Interaction of exogenous refractory nanoparticles of $\text{Al}_2\text{O}_3$ and $\text{MgAl}_2\text{O}_4$ with nonferrous metal impurities in iron melts

S N Anuchkin
A.A.Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences (IMET RAS). Russia
E-mail: AnuchkinSN@yandex.ru

Abstract. The exogenous refractory nanoparticles is proposed for refining iron-based melts from nonferrous metal impurities. Investigated the heterophase interaction of $\text{Al}_2\text{O}_3$ and $\text{MgAl}_2\text{O}_4$ nanoparticles with Sb/Sn/Cu and showed that the degree of removal of nonferrous metal impurities was in the Fe-Sb system up to 30 rel.%, in the Fe-Sn system up to 29 rel. % and in the Fe-Cu system up to 23 rel. %. The existence of refractory nanoparticles in a liquid metal was proved by studying the structural properties of the melt. In the melts, after the introduction of the nanoparticles, inversion of the temperature coefficient of surface tension is observed, as well as multidirectional change depending on the nature of the nanoparticles and the holding time during interfacial interaction. Decompression and compression of the melts after the introduction of nanoparticles and the multidirectional nature of the dependences of properties indicate a possible change in the cluster structure of liquid metal.

1. Introduction

The development of the science of metallic nanomaterials [1], including various methods for producing refractory nanophases, allows implementing non-traditional methods of using nanopowders to develop more efficient and universal methods for improving properties of metal. One of the possible advanced methods is the use of exogenous refractory phase nanoparticles (RPNP) as reagents for refining iron-based melts from harmful impurities, and for inoculation in metal crystallization processes. Many modern studies deal with the interaction of ultrafine particles with iron-, nickel-, and aluminum-based melts during the solidification of commercial metallic parts. For example, in [2], the modification of steel such as Hatfield steel was studied with a fine powder of titanium carbonitride. The authors found that the modification of steel leads to an increase in the coefficient of abrasive wear resistance by 20-25%, impact-abrasive by 3-4 times, as well as grain refinement of austenite to 110-120 μm. It was noted that to ensure a high level of operational properties, it is necessary to introduce a modifier into the melt in an amount of 0.3-0.4% by weight of the alloy. In [3], the modification of low alloy steels was studied and the criteria for selecting nanopowder modifiers were identified: thermodynamic stability in the melt, accordance of the crystal lattices to the matrix metal, and proportionality to the critical radius of the austenite nucleus during crystallization. The authors justified the choice of Ti(CN) nanopowder with a size of less than 100 nm, and showed that the modification of 09G2 and 09G2S steels increases tensile strength by an average of 23%; yield strength - by 19%; δ - by 23%; ψ - by 6% and toughness by 39%. The alloying of 08Kh18N10T steel by nano- and microdispersed $\text{ZrO}_2$ particles during vacuum arc remelting was studied in work [4]. When studying the effect of the melting conditions and the alloying particle size on the $\text{ZrO}_2$ distribution in a
metal ingot, the authors of showed that ZrO2 nanoparticles were more uniformly distributed in the metal volume than ZrO2 microconglomerates did. When analyzing the mechanical properties, they found that the ultimate tensile strength and the yield strength increased as compared to the initial state when the ZrO2 particle content increased to 0.3 wt.% and that these properties decreased at above 0.4 wt.% ZrO2. The effect of nanopowders on the service characteristics of gray iron SCh20 was studied in [5]. Modifiers of two compositions were used in the work: I – obtained by plasma chemical technique in an iron matrix of a composition (α-Fe, TiC,Ny, SiC) of size 30–70 nm; II - obtained by the SHS method, combined with the mechanochemical method, and consisting of a carbide phase (70-80% WC - 20-30% TiC) of size 30 - 35 nm with a metal protector zirconium. The use of nanomodifiers I and II composition in an amount of 0.002 wt.% (I) and 0.038 wt.% (II) increases Brinell hardness by 9.8 (I) and 13.1 (II) rel.%, tensile strength by 11.9 (I) and 19.8 (II) rel. %, relative wear resistance at 21 (I) and 69 (II) rel. %, corrosion resistance in hydrochloric acid at 12.3 (I) and 28 (II) rel. % compared with unmodified samples of cast iron. Studies of the effect of SiC nanoparticles on the structural and mechanical properties of nodular cast iron were carried out in [6]. It was experimentally shown that after the addition of nano-SiC, the spheroidization rate, spheroidization degree and graphitization of the graphite in casting structure are improved. It was noted that nano-SiC can promote the formation of ferrite, reduce pearlite and the content of carbide in the cast structure which is beneficial to improve the impact toughness of casting. In [7], the effect of modification with ultrafine powders of refractory metal oxides and cryolite on the structure and deformation behavior of SCh25 gray iron was investigated. The modifying composition (0.3 wt% of the mass of the melt) consisted of ultrafine powders TiO2 and ZrO2 and cryolite Na3AlF6. The authors found that after modification there is a significant change in the nature of distribution and size of lamellar graphite, as well as an increase in the dispersion of perlite (from 0.57 to 0.32 μm) and increase in tensile strength (by 90 MPa). At the same time, ductility of 0.17-0.18% and hardness of 207 HB ± 5% remain unchanged. This review supports the importance of using RPNP in iron-based melts for increasing the service properties of parts during solidification. However, the physicochemical laws of interaction of nanoparticles with metallic melt components were poorly considered in the reviewed works, and the obtained results are substantially different depending on an RPNP–melt system. The interaction of surfactants with RPNPs in a liquid metal was not considered, and the possible influence of surfactants on the nanoparticle redistribution in the melt volume was not analyzed.

The charge of modern steelmaking units contains significant amounts of nonferrous metal impurities (NMI), in particular copper, tin, antimony, arsenic, etc., and to remove them during metal refining is a complex physicochemical and technical problem, which has not been efficiently and unambiguously solved to date [8,9]. Effective and economically viable methods of metal refining from NMI are only being developed, but there are a large number of scientific papers devoted to this problem [10-13]. However, existing methods do not solve the problem of removal NMI and it remains quite relevant and requires a non-standard approach to solve it. It is note that NMI, as a rule, have surface-active properties in iron melts [14, 15], which suggests the use of these properties for refining melts from NMI.

In [16] have been proposed and experimentally confirmed the hypothesis about the interaction of nanoparticle of refractory phases with metal melt surfactants (SAS). The mechanism was schematically presented as follows: introduction exogenous RPNP (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 M + (RPNP-SAS) 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 M-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 SAS 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, firstly, the choice of RPNP for
introducing into a liquid melt for refining it from NMI (Sb, Sn, Cu). Secondly, the study of heterophase interaction of various types of RPNP with NMI with surface-active properties in model iron melts. Thirdly, the study of the influence of RPNP on the structural properties of melts as proof of their presence in the metal and involvement in the processes of adsorption/desorption of surfactants (Sb, Sn, Cu).

2. Thermodynamic analysis

Based on the physicochemical analysis of the choice of RPNP, including the thermodynamics of dissociation reaction of refractory phase in the melt and information on the interfacial tension of the metal – refractory phase, the Al₂O₃ and MgAl₂O₄ nanoparticles were used in this work. Alumomagnesium spinel was chosen because of an attempt to reveal, first, the influence of a more complicated adsorbent structure and the related cavity content, the strength of cation–anion bonds, nonstoichiometry, and the defect content [17] on SAS adsorption and, second, the possibility of a change in the interfacial characteristics (interfacial tension, wetting contact angle) of the newly formed RPNP due to the dissociation of the nanospinel. The standard Gibbs energy of dissociation in iron was calculated according to the equations [18-20]:

\[
\Delta G_f^0 = 1209255 - 389.72 \cdot T
\]

\[
\Delta G_f^0 = 23600 + 5.91 \cdot T
\]

\[
\Delta G_f^0 = 1961455 - 622.21 \cdot T
\]

| Reaction | \(T_m\) (phase), K | \(\Delta G_f^{1873} \) J/mol | In \(Kp\) | \(\theta\), deg (t, °C) |
|----------|---------------------|-----------------------------|----------|---------------------|
| Al₂O₃(s) = 2[Al]_Fe + 3[O]_Fe | 2327 | 479409 | -30.79 | 141 (1550) [21] |
| MgAl₂O₄(s) = Al₂O₃(s)+ MgO(s) | 34670 | 147 (1550) [22] |
| MgAl₂O₄(s) = 2[Al]_Fe+[Mg]_Fe+4[O]_Fe | 2378 | 7966056 | -51.15 | 107 (1560) [22] |

The calculation results for 1873 K are presented in table 1. The data on the wettability of these compounds with iron melts were analyzed [21, 22], and the values of wetting angle \(\theta\) are also given in table 1. An analysis of these data indicates that oxides can exist in this iron melt, being lipophobic to this melt.

The probability of removing Sn from the Fe-Sn(0.0561 wt.%)-O(0.0059 wt.%) model melt was considered, and the evaporation process was presented as [18.19]: [Sn]_Fe=Sn(g), \(\Delta G_f^{r}=279700-58.32 \cdot T\). Using the equation describing the temperature dependence of the equilibrium constant of the reaction, \(P_{Sn}\) was determined as \(P_{Sn} = a_{Sn} \cdot \exp\left\{ -\Delta G_f^{r}/RT \right\}\), where \(a_{Sn} = f_{Sn}[Sn]\) and \(\lg f_{Sn} = e_{Sn}^{O}[Sn] + e_{Sn}^{O}[O]\). The values of interaction parameters in the calculation were \(e_{Sn}^{O}=0.0017\) [23] and \(e_{Sn}^{O} = -0.11\) [23]. The partial pressure \(P_{Sn}\) at 1873 K was 9.94·10⁻² Pa. Obviously, the amount of tin that passed from the melt to the gas phase under experimental conditions is negligibly small.

The possibility of removing Sb from Fe-Sb(0.0950 wt.%)-O(0.0079 wt.%) model melts was considered, and the process was presented as a reaction [18.24]: [Sb]_Fe=Sb(g), \(\Delta G_f^{r}=120995-14.19 \cdot T\). Note that for the reaction [Sb]_Fe=Fe(l) the values of the reaction coefficients were obtained by extrapolating the data in [24] for [Sb] = 0.1 wt.%. Using the temperature dependence of the reaction equilibrium constant, \(P_{Sb}\) was determined as \(P_{Sb} = a_{Sb} \cdot \exp\left\{ -\Delta G_f^{r}/RT \right\}\), where \(a_{Sb} = f_{Sb}[Sb]\) and \(\lg f_{Sb} = e_{Sb}^{O}[Sb] + e_{Sb}^{O}[O]\). The value of \(e_{Sb}^{O} = -0.2\) [23], and the value of \(e_{Sb}^{O}\) was taken equal to the value of \(e_{Sn}^{O} = 0.0017\) [23]. The value of \(P_{Sb}\) at 1823 K was 17.34 Pa. Apparently, under the assumptions made in the calculations and in the experimental conditions, it indicates on possible evaporation of Sb from the melt, which was taken into account during special experiments.
The probability of a decrease Cu content due to evaporation process in the Fe-Cu(0.0445 wt.%) - O(0.0078 wt.%) system was considered, and the process was presented as a reaction [18,19]:

\[ \text{[Cu]}_{\text{exp}} = \text{Cu}(g), \text{AG}^{0} = 274363 - 69.36\text{T}. \]

Using the equation describing the temperature dependence of the equilibrium constant of the reaction, \( P_{\text{Cu}} \) was determined as \( P_{\text{Cu}} = a_{\text{Cu}} \cdot \exp \left( -\Delta G^{0}/RT \right) \), where \( a_{\text{Cu}} = f_{\text{Cu}}[\text{Cu}] \) and \( \log f_{\text{Cu}} = e^{O}_{\text{Cu}}[\text{Cu}] + e^{Cu}_{\text{Cu}}[\text{O}] \). In the calculation, the interaction parameters \( e^{O}_{\text{Cu}} \) and \( e^{Cu}_{\text{Cu}} \), were equal to -0.0645 [23] and -0.023 [23], respectively. The \( P_{\text{Cu}} \) value at 1873 K was 0.418 Pa, which indicates a low evaporation of Cu under the experimental conditions.

### 3. Methods and materials of research

The material analysis of the RPNP Al\(_2\)O\(_3\), obtained by the plasmachemical method, showed that they were polydisperse and the particle size distribution was close to a logarithmic normal one. The dispersion composition obtained on a Mastersizer 2000 analyzer (Malvern) for a Al\(_2\)O\(_3\) was characterized by the following data: \( d_{10} = 25 \) nm, \( d_{50} = 51 \) nm, and \( d_{90} = 83 \) nm, where \( d_{i} \) is the size below which the fraction contains \( i \% \) particles. The specific surface was analyzed by the Brunauer–Emmett–Teller (BET) method on a Micrometrics TriStar 3000 analyzer and for Al\(_2\)O\(_3\) it was 36.4 m\(^2\)/g. The composition of the RPNP Al\(_2\)O\(_3\) was characterized by the presence of the following phases: \( \delta \) (50–60\%), \( \theta \) (10–20\%), and \( \gamma \) (10–20\%). Spinel MgAl\(_2\)O\(_4\) was obtained mechanochemically by treatment of Al\(_2\)O\(_3\) and MgO RPNP in a Fritsch Pulverisette 7 planetary mill for 10 min followed by annealing in a TK.4-1400.1.F electric resistance furnace at 1000°C for 2 h. The X-ray diffraction pattern obtained on a Rigaku Ultima 4 instrument for the spinel after the treatment is 96.3 wt.\% MgAl\(_2\)O\(_4\), 1.9 wt.\% Al\(_2\)O\(_3\), and 1.8 wt.\% MgO. The specific surface of MgAl\(_2\)O\(_4\) is 24.55 m\(^2\)/g, and the average particle size \( d_{av} \) (BET) is 41 and 65 nm for Al\(_2\)O\(_3\) and MgAl\(_2\)O\(_4\), respectively.

A composite material was prepared from a mixture of the RPNP and iron powders to introduce RPNP into a liquid melt. An analysis of the iron powder (high-purity grade OSCh 6-2) showed the presence of 80\% particles 15–25 \( \mu \)m in size. The composite material Fe(97.5 wt.\%)+RPNP(2.5 wt.\%) was prepared in a Fritsch Pulverisette 6 planetary mill for 1 h in an argon medium. After treatment, the mixture of powders was subjected to uniaxial pressing under a pressure of 35 MPa with degassing at 300°C in argon and in vacuum followed by storage in vacuum at 25°C (for details, see [25]).

Model Fe-Sb, Fe-Sn and Fe-Cu alloys were melted in a vacuum resistance furnace with a graphite heater in a 46 ml corundum crucible at \( P(He+10%H_{2})=0.1 \) MPa. Heterophase interaction was investigated in a vacuum induction furnace (VIF), which has a special conical inductor that provides intensive mixing of the metal with RPNP both on the surface and inside the melt. The experiments were carried out at \( P(He+10%H_{2})=0.2 \) MPa (for details, see [16]). After the metal was melted completely, it was held for 2 min to achieve equilibrium with the gas phase. Then, the composite material (Fe+RPNP) was introduced into the liquid metal followed by the isothermal holding for 300–1200 s depending on the experimental conditions. The RPNP content in the melt after the addition of the composite material was 0.12 wt.\%. The contents of Sb, Sn, and Cu were determined using an Ultim 2 (Jobin Yvon) atomic emission spectrometer with an inductively coupled plasma with a sensitivity of 0.0005\%, and the oxygen content was determined by reducing melting on a TC 436 (LECO) analyzer with a sensitivity of 0.0002\%. Surface tension (\( \sigma \)) and melt density (\( \rho \)) were studied by the sessile drop method: a liquid metal drop was formed in a corundum conic cup (98% Al\(_2\)O\(_3\) plus TiO\(_2\) binder) in a vacuum resistance furnace with a graphite heater and a protective molybdenum tube. The system was pumped out to a residual pressure of 2·10\(^{-3}\) Pa, and a sample was heated to 1000°C after the system was graduated against the melting points of pure metals. The processes of sample melting and drop formation and an equilibrium drop position were detected with a Nikon D70 digital camera upon holding for 600 s when the temperature was changed by 10–15°C above the previous temperature up to 1750°C at \( P_{atm} = 0.1 \) MPa. The photographs were processed using the Drop software package (Laplace calculation) [26]. The theory and practice of the method were described in [27].

### 4. Results of heterophase interaction
More than 40 experiments with the following 8 types of alloys were conducted (wt.%): Fe-Sb (0.0950%); Fe-Sb (0.0950%) - Al₂O₃ (dₐv. = 41nm); Fe-Sn (0.0561%); Fe-Sn (0.0561%) - Al₂O₃ (41nm); Fe-Sn (0.0561%) - MgAl₂O₄ (65nm); Fe-Cu (0.0445%); Fe-Cu (0.0445%) - Al₂O₃ (41nm) and Fe-Cu (0.0445%) - MgAl₂O₄ (65nm), and the results were presented as the degree of removal of surfactants α = (([SAS]initial - [SAS]ending) / [SAS]initial) · 100, rel. %. The experimental results of the heterophase interaction of the RPNP with surfactants using the dependences [SAS] = f(τ), as well as the SAS content in melts without RPNP (special experiments) are shown in figure 1.

**Figure 1.** Dependence of SAS content on the duration of isothermal holding times in melts Fe-Sb (0.0950 wt.%) (a), Fe-Sn (0.0561 wt.%) (b) and Fe-Cu (0.0445 wt.%) (c) and extremum values of the degree of surfactant removal in these systems (d): 1 - Fe-SAS; 2 - Fe-SAS-Al₂O₃; 3 - Fe-SAS-MgAl₂O₄.

An analysis of the result showed that, firstly, the introduction of Al₂O₃ and MgAl₂O₄ RPNP at an isothermal holding time of 300-1200 s. led to a decrease in the content of SAS (Sb, Sn, and Cu), and the degree of removal was in the Fe-Sb system up to 30 rel. %, in the Fe-Sn system up to 29 rel. %, and in the Fe-Cu system up to 23 rel. %. Thermodynamic analysis of the removal processes and experimental data suggest that the recorded decrease is a result of heterophase interaction of RPNP with SAS and the removal of Fe+(RPNP-SAS) ensembles to the Mg-gas/ceramic interface. Secondly, data processing by the least squares method describing by polynomial function showed the presence of an extremum (see Figure 1) in the systems: Fe-Sb-Al₂O₃: [Sb] = 0.0882·4.48·10⁻⁵τ + 2.28·10⁻⁸τ² and R² = 0.64; Fe-Sn-Al₂O₃: [Sn] = 0.0549·2.61·10⁻⁵τ + 1.43·10⁻⁶τ² and R² = 0.94; Fe-Sn-MgAl₂O₄: [Sn] = 0.0551·3.80·10⁻⁵τ + 2.30·10⁻⁸τ² and R² = 0.96; Fe-Cu-Al₂O₃: [Cu] = 0.0440·1.65·10⁻⁵τ + 0.97·10⁻⁴τ² and R² = 0.94; Fe-Cu-MgAl₂O₄: [Cu] = 0.0440·2.13·10⁻⁵τ + 1.13·10⁻⁸τ² and R² = 0.95. The presence of extremum of the equations can serve as evidence of possible processes of surfactant desorption in the melt. Thirdly, a comparison of the dependences after the introduction of Al₂O₃ and MgAl₂O₄ RPNP shows that in all cases the introduction of MgAl₂O₄ leads to a higher degree removal of SAS. This indicates either the higher adsorption properties of spinel, which was indirectly noted in [17], or the
dissociation of spinel nanoparticles into oxides with a surface energy different from the energy of individually introduced exogenous oxides. The extremum values of the functions $[SAS]=f(\tau)$ were determined, which indicate general dependencies of the adsorption/desorption mechanism of metal refining from SAS, and presented them as a histogram in figure 1d. The results showed that $\alpha$ depends on the surface-active properties of investigated nonferrous metal impurities, which probably indicates correlation of the processes of redistribution of nanoparticles and ensembles in a liquid metal with the surface-active properties of the studied impurity. To support the existence of an adsorption mechanism of the removal of RPNP from a metallic melt, we calculated the particle velocities under adsorption forces. Our calculation is based on the diffusion phoresis mechanism proposed and experimentally proved in [28]. This mechanism describes the motion of particles in the concentration gradient field induced by a surface tension gradient. Calculation is presented in detail in [29]. We found that the velocity induced by adsorption forces is equal to $v_a = 6.21 \times 10^{-5}$; $5.86 \times 10^{-5}$ and $4.43 \times 10^{-5}$ m/s for binary systems Fe-Sb, Fe-Sn and Fe-Cu, respectively. The gravitational component of the velocity that appears because of the difference between the densities of the disperse and dispersion phases was estimated, and the value $v_g = 2.01 \times 10^{-9}$ m/s. A comparison of the obtained rates shows that the determining role of the surface phenomena when nanoparticles move in the melt is evident at a difference of four orders of magnitude between the rates under the effect of the adsorption and gravitation forces. In this regard, the effect of the surface properties of impurities and hypothetical ensembles on the change in the structural properties of the melt was investigated.

5. The results of determining the surface tension and density of the melt

The surface tension ($\sigma$) and melt density ($\rho$) were studied after heterophase interaction during melting in a VIF with various isothermal holding times. We studied 7 types of materials: 1 - Fe, 2 - Fe-SAS (Sb, Sn, Cu), 3 - Fe-Sb-Al$_2$O$_3$, 4 - Fe-Sn-Al$_2$O$_3$, 5 - Fe-Sn-MgAl$_2$O$_4$, 6 - Fe-Cu-Al$_2$O$_3$ and 7 - Fe-Cu-MgAl$_2$O$_4$. The oxygen content in all systems was 0.0065-0.0082 wt.%. The experimental results are approximated by least squares method, and the results are presented in table 2 (see $\sigma = f(T)$ and $\rho = f(T)$, where $\sigma$ in mN/m, $\rho$ in g/cm$^3$, $T$ in K). Using the data on the melt densities for the experiments of all series, we estimated the degree of loosening when the temperature was increased by 100°C; to this end, we calculated parameter $\beta = (\rho^{1823} - \rho^{1923})/\rho^{1823} \cdot 100$, rel %.

An analysis of the data of the first and second series of experiments, presented in figure 2a, shows that, firstly, the introduction of low concentrations of Sb, Sn, or Cu into the melt leads to a decrease $\sigma$ at 1873 K (1647, 1439, 1534, and 1584 mN/m for Fe, Fe-Sb(0.0548 wt.%), Fe-Sn(0.0548 wt.%) and Fe-Cu(0.0445 wt.%), respectively). This confirms that even at low concentrations of antimony, tin and copper possess surface-active properties in metallic iron melts. Secondly, there is satisfactory agreement between the values of $\sigma$ and $\rho$ of pure iron and binary systems with published data (for details, see [14, 15]), which indicates the reliability of the results.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Temperature dependences of the surface tension of melts: 1-1 - Fe; 2-1 - Fe-Sb; 2-2 - Fe-Sn; 2-3 - Fe-Cu; (7-1 - 7-3) - Fe-Cu-MgAl$_2$O$_4$ (for details, see table 2).
Table 2. The measurement results of $\sigma$ and $\rho$ of the systems Fe, Fe-(Sb, Sn, Cu) and Fe-(Sb, Sn, Cu)-(Al$_2$O$_3$, MgAl$_2$O$_4$) depending on the type of RPNP and on the holding times in the VIF.

| No. | System      | $\tau^a$, min | [SAS]$^b$, $\cdot 10^4$, wt. % | $\sigma = f(\mathbf{T})$ | $R^2$ | $\sigma^{1873K}$, mN/m | $\rho = f(\mathbf{T})$ | $R^2$ | $\rho^{1873K}$, g/cm$^3$ | $\beta^b$, rel. % |
|-----|-------------|----------------|---------------------------------|--------------------------|-------|--------------------------|-------------------------|-------|-----------------------------|----------------|
| 1-1 | Fe          | 20             | 2027-0.203                      | 0.79                      | 0.79  | 8.871-0.00102T            | 0.82                    | 6.96  | 1.45                        |
| 2-1 | Fe-Sb       | 20             | 881                             | 1905-0.249T               | 0.85  | 7.683-0.00052T            | 0.78                    | 6.71  | 0.77                        |
| 2-2 | Fe-Sn       | 20             | 548                             | 1963-0.229T               | 0.81  | 7.966-0.00057T            | 0.80                    | 6.90  | 0.82                        |
| 2-3 | Fe-Cu       | 20             | 445                             | 2037-0.242T               | 0.74  | 7.990-0.00056T            | 0.93                    | 6.94  | 0.80                        |
| 3-1 | Fe-Sb-Al$_2$O$_3$ | 5        | 590                             | 2116-0.258T               | 0.73  | 8.789-0.00079T            | 0.90                    | 7.31  | 1.08                        |
| 3-2 | Fe-Sn-Al$_2$O$_3$ | 10     | 810                             | 1821-0.119T               | 0.70  | 7.740-0.00028T            | 0.87                    | 7.22  | 0.39                        |
| 3-3 | Fe-Sn-Al$_2$O$_3$ | 20     | 640                             | 1939-0.192T               | 0.75  | 8.576-0.00080T            | 0.85                    | 7.08  | 1.12                        |
| 3-4 | Fe-Sn-Al$_2$O$_3$ | 5      | 457                             | 1069-0.290T               | 0.74  | 8.071-0.00062T            | 0.84                    | 6.91  | 0.89                        |
| 4-2 | Fe-Sn-MgAl$_2$O$_4$ | 10     | 453                             | 1176-0.188T               | 0.72  | 9.059-0.00114T            | 0.75                    | 6.92  | 1.23                        |
| 4-3 | Fe-Cu-MgAl$_2$O$_4$ | 15     | 445                             | 145,1+0.770T              | 0.92  | 7.883-0.00051T            | 0.80                    | 6.93  | 0.73                        |
| 4-4 | Fe-Cu-MgAl$_2$O$_4$ | 20     | 433                             | 1834-0.195T               | 0.68  | 8.332-0.00074T            | 0.89                    | 6.95  | 1.06                        |
| 5-1 | Fe-Sn-MgAl$_2$O$_4$ | 5      | 436                             | 87.9+0.779T               | 0.92  | 8.519-0.00085T            | 0.90                    | 6.93  | 1.22                        |
| 5-2 | Fe-Sn-MgAl$_2$O$_4$ | 10     | 405                             | 665.5+0.502T              | 0.81  | 7.901-0.00060T            | 0.83                    | 6.78  | 0.88                        |
| 5-3 | Fe-Cu-MgAl$_2$O$_4$ | 15     | 416                             | -632.6+1.140T             | 0.88  | 8.458-0.00085T            | 0.80                    | 6.87  | 1.23                        |
| 5-4 | Fe-Cu-MgAl$_2$O$_4$ | 20     | 415                             | -634.7+1.156T             | 0.97  | 8.684-0.00096T            | 0.88                    | 6.89  | 1.38                        |
| 6-1 | Fe-Cu-Al$_2$O$_3$ | 5      | 389                             | 554.2+0.521T              | 0.88  | 8.558-0.00098T            | 0.86                    | 6.72  | 1.45                        |
| 6-2 | Fe-Cu-Al$_2$O$_3$ | 10     | 379                             | 485.8+0.565T              | 0.89  | 8.409-0.00085T            | 0.87                    | 6.82  | 1.24                        |
| 6-3 | Fe-Cu-Al$_2$O$_3$ | 20     | 378                             | 234.1+0.719T              | 0.85  | 8.481-0.00088T            | 0.85                    | 6.83  | 1.28                        |
| 7-1 | Fe-Cu-MgAl$_2$O$_4$ | 5      | 377                             | 373.1+0.616T              | 0.86  | 7.714-0.00066T            | 0.88                    | 6.48  | 1.01                        |
| 7-2 | Fe-Cu-MgAl$_2$O$_4$ | 10     | 349                             | 312.4+0.576T              | 0.90  | 7.615-0.00054T            | 0.76                    | 6.59  | 0.83                        |
| 7-3 | Fe-Cu-MgAl$_2$O$_4$ | 20     | 340                             | 293.0+0.610T              | 0.91  | 7.599-0.00061T            | 0.85                    | 6.46  | 0.94                        |

$^a$ - holding times in the VIF; $^b$ - loosening of a melt.

An analysis of experiments with Fe-SAS-Al$_2$O$_3$ and Fe-SAS-MgAl$_2$O$_4$ melts after the introduction of RPNP showed, firstly, the fact of the inversion of $\partial\sigma/\partial T$ values in the metal, which, unlike the metal without RPNP, indicates a significant change in surface properties melts. Figure 2b shows the typical effect of the MgAl$_2$O$_4$ RPNP on the change in the surface tension of the Fe–Cu system. Secondly, there is a multidirectional change in the values of $\sigma$ at 1873K: in the Fe-Sb system is observed an increase $\sigma$ by 9.7–13.5 rel.%; in the Fe-Sn system – a change in values from -5.1 to +4.2 rel. %, and Fe-Cu – decrease in $\sigma$ by 0.2–12.2 rel.%. This indicates different nature of the ensembles on the surface of melt depending on the surfactant.

To compare the behavior of Sb, Sn, Cu, and RPNP, the values of the temperature coefficient $\partial\sigma/\partial T$ on the exposure time in a VIF in the study of heterogeneous interaction are presented in Figure 3. Firstly, the multidirectional effect of surfactant-NMI on $\partial\sigma/\partial T$ values was found: unlike temperature dependences of the Fe-Sn-RPNP and Fe-Cu-RPNP systems, where the facts of temperature coefficient inversion are observed, this does not occur in the Fe-Sb-Al$_2$O$_3$. Secondly, a different rate of change in the values of $\partial\sigma/\partial T$ is recorded with an increase in the holding times in the VIF, depending on the nature of the RPNP. In the Fe–Sb system is observed a change the values of $\partial\sigma/\partial T$ from -0.258 to -0.192 after the introduction of Al$_2$O$_3$; in the Fe-Sn system – a decrease from +0.290 to -0.195 and an increase from 0.779 to 1.156 after entering Al$_2$O$_3$ and MgAl$_2$O$_4$ RPNP, respectively; in the Fe-Cu system – an increase from 0.521 to 0.719 and a slight change from 0.616 to 0.610 after the introduction of Al$_2$O$_3$ and MgAl$_2$O$_4$ RPNP, respectively. This may be due to the formation of complex ensembles (Fe$_x$+(RPNP$_y$-SAS$_z$)) with long holding times that have different effects on the change in the structure of the surface layer.
The multidirectional effect of RPNP is also observed in analysis of the melt density. Taking for comparison the arithmetic mean of \( \rho \) at 1873 K for experiments with different holding times in the VIF, it was determined that in the Fe-Sb system is observed an increase \( \rho \) of 7.3 rel. % after entering Al\(_2\)O\(_3\). In Fe-Sn and Fe-Cu systems is observed a decrease \( \rho \) by 2.1 and 2.2 rel. % after entering Al\(_2\)O\(_3\) and 3.1 and 6.2 rel. % after entering MgAl\(_2\)O\(_4\), respectively. It can be assumed that, as a result of adsorption of impurity atoms on the surface of nanoparticles, there is a change in the cluster structure [30] both in the metal volume and at the nanoparticle – melt interface. Antimony, tin and copper, having different surface-active properties in iron and different bonding forces with iron atoms, as a result of the formation of ensembles, have different effects on the change of the metal cluster structure. Moreover, in Fe-Sn and Fe-Cu systems, higher values are observed in experiments after entering MgAl\(_2\)O\(_4\), which indicates high adsorption properties of spinel compared to Al\(_2\)O\(_3\), which is also observed in studies of the heterophase interaction of RPNP with SAS.

![Figure 3. Dependence of \( \partial \sigma / \partial T \) values on the nature of the RPNP and the holding times in the VIF (No. see table 2).](image)

![Figure 4. The dependence of the degree of loosening on the nature of the RPNP and the holding time in the VIF (No. see table 2).](image)
The phenomenon of loosening (compression / decompression, see $\beta$ in Table 2 and in Figure 4) was examined. In Figure 4 shows a histogram of changes in the degree of loosening of $\beta$ depending on the nature of the RPNP and the holding time of the melt in the VIF. It can be seen that in the Fe-Sb-Al$_2$O$_3$ and Fe-Cu-Al$_2$O$_3$ systems, the dependence $\beta = f(\tau)$ is characterized by a minimum extremum, and in similar experiments in the Fe-Sn-Al$_2$O$_3$ system the dependence $\beta = f(\tau)$ has a maximum extremum. In all systems a minimum extremum is observed after entering MgAl$_2$O$_4$. Moreover, in most cases, an increase in $\beta$ values (decompression) is observed. These dependences indicate different structures of the melts, which is possibly related to the different influence of the ensembles on the change in the cluster structure of the metal and requires further studies. Thus, due to the surface-active properties of surfactant-NMI in the iron melt as a result of its adsorption interaction with Al$_2$O$_3$ and MgAl$_2$O$_4$ RPNP, a significant change in the structural properties of liquid metal occurs, which affects on the behavior of ensembles in the melt and and their removal under the influence of adsorption nature forces on the M-phase interface.

6. Conclusions:

1. Based on the analysis of literature data, thermodynamic calculations on the dissociation of refractory compounds and the phenomena of wetting them with iron melts, were chose of refractory compounds Al$_2$O$_3$ and MgAl$_2$O$_4$ to study the interaction of these nanophases with Fe-Sb, Fe-Sn and Fe-Cu melts in reducing atmosphere.

2. The heterophase interaction of Al$_2$O$_3$ (41 nm) and MgAl$_2$O$_4$ (65 nm) nanoparticles with surfactant — antimony, tin and copper in Fe-Sb (0.0950 wt.%), Fe-Sn (0, 0561 wt.%) and Fe-Cu (0.0445 wt.%) model double melts was investigated. It was found that, depending on the nature of the nanoparticles and the holding time, the extremum values of the degree of surfactant removal were (rel.%):: Fe-Sb-Al$_2$O$_3$ — 30,3 %; Fe-Sn-Al$_2$O$_3$— 23,4 %; Fe-Sn-MgAl$_2$O$_4$— 29,8 %; Fe-Cu-Al$_2$O$_3$ — 16,8 % and Fe-Cu-MgAl$_2$O$_4$— 23,6 %.

3. The surface tension and density of Fe-(Sb, Sn, Cu) and Fe-(Sb, Sn, Cu)-(Al$_2$O$_3$, MgAl$_2$O$_4$) melts were studied by the sessile drop method and showed that in systems after the introduction of nanoparticles, in most cases, an inversion of the temperature coefficient is observed, as well as its multidirectional change depending on the nature of the nanoparticles and the holding time in the VIF. This indicates the influence of ensembles (Fe+(RPNP-SAS)) on the surface properties of melts. Decompression of Fe-Sn and Fe-Cu melts and compression of Fe-Sn melts after nanoparticles are introduced and the multidirectional character of the loosening dependences $\beta = f(\tau)$ indicates a possible change in the cluster structure of liquid metal.

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