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Phase composition and microstructure

of the doping alloy obtained by regenerative

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### IDENTIFYING THE FEATURES OF STRUCTURAL AND PHASE TRANSFORMATIONS IN PROCESSING THE WASTE OF METALLURGICAL PRODUCTS DOPED WITH REFRACTORY ELEMENTS

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1. Introduction

Large volumes of industrial waste and secondary raw materials doped with refractory elements are not used effectively enough in practice. Wastes of doped refractory, heat-resistant, and corrosion-resistant steel and alloy grades contain valuable elements such as Mo, W, Ni, Cr, Nb, Ti. In the agro-industrial complex, waste includes particles of

smelting of technogenic wastes were studied. This is necessary to determine technological characteristics that increase the degree of extraction of doping elements during the processing of technogenic raw materials and subsequent use of the alloying material. It was determined that at a Si:C atomic ratio in the charge at a level of 0.05-0.19 (O:C atomic ratio is 1.25), a solid solution of carbon and doping elements in  $\gamma$ -Fe, Fe<sub>3</sub>Si, and Fe<sub>5</sub>Si<sub>3</sub> was found in the alloy. At Si:C atomic ratio at a level of 0.05 in the alloy, a solid solution of carbon and alloying elements in y-Fe was dominating with a weak manifestation of Fe<sub>3</sub>Si. When the value of Si:C atomic ratio was increased to 0.09, Fe<sub>5</sub>Si<sub>3</sub> was found together with Fe<sub>3</sub>Si. A gradual increase in Si:C atomic ratio to 0.09, 0.12, and 0.19 led to a higher manifestation of Fe<sub>3</sub>Si and Fe<sub>5</sub>Si<sub>3</sub>. The microstructure of the alloy in the entire studied range of Si:C ratio values in the charge was characterized by the presence of several phases with different contents of doping elements. The content of elements in the studied areas (at. %) was 1.65-52.10 for Ni, 2.80-53.92 for Cr, 0.19-13.48 for Mo, 0.40-12.21 for W, 13.85-33.85 for Nb, 2.40-6.63 for Ti. An increase in Si:C atomic ratio in the charge from 0.05 to 0.19 caused an increase in silicon concentration in the studied areas of the microstructure (from 0.28 at. %) to 6.31 at. %. According to an analysis of the sample areas, carbon content was characterized by figures from 2.07 at. % to 14.23 at. %). Some of the investigated particles with a high content of W, Mo, Nb corresponded to complex carbide compounds with a high probability. Based on the study results, it can be pointed out that the most favorable Si C atomic ratio in the charge is 0.12 (with an O:C atomic ratio of 1.25). The resulting product had a relatively low content of silicon and carbon but was sufficient enough to provide the required reducing and deoxidizing strength of the alloy

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residues from knives of feed preparing machines. Oxide and fine waste products including grinding dust and scale form a significant share. The effective processing of such waste is complicated. This causes problems in ensuring product manufacturability and reasonable production price. Main alloying elements are present in these wastes in a form of complex oxide compounds. That is, the development of technological parameters of processing doped oxide waste creates the need to take into account the peculiarities of the complex interaction of the elements.

According to [1], the production of 1 t of rolled steel accounts for 0.043 t of scale and sludge. Metal losses during processing in fire stripping machines measure 5-15 %. Particle size in the processing of stainless corrosion-resistant steels with a nickel content of 19 wt. % is 240-450 µm. According to [2], with scale in the production of small-size commercial billets of high-alloy steels, at best, 12 % of the production volume is lost. According to [1], the amount of scale formation (in thousand tons) at metallurgical enterprises of the Ural Federal District (Russia) is 404.4 at Magnitogorsk Metallurgical Plant; 24.9 at Chelyabinsk Metallurgical Plant; 27.2 at Zavolzhsky Motor Plant; 1.0 at Chelyabinsk Tube Rolling Works; 2.1 at Uralskaya Kuznitsa OJSC.

The doped scale is used in the charge of electric furnaces [1]. The problem consists in that to increase the degree of assimilation of alloying elements by molten steel, it is necessary to perform pre-treatment of scale and other fine dispersed wastes. At the same time, there are additional problems in processing the oil-contaminated scale [3]. That is, before adding to the charge, it should be cleaned from harmful impurities. According to [2], when introducing fine waste of high-alloy steels into the puddle without prior preparation, burnout of refractory elements reaches 40 %.

Hence, reduction of doping element loss and introduction of resource-saving technologies when processing technogenic doped waste in metallurgical production are rather pressing problems. To solve these problems, it is necessary to expand the understanding of structural-phase transformations occurring during the recycling of oxide waste by reductive smelting.

#### 2. Literature review and problem statement

According to [4], Fe<sub>3</sub>C and carbon were found in the reduction products after the carbothermal treatment of iron scale together with the iron phase. Similar results with a manifestation of iron carbide were obtained in [5] during the reduction of carbon oxide waste of chromium and nickelcontaining steel. The presence of Fe<sub>3</sub>Si together with a solid solution of carbon and alloying elements in the  $\gamma$ -Fe lattice was found in [6] in the products of the reductive smelting of chromium and nickel-containing doped wastes with the participation of carbon and silicon. Among shortcomings, lack of studies on the physicochemical properties of reduction products including refractory elements such as W and Nb can be pointed out. The unsolved parts of the problem relate to the determination of the most favorable conditions for the recovery of doped technogenic raw materials in the Fe-Ni-Cr-Mo-W-Nb-O-C-Si system.

Reduction of  $FeO \cdot Cr_2O_3$  oxides at different C:Fe atomic ratios and temperatures from 1,373 K to 1,523 K was investigated in [7]. It was found that with an increase in atomic ratio C:Fe from 0.8 to 1.4, degree (%) of chromium extraction increased from 9.6 to 74.3, respectively. An increase in temperature to 1,523 K led to an increase in carbide formation. According to the results of [8], some carbon residue is inevitably present in the products of carbothermal reduction. In this case, residual carbon may be present in a form of carbide compounds. At C:Fe atomic ratios below 0.8, a significant decrease in the degree of chromium extraction and a decrease in carbide formation was observed. The formed chromium carbides were found dissolved in the iron phase [7]. A study of reduction reactions involving oxides and carbon in the Fe–Ni–O system at temperatures up to 1,373 K was performed in [9]. With an increase in processing temperature, reduction products appeared in the following sequence:

 $Fe_3O_4$ +NiO $\rightarrow$ Fe\_3O\_4+Ni $\rightarrow$ FeO+Fe<sub>x</sub>Ni<sub>y</sub> $\rightarrow$  $\rightarrow$ Fe<sub>x</sub>Ni<sub>y</sub>+Fe (Fe<sub>n</sub>C<sub>m</sub>).

That is, there was a relatively greater tendency to reduce nickel oxide than iron oxides. At some stages, the formation of metallic nickel and iron was observed. The possibility of the presence of iron carbides and iron and nickel-containing phase  $Fe_xNi_y$  which can also occur during the reduction of oxide alloyed waste was noted. The disadvantage is the lack of data on the reduction of complex oxide compounds which may be part of technogenic raw materials. This can lead to probable differences in the course of reduction reactions. Unsolved parts of the problem relate to expanding the notion of the nature of the presence of elements in the reduction products with integrated use of X-ray phase analysis, scanning electron microscopy, and X-ray microanalysis.

It was shown in [10] that reduction of oxides in the Mo–O–C system occurs with the transformation of molybdenum trioxide to dioxide and free molybdenum with the formation of carbides. The reduction process in the W-O-C system which was studied in [11] was also characterized by the formation of intermediate products:  $WO_{2,72}$  and  $WO_{2}$ . Tungsten dioxide was subsequently converted into tungsten metal and carbide component. Similar results are also given in [12]. The disadvantage is that the form of presence of molybdenum- and tungsten-containing compounds in the oxide waste of high-alloy steels can be more complex and differ from individual pure oxides. The unresolved parts of the problem include the determination of conditions for the reduction of oxide complex-doped raw materials to obtain products without compounds and phases prone to sublimation. This eliminates the need to create special conditions preventing evaporation and loss of refractory alloying elements with a gas phase.

In [13], a study of the influence of the O:C ratio in a charge on properties of the alloy obtained from a mixture of waste of refractory, heat-resistant, and corrosion-resistant steels and alloys is presented. It is noted that the most acceptable O:C mass ratio in the charge is 1.67. This provided a predominance of carbon and alloying elements in the phase composition of solid solution in  $\gamma$ -Fe with a relatively weak manifestation of residual carbon in a form of Fe<sub>3</sub>C. Phase formation in the Fe–Ni–Si system was studied in [14]. It was found that the FeSi and Fe<sub>3</sub>Si phases have relatively high solubility values for Ni in contrast to the FeSi<sub>2</sub> phase. Formation of Fe<sub>3</sub>Si silicide was found in the Fe–Cr–C–Si system in [15] in a coating of 45Fe39Cr6C10Si alloy. It follows from the results of [14, 15] that reduction of oxide waste

of alloy steels and alloys using silicon may be accompanied by the formation of iron silicides with dissolved alloying elements. The disadvantage is the inability to trace the impact of carbide and silicide formation of Mo, W, and other refractory elements that are present in a complex in the oxide waste of alloys and alloys on the reduction process. The unsolved parts of the problem include establishing the phase composition and microstructure of the reduction products of complex-alloyed refractory elements of technogenic raw materials when changing the silicon/carbon ratio in the charge.

The study of carbon recovery of non-doped technogenic waste in [4] should be mentioned. Iron phase, iron carbide, and carbon were found in the reduction products. Similar results were obtained in [5, 6] in the recovery of waste steels doped with carbon and silicon. Both iron carbides and silicide, together with a solid solution of carbon and alloying elements in the  $\gamma$ -Fe lattice were detected in the reduction products. In studies of the Fe-Cr-Ni-O-C system [7,9], the occurrence of the metal phase, carbides, and intermetallics should be noted. Fe<sub>x</sub>Ni<sub>y</sub> and Fe (Fe<sub>n</sub>C<sub>m</sub>) phases as well as chromium carbides were found. Reduction of individual oxides in Mo-O-C [10] and W-O-C [11, 12] systems determines the two-stage process. A decrease of higher oxides to lower ones with subsequent formation of metal and carbide components is observed. Formation of FeSi and Fe<sub>3</sub>Si found in studies of the Fe-Ni-Cr-O-C-Si system [14, 15] should be noted. However, phase composition and microstructure of the reduction products of technogenic raw materials complex doped with refractory elements when changing the silicon/carbon ratio in the charge were not found yet. At the same time, the use of X-ray phase analysis, scanning electron microscopy, and X-ray microanalysis would expand the idea of the nature of the presence of elements in the recovered material.

It is advisable to study features of the structural-phase composition of the doping alloy obtained by reduction smelting based on a mixture of doped technogenic waste by changing the silicon/carbon ratio in the charge. It is also necessary to determine conditions for the reduction of complex doped technogenic raw materials to obtain products without compounds and phases prone to sublimation. This can reduce losses of Cr, Ni, Nb, Mo, W by sublimation of oxide compounds during production and use of the reduced alloying material.

#### 3. The aim and objectives of the study

The study objective was to identify features of structural and phase changes in processing metallurgical technogenic waste doped with Cr, Ni, Mo, W, Ti, Nb in obtaining a doping alloy by reduction smelting. This is necessary to increase the degree of extraction of doping elements in the process of processing technogenic raw materials and subsequent use of the alloy during doping.

To achieve this goal, the following tasks were set:

 to determine the phase composition of an alloy obtained using doped technogenic waste when changing the silicon/carbon ratio in the charge;

– to study the features of microstructure and chemical composition of individual phase formations of the alloy based on the doped waste with different silicon/carbon ratios in the charge using scanning electron microscopy and X-ray microanalysis.

### 4. Materials and methods used in studying the properties of the obtained alloy

### 4.1. Materials and equipment used in the experiment

A mixture of the scale of chromium-nickel steels of 18-10 type and chips formed in grinding heat-resistant alloys based on nickel EI893 and EP709 at facilities of metallurgical production was used as a raw material. Carbon in a form of ultrafine dust taken from a carbon and graphite production facility (carbon content: 98 wt. %) was used as a reducer. Its addition provided an O:C mass ratio in the charge at a level of 1.67 (the atomic ratio was 1.25, respectively). Variation in the amount of silicon in the alloy was ensured by adding FS-65 grade ferrosilicon to the charge with the regulation of Si:C mass ratio in the charge within 0.12–0.45 (atomic ratio of 0.05-0.19, respectively). The addition of metal chips provided an intensification of heat transfer at the initial stages of heating the charge and an additional increase in doping degree. The study samples were smelted in alundum crucibles placed in an indirect heating furnace with a coal lining. Smelting temperature was 1,873–1,913 K. Alundum crucibles together with the alloy were removed from the furnace after smelting and cooled at ambient temperature.

X-ray phase analysis of the samples was performed using the DRON-6 diffractometer (Russian Federation).

Images of microstructure and chemical composition of individual areas of the sample surface were obtained using a JSM 6360LA scanning electron microscope equipped with an X-ray microanalysis system JED 2200 manufactured by JEOL (Japan).

### 4. 2. The procedure used in the experiments and determination of indicators of sample properties

The phase composition of the samples was determined by X-ray phase analysis using monochromatic radiation of Cu K<sub> $\alpha$ </sub> ( $\lambda$ =1.54051 Å). Measurements were performed at the tube voltage U=40 kV and anode current I=20 mA. The composition of the phases was determined using a set of PDWin 2.0 programs (Russia). In order to present the most pronounced indicative diffraction maxima in the study, areas of diffractograms with angle intervals of 20 within 40 to 50 degrees were selected and presented.

Microstructural studies of the samples were performed at an accelerating voltage of 15 kV. The electronic probe diameter was 4 nm. The phase composition was determined by a non-standard method of calculating the fundamental parameters.

### 5. The results obtained in the studies of properties of the obtained doping alloy

### 5. 1. Determination of features of phase composition of the alloy at different Si:C ratio in the charge

The phase composition of the alloy with Si:C atomic ratio in the charge of 0.05 consisted mainly of a solid solution of alloying elements and carbon in  $\gamma$ -Fe with a manifestation of Fe<sub>3</sub>Si of relatively low intensity (Fig. 1, *a*). At Si:C atomic ratio in the charge of 0.09, the manifestation of Fe<sub>5</sub>Si<sub>3</sub> and some increase in the intensity of Fe<sub>3</sub>Si were observed. At Si:C atomic ratio of 0.12–0.19 in the charge, a decrease in manifestation of the solid solution of alloying elements and carbon in  $\gamma$ -Fe and an increase in the intensity of the diffraction maxima of Fe<sub>3</sub>Si and Fe<sub>5</sub>Si<sub>3</sub> were found. Fe<sub>3</sub>C carbide as well as carbides of doping elements in the entire studied range of Si:C ratios were manifested in fragments with a relatively low intensity of diffraction maxima approaching the background level.



Fig. 1. X-ray phase studies of the doping alloy with different Si:C atomic ratios in the charge at O:C atomic ratio of 1.25 and the corresponding images of microstructure with magnification  $\times$ 1,500: *a* – areas of diffractograms; *b* – 0.05; *c* – 0.12; *d* – 0.19; 1–12: areas of X-ray microanalysis of samples

## 5. 2. Study of the microstructure of the doping alloy with different Si:C ratios in the charge

Inclusions with a relatively high content of Nb, W, Mo, and Ti (Fig. 1, 2, Table 1, points 1, 7, 10) were found in the studied samples with various Si:C ratios in the charge. Irregular phase formations with increased content of W and Mo at the level of 3.69–10.21 at. % and 4.02–9.63 at. %, respectively (Fig. 1, Table 1, points 3, 8, 9) were found as well. With a gradual increase in Si:C atomic ratio in the charge from 0.05 to 0.19, there was an increase in the particle number and size of the above phases. There was also an increase in silicon content at the studied points from 0.28 at. % up to 6.31 at. %. Carbon content was from 2.07 to 14.23 at. % in the studied points of the alloy surface.



Fig. 2. Spectrograms of some of the studied areas of X-ray microanalysis of the samples, respectively, Fig. 1: a-5; b-6; c-7; d-8

Determination of element concentrations in the studied area of the sample surface indicates a clear distribution between phases differing in the content of Cr and Ni (Fig. 3, b, c). The Fe content is relatively uniform throughout the studied area (Fig. 3, a), except for inclusions with niobiumcontaining phases (Fig. 3, e). W and Mo, like Nb, were mainly concentrated in individual inclusions (Fig. 3, d, e).

Table 1

The results of X-ray microanalysis of the doping alloy, respectively, Fig. 1

Analysis points	Element content, at. %										
	С	Si	Ti	Cr	Mn	Fe	Ni	Nb	Mo	W	Total
1	14.32	0.00	2.40	12.52	0.00	10.96	1.65	33.85	13.44	10.86	100
2	6.29	0.00	0.00	41.22	0.00	46.50	4.64	0.00	0.61	0.75	100
3	6.76	0.00	0.00	6.63	0.00	50.10	1.68	0.00	9.63	10.21	100
4	2.07	0.28	0.00	3.97	0.00	53.36	39.60	0.00	0.19	0.53	100
5	2.26	4.00	0.00	2.80	0.73	52.49	37.06	0.00	0.26	0.40	100
6	4.92	0.00	0.00	45.98	0.00	43.68	3.97	0.00	0.69	0.75	100
7	14.23	0.00	5.73	14.39	0.00	19.14	6.96	13.85	13.48	12.21	100
8	9.15	0.00	0.00	6.53	0.73	45.24	30.63	0.00	4.02	3.69	100
9	6.57	0.00	0.00	11.03	0.81	33.33	39.07	0.00	4.87	4.33	100
10	14.25	0.00	6.63	13.58	0.00	13.39	5.00	21.70	13.52	11.93	100
11	2.54	6.31	0.00	4.38	0.53	32.98	52.10	0.00	0.25	0.91	100
12	8.87	0.00	0.00	53.92	0.00	29.58	5.69	0.00	0.93	1.01	100



Fig. 3. The results of X-ray microanalysis in the mode of distribution of main elements in characteristic X-rays, respectively, Fig. 1, c (magnification ×1500). A more intense color corresponds to larger element content: a - Fe; b - Ni; c - Cr; d - Mo; e - W; f - Nb

### 6. Discussion of the results obtained in studying the properties of technogenic raw materials and the obtained doping alloy

Phase analysis of an alloy with different Si:C ratios in the charge (Fig. 1) indicates that the alloying elements and carbon were mainly in a solid solution in the  $\gamma\text{-}\text{Fe}$  lattice which is consistent with the results of [5]. Some of the alloying elements may be substitutional atoms in Fe<sub>3</sub>Si and Fe<sub>5</sub>Si<sub>3</sub> compounds. This is consistent with the results of [6, 15] where the formation of iron silicide Fe<sub>3</sub>Si was found. There is also a correspondence with studies [14] which pointed out relatively high solubility of Ni in the Fe<sub>3</sub>Si phase. However, Fe<sub>5</sub>Si<sub>3</sub> was not detected in the materials studied in the above works [14]. FeSi and FeSi2 silicides were additionally manifested in the study. The absence of clear manifestation of diffraction maxima of compounds of refractory metals Mo, W, Nb cannot indicate the complete absence of such compounds in the studied samples. Moreover, some local phase formations have a relatively high content of such elements (Fig. 1, Table 1, points 1, 7, 10) and, probably, may contain compounds of refractory metals. These results are probably due to the fact that the quantitative component of refractory metal compounds is relatively small. Therefore, diffraction maxima of manifestation of refractory metal compounds have a relatively low intensity close to the background level.

The microstructure study in combination with X-ray microanalysis of the obtained alloy additionally indicates the concentration of atoms of alloying elements in Fe<sub>3</sub>Si and Fe<sub>5</sub>Si<sub>3</sub> and in the  $\gamma$ -Fe lattice (Fig. 1, Table 1). It should be noted that some of the studied areas of the sample surface had a high content of carbon and chromium (Fig. 1, 2, Table 1, points 2, 6, 12) which may indicate local areas of the presence of complex chromium and iron-containing carbides. This is consistent with the data of [7] which describes the course of carbide formation in the iron and chromium-containing oxide system in parallel with reduction. In addition, this is indicated by the results of [8] which states that due to carbide formation, it is unlikely to obtain a completely carbon-free reduction product in practice. Some local part of the carbide component after formation can be dissolved in

the  $\gamma$ -Fe lattice at the contact of two phases, as evidenced by the studies performed in [7]. The investigated areas of microstructure with phase formations having a relatively high content of nickel (Fig. 1, Table 1, points 4, 5, 11) can be a solid solution of alloying elements and carbon in γ-Fe. This is in good agreement with the results of [13] in which the distribution of elements between phases was similar after the reductive smelting of doped waste. Additionally, confirmation of reduction efficiency of the iron-nickel component in the Fe-Ni-O-C system was obtained in [9] where reduction products were characterized by the presence of Fe<sub>x</sub>Ni<sub>y</sub> and Fe  $(Fe_nC_m)$  phases. However, in contrast to [9, 13], the studies conducted with carbon in the reduction process involved silicon which affected the nature of transformations, microstructure, and phase composition. For example, with a gradual increase in Si:C atomic ratio in the charge from 0.05 to 0.12 and 0.19, residual silicon content at. % at the above points increased from 0.28 to 4.00 and 6.31, respectively. The concentration of residual silicon in the nickel-enriched phase should be pointed out (Fig. 1, Table 1).

Based on the obtained images of elements distribution in characteristic X-rays (Fig. 3, d, e), tungsten, molybdenum, and niobium in a certain amount were concentrated in local particles. The relatively high carbon content (Fig. 1, Table 1) indicates the carbide nature of such phase formations. That is, the presence of refractory metal carbide compounds in the studied samples is quite possible, however, the number of such formations is probably relatively small for a clear manifestation on the diffractograms relative to the background level. This is consistent with the results of a study in which the course of carbide formation during the reduction of carbon oxides of molybdenum [10] and tungsten is noted [11, 12]. However, the recovery of technogenic waste doped with several refractory elements is somewhat more complex. The complex content of refractory elements in the formed inclusions was traced which may indicate the presence of complex carbide compounds with the participation of refractory alloying elements.

The obtained samples do not contain compounds and phases with a relatively high tendency to sublimation. That is, there is no need to create special conditions that prevent evaporation and loss of alloying elements with a gas phase. This also leads to an increase in the use of alloying elements.

It follows from the study results that the most acceptable Si:C atomic ratio in the charge is 0.12 (the mass ratio of 0.29, respectively). In this case, the reduction is provided with a predominance in the phase composition of a solid solution of carbon and alloying elements in  $\gamma$ -Fe and a manifestation of residual silicon in a form of a silicic component. The content of residual carbon and silicon was relatively low and sufficient to provide the necessary reduction and deoxidizing ability in the use of the alloy. The alloy performance provides the possibility of replacing some of the standard ferroalloys in the smelting of steels which have some restrictions on silicon and carbon content. From this point of view, heat-resistant steels of the austenitic class have a good perspective.

Some limitations in the alloy use are explained by complex alloying ability. This is because of the need to select certain grades of steels similar in content to the alloying elements for their alloying. Problems can arise when one or more components of the alloy are strictly limited in the target product and can lead to exceeding permissible limits of the elements in the composition. To avoid such problems and ensure relatively high cost factors, it is necessary that the content of elements in the alloy and the target product was close.

The study disadvantages include a lack of images of microstructure with varying magnification. This would give better visualization when familiarizing with the microstructure features.

Development of this direction is possible in the course of involvement of other classes of steels and alloys for processing doped waste by the method of reductive smelting. Also, a much deeper study of the phase structure in obtained alloys concerning the form of presence of refractory metals is possible in future studies within the frames of further development. Difficulties in trying to develop this study related to the lack of a sufficient experimental base.

Positive results were obtained in experimental-industrial steel smelting in an electric arc furnace when using a complex doping alloy based on metallurgical Cr and Ni containing waste as a charge additive. Partial replacement of standard ferroalloys was provided by a discharge coefficient of 270–330 kg/t of steel. Burnout of alloying elements has decreased by 3–4 wt. %. When using the doping alloy, the consumption of nickel and chromium was reduced by 27–31 wt. % and 25–29 wt. %, respectively [5].

Simultaneously, ecological tension and environmental pollution of industrialized regions were reduced with processing the technogenic metallurgical waste and its return to production.

#### 7. Conclusions

1. It was determined that there are such phases in the alloy as a solid solution of alloying elements and carbon in  $\gamma$ -Fe, Fe<sub>3</sub>Si, and Fe<sub>5</sub>Si<sub>3</sub> at Si:C atomic ratio in the charge in the range of 0.05–0.19 (O:C atomic ratio is 1.25). In the case where the Si:C atomic ratio was 0.05, phase composition mainly consisted of a solid solution of alloying elements and carbon in  $\gamma$ -Fe with a manifestation of Fe<sub>3</sub>Si. The gradual increase of Si:C atomic ratio in the charge up to 0.09, 0.12, and 0.19 resulted in an increase in Fe<sub>3</sub>S manifestation. At values of Si:C atomic ratio in the charge from 0.09 and above, Fe<sub>5</sub>Si<sub>3</sub> took place in the diffraction patterns. Fe<sub>3</sub>C has manifested itself fragmentarily with relatively low intensity.

2. The alloy microstructure at different Si:C ratios in the charge had a clear manifestation of several phases with different contents of main alloying elements. Content of elements in the studied areas (at. %) was 1.65–52.10 for Ni, 2.80–53.92 for Cr, 0.19–13.48 for Mo, 0.40–12.21 for W, 13.85–33.85 for Nb, 2.40–6.63 for Ti. A gradual increase in Si:C atomic ratio in the charge from 0.05 to 0.19 has led to an increase in the silicon content in the studied areas of the samples from 0.28 at. % to 6.31 at. %. The carbon content was 2.07 at. % up to 14.23 at. %. Local phase formations with a high content of W, Mo, Nb, and C which can be complex carbide compounds, have been revealed.

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This paper reports the analytical and experimental studies aimed at designing and modeling fluoropolymer anti-friction materials. The optimal ratios of the total surface of polymer particles to the total surface of filler particles for different brands of fluoropolymer-4 have been determined, as well as the critical concentrations of the modifiers of fluoropolymer anti-friction materials. The calculations of antifriction carboplastics' elasticity modules indicate the existence of adhesion between carbon fiber and polytetrafluoroethylene. When constructing composites that combine high durable and tribotechnical characteristics, it is advisable to combine modifiers with different dispersion and polymer-oligomeric matrices, which enables the implementation of the principle of multilevel modifying. It has been established that the adhesion between carbon fiber and polytetrafluoroethylene can be improved by applying a fluoropolymer coating onto the surface of carbon fibers or by modifying with zirconium oxide nanopowders. The binary fluoropolymer matrix applied to the surface of carbon fiber can be used as an effective base for composite materials. This study has demonstrated that filling polytetrafluoroethylene (PTFE) with coke, carbon fibers (18-19.5 % by weight), and zirconium oxide nanopowders in the amount of up to 2 % by weight produces materials with high mechanical characteristics and durability. It has been shown that the existence of an oligomer component improves the thermodynamic compatibility at the interface and promotes the plasticization of the PTFE boundary layers. Molecular structure with a certain orientation of coke and carbon fiber in the interphase areas is inherent in the materials with improved physical and mechanical properties

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Keywords: anti-friction materials, composite, durability, fluoropolymer coatings, nanopowder, zirconium oxide, carboplastics

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# DESIGN AND STUDY OF NANOMODIFIED COMPOSITE FLUOROPOLYMER MATERIALS FOR TRIBOTECHNICAL PURPOSES

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### 1. Introduction

The development of technology for the development and creation of polymeric composite materials based on polytetrafluoroethylene (PTFE) has for a long time been based mainly on empirical research, due to the complexity of interphase interactions in the multicomponent polymeric composite systems. The combination of theoretical research into the structural and phase transformations occurring during the introduction of fillers to the composite's fluoro-