidorov V V, Kablov D E and Rigin V E 2016 Metallurgy of foundry heat-resistant alloys: technology and equipment (Moscow: VIAM) p 368.
[15] Glebovsky V G and Burtsev V T 1974 Melting of metals and alloys in the suspended state (Moscow: Metallurgy) 176 p.
[16] Minaev Yu A 1984 Surface phenomena in metallurgical processes (Moscow: Metallurgy) p 152
[17] Nasuta L Y and Saenko A 2017 Peculiarities of application of zirconia as microlaserpeel element in the smelting high-quality steels: a literature review. Proc. abstracts of International scientific-technical conference "University science – 2017". Mariupol: state higher educational institution "Priazovskiy state technical University" Vol.1. pp 122-126.
[18] Aleksandrov A A 2016 Influence of zirconium on the solubility of oxygen in liquid nickel and melts of Ni-Fe. Metal. No.5 pp 61-68.
[19] Aleksandrov A A 2018 Thermodynamics of solutions of oxygen in melts of the system Fe-Ni containing boron. Aleksandrov A A, Dashevskiy V Ya and Leont'ev L I 2018 Izv. higher educational. Ferrous metallurgy No. 3 pp 201-210.
[20] Buzek Z 1979 Fundamental Thermodynamic Data on Metallurgical Reactions and Interactions of Elements in System Significant for Metallurgical Theory and Practice. Buzek Z (Ostrava: Vyzkumný ustav hutníctví zeleza) 110 p.
[21] Turdogan E T 1985 Physical chemistry of high-temperature processes (M.: Metallurgy) 344 p.