

Досліджено фізико-хімічні властивості сплаву, отриманого за допомогою відновлювальної плавки з використанням відходів виробництва високолегованих сталей та сплавів. Це необхідно для визначення технологічних аспектів, що забезпечують зниження втрат легуючих компонентів під час отримання та використання легуючого сплаву. Результати досліджень вказують, що при співвідношенні кисню до вуглецю в шихті 2,25 сплав складався в основному з твердого розчину легуючих елементів в γ -Fe. При співвідношенні кисню до вуглецю в шихті на рівні 1,67 додатково прослідковувався Fe_3C з подальшим підвищенням інтенсивності прояву карбиду при співвідношенні кисню до вуглецю 1,19. На фотографіях мікроструктури чітко проявлялися декілька фаз з різним співвідношенням легуючих елементів. Вміст Ni у досліджених ділянках різних фаз змінювався в межах 1,38–46,38 % мас., Cr – 3,45–45,32 % мас., W – 1,51–27,32 % мас., Mo – 0,48–10,38 % мас. Mo, W, Nb в більшій мірі концентрувалися в окремих частках. Вміст Nb в деяких включеннях досягав 47,62 % мас. Аналіз результатів досліджень показав, що найбільш вигідним співвідношенням кисню до вуглецю в шихті є 1,67. При цьому переважання у фазовому складі має твердий розчин легуючих елементів в γ -Fe. Частка залишкового вуглецю, що знаходилася у вигляді карбідної складової, мала значення в межах значення в межах 0,52–2,32 % мас., при цьому забезпечуючи необхідну відносну здатність під час використання сплаву. Проведені дослідження визначили нові технологічні аспекти переробки високолегованих техногенних відходів щодо отримання сплаву з відносно невисоким залишковим вмістом вуглецю. Отримані параметри ресурсозберігаючого легуючого матеріалу забезпечують можливість заміни частинки стандартних феросплавів щодо виплавки сталей з деякими обмеженнями по вмісту вуглецю.

Ключові слова: оксидні техногенні відходи, окалина легованих сталей, відновна плавка, рентгенофазові дослідження

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FEATURES OF THE PHASE AND STRUCTURAL TRANSFORMATIONS IN THE PROCESSING OF INDUSTRIAL WASTE FROM THE PRODUCTION OF HIGH-ALLOYED STEELS

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1. Introduction

One of the alternative sources to obtain doping materials is the processing and return to production of doped

anthropogenic waste the large volumes of which are not used in practice effectively enough. The waste of doped heat-stable, heat-resistant, corrosion-resistant, as well as other grades of steel and alloys, whose utilization can

be accompanied by the influence of aggressive environments, temperature, and mechanical factors, contains expensive elements. These include Ni, Cr, W, Mo, and others. These materials are widely used in all sectors of the national economy – from the aviation industry to the agricultural sector (for example, wearable blades in agricultural production). The specific feature of the waste is the presence of doping elements in the form of oxide and complex compounds. This necessitates taking into consideration the complex nature of the physical and chemical interaction between elements in the development of technological processing conditions. A significant part is the oxide and finely-dispersed waste (scale, grinding dust), whose efficient processing is complicated, which negatively affects the technology of production and the cost of production.

According to work [1], the production of 1 ton of rolled steel yields 0.043 tons of scale and sludge. The loss of metal in the processing at fire stripping machines reaches 5–15 %. The size of particles in the treatment of stainless corrosion-resistant steels with the content of Ni of 19 % is equal to 240–450 μm . According to study [2], 12 % of the production volumes are lost, at best, because of the scale, at small-grade manufacturing of highly-alloyed steel billets. As argued by work [1], the amount of scale formation at the metallurgical plants in the Ural Federal District (Russia) is, in thousand tons: Magnitogorsk Metallurgical Plant – 404.4; Chelyabinsk Metallurgical Plant – 244.9; Volga Motor Plant – 27.2; Chelyabinsk tube-rolling plant – 1.0; OAO Ural Forge – 2.1.

The doped scale is used in the charge of electric furnaces [1]. The difficulty is that pre-processing of scale and other finely-dispersed wastes is required to increase the level of absorption of doping elements by melting steel. At the same time, there are additional difficulties in processing oil (dirty) scale [3]. That is, before adding it to the charge, it requires cleaning of harmful impurities. According to study [2], when the finely-dispersed waste of highly-alloyed steels is introduced into the liquid bath, without preliminary preparation, the loss of refractory elements reaches 40 %.

Therefore, it is a relevant issue to reduce the loss of refractory elements when processing the waste from highly-alloyed steels and alloys. That necessitates research into the features of the physical and chemical transformations at the reduction smelting involving doped oxide metallurgical waste.

2. Literature review and problem statement

A technique to process the oxide anthropogenic raw materials that has demonstrated practical positive results is the reduction by carbon [4], as well as by a complex of C and Si [5], whereby the smelted products are received. The use of reduction smelting is possible when processing the scale and other finely-dispersed anthropogenic waste contaminated with mineral oils and emulsions, which require refining from harmful impurities.

According to work [6], Fe_3C and C were identified in the reduced products after the carbon-thermal treatment of iron scale together with Fe. Similar results were obtained by the authors of [5] during the carbon-thermal reduction of dross from chromium-nickel-containing steel. In [7],

at different stages of the carbon reduction of scale from the highly-alloyed steel P18, the authors observed the formation of $(\text{Fe}, \text{Cr})_7\text{C}_3$, $\text{Fe}_3\text{W}_3\text{C}$, W_2C , VC, Fe_2C , Fe_3C . According to the results of X-ray phase analysis reported in [5, 7], the doping elements are present not only in the form of individual compounds but also as a solid solution in the Fe phase. These technological aspects should be taken into consideration when developing the parameters for the reduction smelting of highly-alloyed oxide waste. Among the drawbacks is the lack of data on the physical and chemical properties of the reduced products when the carbon content in the charge changes. The unresolved issues relate to determining the most favorable conditions for reducing the alloyed anthropogenic raw materials in the system Fe–Ni–Cr–Mo–W–O–C.

The authors of paper [8] investigated the reduction of nickel-iron-containing laterite ores with carbon. After processing for 60 minutes at 1,623 K and a molar ratio of C:O 1.4, the Ni and Fe extraction degree was 96.6 % and 97.9 %, respectively. At the same time, the content of Ni and Fe in the product was 9.4 % and 87.5 %, respectively. Similar studies with laterite ore were carried out by the authors of work [9]. Processing at 1,773 K for 90 minutes, at the C:O ratio of 1.0, yielded the product containing Ni in the amount of 8.33 % by weight, and Fe in the amount of 84.71 % by weight. The authors of paper [10] reported a study of reduction reactions involving oxides and carbon in the system Fe–Ni–O system at temperatures up to 1,373 K. With the increase in processing temperature, the reduced products manifested themselves in the following sequence: $\text{Fe}_3\text{O}_4 + \text{NiO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Ni} \rightarrow \text{FeO} + \text{Fe}_x\text{Ni}_y \rightarrow \text{Fe}_x\text{Ni}_y + \text{Fe}$ (Fe_nC_m). That is, there was a relatively greater propensity to reduce the Ni oxide rather than the Fe oxides. Metallic Ni and Fe were observed at some stages. The possibility of the presence of Fe carbides and the Fe_xNi_y iron-nickel-containing phase was noted, which can also occur when reducing the oxide doped waste. In other words, the possibility to reduce the iron-nickel component was confirmed, with a relatively high degree of the extraction of target elements from oxides. The downside is the lack of data on the reduction of complex oxide compounds, which may form a part of anthropogenic raw materials. That may lead to likely differences in the course of reduction reactions. The unresolved issues are related to determining the phase composition and microstructure of the reduced products of the anthropogenic raw materials that are complexly alloyed by refractory elements when the ratio of oxygen to carbon in the charge changes.

The authors of work [11] investigated the reduction of oxides in the Fe–Cr–O–C system at the different ratios of carbon to iron and temperatures of 1,373–1,523 K. A temperature rise led to an increase in the formation of carbides, the remainder of which is inevitably present in reduction products [12]. The Cr extraction degree increased from 9.6 % to 74.3 % when increasing C:Fe from 0.8 to 1.4. At the same time, the formation of carbides increased. Some of the carbides dissolved in the iron phase [11]. The authors of papers [13, 14] identified the possibility of the formation of Cr_3C_2 , Cr_{23}C_6 , Cr_7C_3 carbides at temperatures 1,273–1,773 K. They established the possibility to form the iron-chrome-containing materials with a limited carbon content, which makes it possible to expand the scope of application, including the doping of heat-resistant steels. The downside is the inability to trace the

impact exerted on the process of reduction and carbide formation by Ni and other refractory elements, which are in the complex present in the oxide waste from complexly-alloyed steel and alloys. The unresolved issues relate to expanding the understanding the nature of the presence of elements in the reduced products with a combined use of X-ray phase analysis, raster electron microscopy, and X-ray microanalysis.

The authors of study [15] show that the reduction of oxides in the W–O–C system occurs with the transition of tungsten trioxide to $WO_{2,72}$, tungsten dioxide, and W, with the formation of carbides. Similar results were also reported in paper [16]. The reduction process in the system Mo–O–C, which was investigated by the authors of work [17], was also characterized by the formation of an intermediate product, molybdenum dioxide. MoO_2 was later transferred to molybdenum and a carbide component. The downside is that the form of the presence of tungsten and molybdenum-containing compounds in the oxide waste from highly-alloyed steels may prove to be more complex and be different from the individual pure oxides. The unresolved issues are related to determining the conditions for the reduction of the oxide complexly-alloyed raw materials yielding products without compounds and the phases prone to sublimation. That would eliminate the need to create special conditions that prevent the evaporation and loss of refractory doping elements with the gas phase.

It is worth noting the research of the mechanism of carbon-thermal treatment of the unalloyed anthropogenic waste reported by the authors of work [6]. Fe, Fe_3C , and C were identified in the reduced products. Similar studies into the reduction of waste from some alloyed steel grades were carried out by the authors of [5, 7]. Both iron carbides and refractory doping elements were identified in the reduction products. But, at the same time, the issue of reducing a complex mixture of waste, from different sources, alloyed by refractory elements was not studied in detail. That could define the most preferable conditions for the reduction of the alloyed anthropogenic raw materials in the system Fe–Ni–Cr–Mo–W–O–C.

In the studies of the systems Fe–Ni–O–C [10], Fe–Cr–O–C [13, 14], and the degree of extraction of Ni, [8, 9], Cr [11], it is worth noting the emergence of the metallic phase, carbides, and intermetallides. The Fe_xNi_y and Fe (Fe_nC_m) phases were identified, as well as Cr_3C_2 , $Cr_{23}C_6$, Cr_7C_3 . At the same time, studies into the reduction of individual oxides in the W–O–C [15, 16] and Mo–O–C [17] systems determine the two-stage reduction. There is a decrease in the higher oxides to the lower ones, followed by the formation of a metal and carbide component. But, at the same time, it remains to be determined the phase composition and microstructure of the reduced products from anthropogenic raw materials, which are complexly doped with refractory elements, when the amount of oxygen to carbon in the charge is changed. At the same time, the use of X-ray phase analysis, raster electron microscopy, and X-ray microanalysis would expand the understanding of the nature of the presence of elements in the reduced material. There is also a need to determine the conditions for the reduction of complexly doped anthropogenic raw materials in order to obtain products without compounds and phases prone to sublimation. That could reduce the loss of Ni, Cr, W, Mo by sublimating oxide

compounds when obtaining and using the reduced doping material.

Therefore, it is advisable to study the features of the phase composition, the microstructure of doping raw materials obtained through reduction smelting, when changing the parameters of the charge based on a mixture of anthropogenic waste from steels and alloys doped with refractory elements. This would help define the nature of the presence of elements in the material. At the same time, the use of X-ray microanalysis of individual inclusions and phases could enhance the perception of the distribution of doping elements in the resulting alloy.

3. The aim and objectives of the study

The aim of this study was to identify the features of the phase and structural transformations in the processing of highly-alloyed steel waste using reduction smelting and obtaining an alloy containing Ni, Cr, W, Mo. This is necessary to determine the parameters that reduce the loss of doping elements by sublimation in the processing of the oxide doping raw materials and when using the resulting doping additive.

To accomplish the aim, the following tasks have been set:

- to determine the features of the phase composition of the doping alloy based on anthropogenic waste with a different ratio of O:C in the charge with respect to the nature of the presence of the elements;
- to investigate the microstructure and chemical composition of individual phases and inclusions in a resource-saving doping alloy with a different ratio of O:C in the charge.

4. Materials and methods to study the properties of the resulting alloy

4.1. The examined materials and the equipment used in the experiment

The starting raw material is a mixture of scale from the chrome-nickel-containing steels of type 18-10 and grinding shavings from heat-resistant alloys on the nickel base EI893 and EP709, formed in the areas of metallurgical production. The addition of metal shavings ensured the intensification of heat exchange at the initial stages of charge heating and an additional increase in doping. A reducing agent is carbon-based, in the form of ultra-dispersed dust from carbon fiber production (the share of carbon is 98 % by weight), the adjustment of the amount of which ensured a change in the ratio of O:C in the charge within 1.19–2.25. Samples for our study were smelted in an indirect heating furnace with a coal lining in alundum crucibles. The smelting temperature is 1,873–1,913 K. After smelting, the alundum crucibles were removed from the furnace with the alloy and cooled at the ambient air temperature.

The X-ray phase analysis of the samples was carried out at the diffractometer “DRON-6” (Russia).

Photographs of the microstructures of the samples were acquired from the “JSM 6360LA” (Japan) electron microscope. The microscope is equipped with the JED 2200 X-ray microanalysis system manufactured by JEOL (Japan) to determine the chemical composition of individual parts of the surface of the samples.

4. 2. Procedure to determine the samples' properties indicators

The phase composition of the examined samples was determined by X-ray phase analysis using the Cu monochromatic radiation $K\alpha$ ($\lambda=1.54051 \text{ \AA}$). Measurements were performed at a voltage on the tube of $U=40 \text{ kV}$ and an anode current of $I=20 \text{ mA}$. The composition of the phases was determined using the software suite PDWin 2.0 (Russia).

The microstructure of the samples was studied at an accelerating voltage of 10–25 kV and a current of the electro probe of 52–96 μA . The work distance to the surface under study was 10.5–11.7 mm.

5. Results of studying the properties of the resulting doping alloy

5. 1. Determining the features of the phase composition of the alloy with a different O:C ratio in the charge

The phase composition of the alloy with an O:C ratio in the charge of 2.25 consisted mainly of a solid solution of doping elements in $\gamma\text{-Fe}$ (Fig. 1, *a*). At an O:C in the charge of 1.67, the diffraction maxima of Fe_3C and a slight decrease in the intensity of the $\gamma\text{-Fe}$ manifestation were observed. The O:C ratio in the charge of 1.19 provided the dominating manifestation of Fe_3C in the alloy, together with the relatively low intensity of the $\gamma\text{-Fe}$ manifestation. It is also possible that some of the individual doping compounds may be present but they demonstrated a fragmented character of the diffraction maxima with relatively low intensity.

5. 2. Studying the microstructure of a doping alloy with a different O:C ratio in the charge

The microstructure of the alloy consisted of several phases (Fig. 1, *b–d*) of different particle shapes and sizes. Phases with a relatively high Ni content (points 3, 5, 9) and Cr content (points 2, 4, 8) were identified in the studied areas, to 46.38 % by weight and to 45.32 % by weight, respectively (Fig. 1, 2, Table 1).

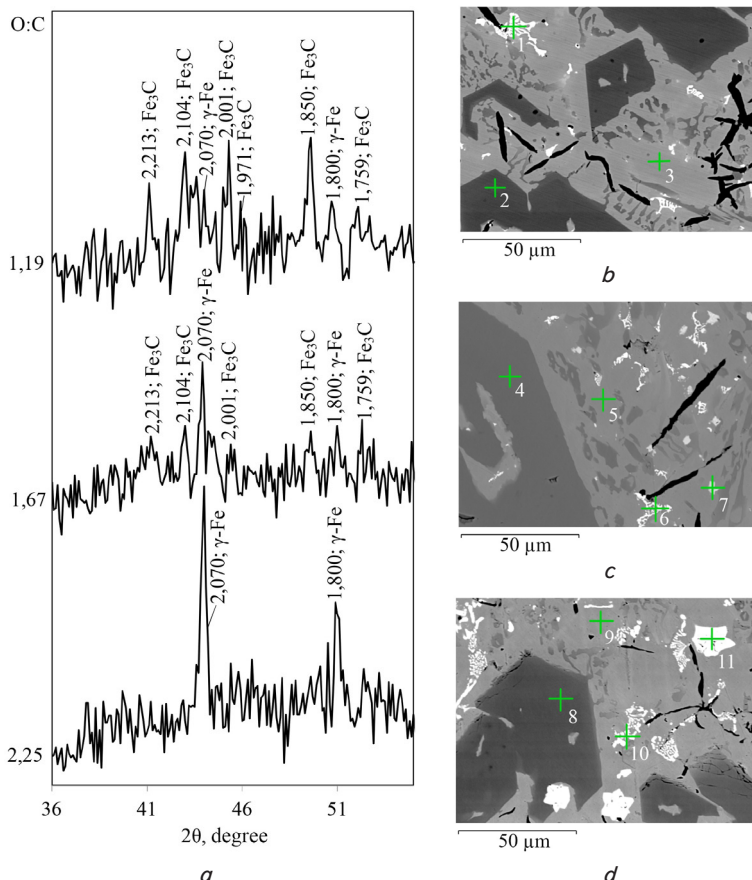


Fig. 1. The X-ray phase studies of the doping alloy with various O:C in the charge and the corresponding photographs of the microstructure, magnification $\times 1,000$: *a* – sections of diffractograms; *b* – 2.25, *c* – 1.67, *d* – 1.19, 1–11 – sections of the samples X-ray microanalysis

Some particles had an increased Mo and W content (1, 6, 7, 10, 11), to 10.38 % by weight and to 27.32 % by weight, respectively. The carbon content was between 0.47 and 2.32 % by weight. At the same time, the particles containing Nb (points 1, 7, 11) and Ti (points 7, 11) were identified. The content of Nb in individual particles reached 47.62 % by weight, the Ti content – 15.92 % by weight (Fig. 1, 2, Table 1).

When the O:C ratio in the charge decreased from 2.25 to 1.19, there was an increase in phase particles with a relatively high value of W, Mo, Mo, Nb.

Table 1

Results of the X-ray microanalysis of the doping alloy according to Fig. 1

Examined point	Element content, % by weight										
	C	Al	Ti	Cr	Mn	Fe	Ni	Nb	Mo	W	Total
1	2.18	0.13	0.00	7.10	0.00	39.79	21.88	0.98	9.48	18.46	100
2	1.24	0.06	0.00	44.67	0.00	43.99	5.70	0.00	1.43	2.91	100
3	0.47	0.09	0.00	3.45	0.10	48.56	45.45	0.00	0.37	1.51	100
4	1.09	0.16	0.00	34.61	0.00	53.64	5.37	0.00	1.76	3.37	100
5	0.52	0.22	0.00	3.54	0.00	54.76	38.57	0.00	0.48	1.91	100
6	1.93	0.00	0.00	6.92	0.00	45.25	15.39	0.00	10.38	20.13	100
7	2.32	0.00	2.46	3.99	0.00	19.94	1.96	47.62	7.95	13.76	100
8	1.32	0.13	0.00	45.32	0.00	40.91	6.93	0.00	1.96	3.43	100
9	0.70	0.17	0.00	4.02	0.70	45.95	46.38	0.00	0.53	1.55	100
10	2.27	0.00	0.00	9.43	0.67	29.9	38.54	0.00	6.79	12.4	100
11	2.14	0.00	15.92	7.12	0.00	18.03	1.38	20.46	7.63	27.32	100

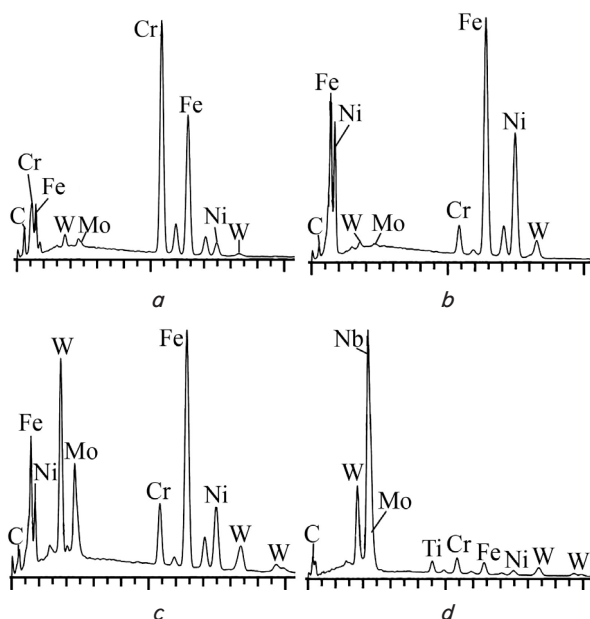


Fig. 2. Spectrograms of certain examined points according to Fig. 1, respectively: *a* – 4, *b* – 5, *c* – 6, *d* – 7

6. Discussion of results of studying the properties of the doping alloy

The phase analysis of the alloy with O:C in the charge from 2.25 to 1.19 (Fig. 1, *a*) indicates that the doping elements were in a solid solution in the lattice of γ -Fe. Some of the doping elements could serve substitution atoms in Fe_3C . This is consistent with the results reported in work [5], where only iron-containing compounds clearly manifested themselves on the diffractogram of the reduced doped product. At O:C in the charge of 2.25, the manifestation of Fe_3C was fragmented. A relatively weak but clear manifestation of the Fe_3C presence was observed at O:C in the charge of 1.67. This is consistent with the results reported in work [12] on the parallel reduction and carbide evolution and the inability to obtain a fully carbon-free product in practice. Changing O:C in the charge to 1.19 led to an increase in the manifestation of Fe_3C relative to γ -Fe. The resulting sequence of transformations is well consistent not only with the data from [6] on the reduction of non-alloyed oxide waste but also with the results reported in [7]. However, in [7], at different stages of reduction, carbide compounds of alloying elements were found in the obtained products together with iron carbides ($(\text{Fe}, \text{Cr})_7\text{C}_3$, $\text{Fe}_3\text{W}_3\text{C}$, W_2C , VC. At the same time, the lack of a clear manifestation of the compounds of refractory elements in the current research is apparently associated with the concentration of most of the doping elements as substitution atoms in Fe_3C and a solid solution of γ -Fe.

Our study of the microstructure in combination with X-ray microanalysis of the resulting alloy additionally indicates the concentration of doping elements' atoms in Fe_3C and in the lattice of γ -Fe (Fig. 1, 2, Table 1). Phases that have elevated Ni and Fe content (points 3, 5, 9) may prove to be a solid Fe_xNi_y solution. This agrees well with the results reported in [8–10], which confirm the relatively high efficiency of the reduction of the iron-nickel oxide component by carbon. At the same time, in [10], with the occurrence of reduction processes, together with Fe_xNi_y , the iron-containing carbide component $\text{Fe}(\text{Fe}_n\text{C}_m)$ occurred. One sees that

some phases were characterized by the elevated content of Cr and Fe (Table 1, points 2, 4, 8). Such phases may probably consist of Fe_3C , where Fe atoms are partially replaced with Cr atoms. This is consistent with the results reported in [13, 14], which note the formation of chromium-containing carbides in parallel with the reduction. However, in works [13, 14], the reduction is accompanied by the formation of carbides Cr_3C_2 , Cr_{23}C_6 , Cr_7C_3 . The absence of chromium carbide manifestation on the diffractograms in our study is due to the fact that it is possible to dissolve some part of the carbides in a solid solution of γ -Fe when two phases are in contact. This is also noted by the authors of paper [11].

Some particles with the elevated levels of Mo, W, Nb, and C (Fig. 1, points 1, 6, 7, 10, 11) may prove to be carbide phases. This agrees well with the results of studies into the reduction mechanism of W oxides [15, 16] and Mo oxides [17]. They revealed that at the final stage of reduction there is a parallel formation of the metal and carbide component. At the same time, as a difference, in the current study the alleged particles of the carbide phase are characterized by an increased content of the entire complex of the doping elements. This indicates a more complex nature of the compounds of refractory elements. It should also be noted that individual inclusions with a relatively high Nb content are clearly visible only with an increase in the carbon content in the charge, at O:C 1.67 and 1.19. Accordingly, the size of such particles increased from a few micrometers to more than ten micrometers. This may be due to an increase in the residual carbon level to the required amount for the detection of a separate niobium-containing carbide phase. There are no compounds and phases in the obtained samples with a relatively high propensity for sublimation. That is, there is no need to create special conditions that prevent the evaporation and loss of doping elements with the gas phase. It also leads to an increase in the utilization degree of doping elements.

Analysis of our study results showed that the most favorable ratio of O:C in the charge is 1.67. At the same time, dominating in the phase composition is a solid solution of doping elements in γ -Fe. The proportion of residual carbon, which was in the form of a carbide component, had a relatively low manifestation, while providing the necessary reducing capacity during the use of the alloy. Our study has identified new technological aspects in the processing of highly-alloyed anthropogenic waste to produce an alloy with a relatively low residual carbon content. The resulting parameters for a resource-saving doping material ensures the possibility of replacing some of the standard ferroalloys when smelting steels that have some carbon limitations. The heat-resistant steels from the austenite class are promising from this point of view.

The limitations of our study results are the use of the resulting doping alloy for the steels from a defined class, based on the complex of the elements contained. For example, in some heat-stable and heat-resistant steels, the complex of Ni, Cr, Mo, W elements determines the required quality properties of the product. For tool fast-cutting steels, unlike Cr, Mo, W, the Ni content is strictly limited by tenths of a percent. Therefore, the problem may be that the composition of the elements in a target product exceeds the acceptable limits. Similar problems are not ruled out for other grades of steel, which have strict restrictions on the content of one or more elements of the doping alloy. Therefore, in order to avoid the related issues and the increased cost indicators of raw material utilization, one should adhere to close ratios of the elements' content in the doping alloy and a target product.

The lack of results from X-ray microanalysis related to the distribution of elements under the characteristic X-rays can be noted as a disadvantage. This could make it possible to monitor the distribution of the main elements throughout the entire surface of the examined samples, which would better characterize the nature of phases and inclusions.

This study could be advanced towards expanding the range of grades of steel, whose oxide wastes would be used in processing by a reduction smelting technique. The difficulties in attempting to develop the current study are related to the lack of a sufficient database of experimental data. The most promising are the wastes with an increased level of doping.

The use of a complex doping alloy based on the chromium-nickel-containing anthropogenic waste during the experimental smelting in the arc electric furnace produced positive results. The alloy was used as a charge additive. The cost ratio was at the level of 270–330 kg/t of steel. This ensured a partial replacement of standard doping materials. The use of the doping alloy reduced the Ni and Cr consumption by 27–31 % by weight and 25–29 % by weight, respectively. The loss of the alloying elements decreased by 3–4 % by weight [4].

Recycling and returning industrial anthropogenic waste from steel-making to production ensures not only the development of resource savings but also reduces pollution, along with the reduction of environmental tension in industrial regions.

7. Conclusions

1. It has been determined that the alloy at O:C in the charge within the interval 1.19–2.25 demonstrated the phases of γ -Fe and Fe_3C with the doping elements as replacement atoms. At O:C=2.25, the phase composition consisted of a solid solution of the doping elements in γ -Fe. The carbide component had a fuzzy fragmentary manifestation. At O:C=1.67, there was a relatively weak but clear manifestation of Fe_3C . Changing O:C in the charge to 1.19 led to an increase in the manifestation of Fe_3C on diffractograms. The presence of some of the individual compounds of alloying elements is not excluded but they were characterized by the fragmented nature of the manifestation of diffraction maxima with relatively low intensity.

2. The microstructure of the doping alloy with a different O:C in the charge had a clear manifestation of several phases, characterized by a difference in the content of the main doping elements. The Ni content in the examined sections of various phases varied within 1.38–46.38 % by weight, Cr – 3.45–45.32 % by weight, W – 1.51–27.32 % by weight, Mo – 0.48–10.38 % by weight. The carbon content was between 0.47 and 2.32 % by weight. Mo, W, Nb were more concentrated in individual particles. The Nb content in some inclusions reached 47.62 % by weight.

References

- Maksimov, E. A., Vasil'ev, V. I. (2016). The Utilization of the Wastes of the Rolling and Pipe-Rolling Shops of the Metallurgical Plants and their Processing. *Ferrous Metallurgy. Bulletin of Scientific, Technical and Economic Information*, 3, 99–107.
- Grigor'ev, S. M., Petrishchev, A. S. (2012). Assessing the phase and structural features of the scale on P6M5 Φ 3 and P12M3K5 Φ 2 steel. *Steel in Translation*, 42 (3), 272–275. doi: <https://doi.org/10.3103/s0967091212030059>
- Demydyk, V. N. (2014). Sustainable development and waste recycling in ferrous metallurgy. *Metall i lit'e Ukrainy*, 8, 36–40.
- Petryshchev, A., Milko, D., Borysov, V., Tsybmal, B., Hevko, I., Borysova, S., Semenchuk, A. (2019). Studying the physical-chemical transformations at resourcesaving reduction melting of chrome–nickelcontaining metallurgical waste. *Eastern-European Journal of Enterprise Technologies*, 2(12 (98)), 59–64. doi: <https://doi.org/10.15587/1729-4061.2019.160755>
- Hryhoriev, S., Petryshchev, A., Shyshkanova, G., Zaytseva, T., Frydman, O., Krupey, K. et. al. (2018). A study of environmentally friendly recycling of technogenic chromium and nickel containing waste by the method of solid phase extraction. *Eastern-European Journal of Enterprise Technologies*, 1 (10 (91)), 44–49. doi: <https://doi.org/10.15587/1729-4061.2018.121615>
- Mechachti, S., Benchiheub, O., Serrai, S., Shalabi, M. (2013). Preparation of iron Powders by Reduction of Rolling Mill Scale. *International Journal of Scientific & Engineering Research*, 4 (5), 1467–1472.
- Hryhoriev, S., Petryshchev, A., Belokon', K., Krupey, K., Yamshinskij, M., Fedorov, G. et. al. (2018). Determining the physical-chemical characteristics of the carbon-thermal reduction of scale of tungsten high-speed steels. *Eastern-European Journal of Enterprise Technologies*, 2 (6 (92)), 10–15. doi: <https://doi.org/10.15587/1729-4061.2018.125988>
- Huang, D. H., Zhang, J. L., Lin, C. C., Mao, R. (2011). Production of ferro-nickel granules from nickel laterite ore/coal composite briquettes by direct reduction. *Beijing Keji Daxue Xuebao*, 33 (12), 1442–1447.
- Wang, L., Lü, X., Liu, M., You, Z., Lü, X., Bai, C. (2018). Preparation of ferronickel from nickel laterite via coal-based reduction followed by magnetic separation. *International Journal of Minerals, Metallurgy, and Materials*, 25 (7), 744–751. doi: <https://doi.org/10.1007/s12613-018-1622-7>
- Zhang, Y., Wei, W., Yang, X., Wei, F. (2013). Reduction of Fe and Ni in Fe-Ni-O systems. *Journal of Mining and Metallurgy, Section B: Metallurgy*, 49 (1), 13–20. doi: <https://doi.org/10.2298/jmmb120208038z>
- Zhao, L., Wang, L., Chen, D., Zhao, H., Liu, Y., Qi, T. (2015). Behaviors of vanadium and chromium in coal-based direct reduction of high-chromium vanadium-bearing titanomagnetite concentrates followed by magnetic separation. *Transactions of Nonferrous Metals Society of China*, 25 (4), 1325–1333. doi: [https://doi.org/10.1016/s1003-6326\(15\)63731-1](https://doi.org/10.1016/s1003-6326(15)63731-1)
- Ryabchikov, I. V., Belov, B. F., Mizin, V. G. (2014). Reactions of metal oxides with carbon. *Steel in Translation*, 44 (5), 368–373. doi: <https://doi.org/10.3103/s0967091214050118>
- Simonov, V. K., Grishin, A. M. (2013). Thermodynamic analysis and the mechanism of the solid-phase reduction of Cr_2O_3 with carbon: Part 1. *Russian Metallurgy (Metally)*, 2013 (6), 425–429. doi: <https://doi.org/10.1134/s0036029513060153>
- Simonov, V. K., Grishin, A. M. (2013). Thermodynamic analysis and the mechanism of the solid-phase reduction of Cr_2O_3 with carbon: Part 2. *Russian Metallurgy (Metally)*, 2013 (6), 430–434. doi: <https://doi.org/10.1134/s0036029513060165>
- Shveikin, G. P., Kedin, N. A. (2014). Products of carbothermal reduction of tungsten oxides in argon flow. *Russian Journal of Inorganic Chemistry*, 59 (3), 153–158. doi: <https://doi.org/10.1134/s0036023614030206>

16. Smirnyagina, N. N., Khaltanova, V. M., Kim, T. B., Milonov, A. S. (2012). Thermodynamic modeling of the formation of borides and carbides of tungsten, synthesis, structure and phase composition of the coatings based on them, formed by electron-beam treatment in vacuum. *Izvestiya vysshih uchebnyh zavedeniy. Fizika*, 55 (12 (3)), 159–163.
17. Zhu, H., Li, Z., Yang, H., Luo, L. (2013). Carbothermic Reduction of MoO₃ for Direct Alloying Process. *Journal of Iron and Steel Research International*, 20 (10), 51–56. doi: [https://doi.org/10.1016/s1006-706x\(13\)60176-4](https://doi.org/10.1016/s1006-706x(13)60176-4)

В статті на основі аналізу прогнозних моделей стану поверхневих об'єктів доведено, що при створенні системи оперативного прогнозування та нормування техногенних навантажень доцільно використовувати більш прості моделі, які дозволяють оперативно проводити розрахунки. В якості підходу для проведення оперативного прогнозування техногенного навантаження запропоновано застосування орієнтовно необхідного рівня зниження шкідливого впливу на ділянку поверхневого водного об'єкта по надходженню забруднюючих речовин.

На основі ретроспективного аналізу даних проведено математичне моделювання показників екологічного стану Дніпра. Встановлено, що залежність збільшення концентрацій забруднюючої речовини від збільшення її маси, в межах ділянок водотоку, обмежених існуючими стаціонарними сторами, описується лінійною залежністю.

Аналіз отриманих залежностей дозволив встановити, що незалежно від виду забруднюючої речовини, вони мають IV характерні точки, які дозволяють оперативно прогнозувати приріст масової витрати розглянутої забруднюючої речовини та зміну її концентрації.

Встановлено, що при рівних значеннях збільшення концентрацій для неконсервативних речовин, збільшення масової витрати буде менше, ніж для умов «чистого розведення». Тобто в реальному водному об'єкті зі збільшенням приросту концентрації ЗР посилюються природні процеси самоочищення.

Проведена перевірка адекватності запропонованого підходу в умовах реального поверхневого водного об'єкта, яка дозволила встановити лінійні залежності для зміни вмісту сульфатів: $\Delta C_{\text{сульф}} = 0,022 \cdot \Delta t_{\text{сульф}} - 0,001$ та хлоридів: $\Delta C_{\text{хлорид}} = 0,0143 \cdot \Delta t_{\text{хлорид}} - 0,033$. В свою чергу залежність вмісту сульфатів від вмісту хлоридів має вид: $\Delta C_{\text{сульф}} = 1,559 \cdot \Delta t_{\text{хлорид}} + 2,286$.

Встановлено, що для ділянки водотоку в умовах Дніпра лінійна залежність для фосфатів має вигляд: $\Delta C_{\text{фосф}} = 0,019 \cdot \Delta t_{\text{фосф}} - 0,020$; сульфатів: $\Delta C_{\text{сульф}} = 0,022 \cdot \Delta t_{\text{сульф}} - 0,001$; хлоридів: $\Delta C_{\text{хлорид}} = 0,0143 \cdot \Delta t_{\text{хлорид}} - 0,033$. Залежність вмісту фосфатів від вмісту сульфатів має вигляд: $\Delta C_{\text{фосф}} = 0,066 \cdot \Delta C_{\text{хлорид}} + 0,422 \Delta C_{\text{сульф}} - 0,017$. Наведені рівняння дозволяють в першому наближенні проводити розрахунок збільшення концентрації однієї забруднюючої речовини за умови, що приріст концентрації іншої відомий, що зменшує обсяги даних та збільшує оперативність прогнозних розрахунків

Ключові слова: поверхневий водний об'єкт, забруднююча речовина, екосистема, шкідливий вплив, оперативний контроль

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DETERMINING THE EFFECT OF ANTHROPOGENIC LOADING ON THE ENVIRONMENTAL STATE OF A SURFACE SOURCE OF WATER SUPPLY

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1. Introduction

At present, even for a fairly large surface water object, the effectiveness of the forecasting models of water qualitative

composition is largely determined by the completeness and adequacy of the source information. A review of approaches to using such models is given in scientific papers [1, 2]. Traditional forecasting methods, developed for using mod-