

*Peculiarities of phase and structural transformations during the carbon-thermal recovery of high-speed steel slag with the production of an alloying additive were investigated. This is necessary to determine the technological indicators that allow reducing the loss of high-value elements during the production and use of the alloying additive. A gradual change in the degree of scale reduction from 32 % to 69 % and 77 % led to an increase in the appearance of the solid solution of alloying elements and carbon in the  $\alpha$ -Fe lattice with respect to  $\text{FeWO}_4$  and  $\text{Fe}_3\text{O}_4$ . Along with this,  $\text{Fe}_3\text{C}$ ,  $\text{FeW}_3\text{C}$ , WC, VC,  $\text{V}_2\text{C}$ , and  $\text{Cr}_7\text{C}_3$  were manifested. At the same time, the formation of polyhedral and rounded particles of different chemical composition and the formation of a spongy microstructure was observed. It was determined that the most acceptable degree of recovery is 77 %. At the same time, the degree of reduction of 69 % is also sufficient since due to the residual carbon in the form of carbides, an increased reduction capacity is ensured with additional reduction of the oxide component in the liquid metal during alloying. The spongy microstructure provides relatively fast dissolution compared to standard ferroalloys, which causes a reduction in the total melting time while reducing the resources spent. No phases and compounds characterized by an increased tendency to sublimation were detected in the obtained alloying additive. That is, there is no need to provide additional conditions that prevent the loss of high-value elements during evaporation with the gas phase, which causes an increase in the degree of extraction of alloying elements. The indicators of the obtained alloying additive make it possible to melt alloyed steel in an electric arc furnace with respect to brands whose composition does not have strict restrictions on carbon, while replacing a part of standard ferroalloys*

*Keywords: carbon thermal recovery, slag of high-speed steels, oxide man-made waste, structural-phase transformations*

# IDENTIFYING THE FEATURES OF STRUCTURAL AND PHASE TRANSFORMATIONS DURING THE PROCESSING OF OXIDE WASTE FROM THE PRODUCTION OF HIGH-SPEED STEEL

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## 1. Introduction

Processing and return to production of alloyed industrial waste belong to alternative sources of alloying additives

containing tungsten, molybdenum, vanadium, chromium, etc. Quite a lot of man-made wastes do not find relatively effective use in practice, which in some cases is due to their finely dispersed, oxide nature, and the unpredictable nature

of the interaction between alloying elements [1]. That is, alloying elements can be part of complex chemical compounds. A representative of such waste is the slag of high-speed steels, which is characterized by a high level of alloying with tungsten and other high-value elements, the prices of which tend to increase [2]. Such specific features cause problems in ensuring the manufacturability of production and satisfactory production cost [3], which is a necessary component for maintaining competitiveness on the world and domestic markets.

It follows from the above that the problem of reducing the loss of alloying elements during the resource-saving processing of the slag of high-speed steels and the use of the resulting product in metallurgical production is urgent. To solve this task, we need to study the specifics of recovery of oxide man-made waste containing refractory elements, with the determination of structural and phase transformations.

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## 2. Literature review and problem statement

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Studies of iron slag carried out by the authors of [4] indicate the content of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeO}$ . At the same time, the increased alloying of high-speed steel slag determined the additional content in the composition of  $\text{WO}_2$  and  $\text{W}_2\text{C}\cdot\text{Mo}_2\text{C}$ , which is reported in paper [5]. Recovery of iron slag in the temperature range of  $750\text{ }^\circ\text{C}$  to  $1050\text{ }^\circ\text{C}$  was studied by the authors of paper [4]. It was noted there that the highest degree of reduction can be achieved at  $1050\text{ }^\circ\text{C}$  with an iron content of 98.40 % by weight in the reduced material. Depending on the processing temperature, C and  $\text{Fe}_3\text{C}$  appeared in the recovered raw materials along with the iron phase. The presence of  $\text{Fe}_3\text{C}$  also took place during the study of the recovery of alloyed oxide raw materials with contents, including Cr and Mo, which was presented by the authors of paper [6]. Among the carbides in the reduction products,  $\text{Fe}_2\text{C}$  carbide was additionally detected. Alloying elements were mostly in iron-containing phases as substitutional atoms. Another relationship of alloying elements in the products of reduction of tungsten-containing high-speed steel scale, reported by the authors of work [7], had an impact on the nature of the phase composition. During the recovery process, the oxide compounds  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{FeWO}_4$  were transformed into a solid solution of carbon and alloying elements into  $\alpha\text{-Fe}$  and carbides at various stages. At the same time, the presence of  $\text{W}_2\text{C}$ ,  $\text{Fe}_3\text{W}_3\text{C}$  was relatively clearly observed at the initial stages of recovery, in contrast to  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_2\text{C}$ , which had a greater intensity of manifestation at the final stage of processing.  $\text{V}_2\text{C}$  and  $(\text{Fe}, \text{Cr})_7\text{C}_3$  carbides were found fragmentarily. But there are unsolved questions regarding the nature of the presence of target alloying elements in the formed phases in the products of recovery of oxide finely dispersed raw materials from the production of tungsten-molybdenum-containing high-speed steels with an increased content of vanadium. Some unsolved parts of the problem are related to the identification of the most acceptable indicators of recovery of oxide man-made material in relation to the Fe-W-Cr-V-Mo-O-C system.

Two-stage reduction processes in the Mo-O-C system during the stepwise transition of  $\text{MoO}_3$  to  $\text{MoO}_2$  and,

subsequently, to Mo together with carbides were presented by the authors of [8]. The authors of work [9] showed the possibility of a more complete recovery of the oxide component with the participation of residual carbon with the predominance of metallic molybdenum in the phase composition using low-temperature plasma treatment. As a difference, the formation of intermediate compounds of the  $\text{WO}_x$  type was found in [10] during carbonization of tungsten trioxide. At the same time, there was a staged transformation, similar to the case of the reduction of molybdenum oxides. This is also confirmed by the results of research in accordance with the heat treatment temperature range of  $750\text{--}900\text{ }^\circ\text{C}$ , given in [11], but with an increase in temperature at  $1450\text{ }^\circ\text{C}$ , an increase in the intensity of carbide formation took place. As a disadvantage, it can be noted that due to the different composition of elements in alloyed man-made waste from steel production, the nature of the presence of tungsten- and molybdenum-containing compounds can be more complex. Parts of the problem that require further resolution relate to the determination of indicators of heat treatment of complex alloyed man-made raw materials when obtaining recovered material that does not contain phases and compounds prone to sublimation. This will make it possible to avoid the need to create additional conditions during heat treatment that prevent evaporation of high-value elements and loss with the gas phase.

The authors of work [12], while studying the carbon reduction of the iron-vanadium oxide ore component  $\text{FeV}_2\text{O}_4$ , determined that the most acceptable results can be achieved by processing at  $1350\text{ }^\circ\text{C}$ . At the same time, the extraction of vanadium and iron is achieved at the level of 71.60 % and 95.07 %, respectively. The authors of paper [13] investigated the reduction of  $\text{FeO}\cdot\text{Cr}_2\text{O}_3$  and  $\text{FeO}\cdot\text{V}_2\text{O}_3$  oxide compounds when the ratio of carbon to iron is changed in the temperature range of  $1100\text{--}1250\text{ }^\circ\text{C}$ . It was found that increasing the latter from 0.8 to 1.4 provided an increase in the degree of extraction (%) of chromium and vanadium from 9.6 to 74.3 and from 10.0 to 45.3, respectively. Increasing the processing temperature to  $1250\text{ }^\circ\text{C}$  ensured an increase in the intensity of carbide formation. A change in the ratio of carbon to iron below 0.8 led to a sharp decrease in the degree of extraction of chromium and vanadium while reducing the level of carbide formation. As a drawback, we can note the lack of results regarding the carbonation of complex oxide compounds, which can be components of doped man-made waste. This specificity of the content of elements can cause differences in the course of reduction reactions. The part of the problem that remained unsolved is related to the research of the phase and structural composition of man-made waste complex-doped with refractory elements using X-ray phase analysis and scanning electron microscopy.

It is possible to note the results of studies of the composition of slag from the production of carbon steels [4] and those alloyed with refractory elements [5], as well as the features of carbon reduction. A solid solution of carbon in the iron lattice, iron carbides, and residual oxides were found in the products of recovery of unalloyed slag. Similar to the above-mentioned results were the data given in [6], in which research was carried out on the recovery of oxide-doped waste. As a difference, accord-

ing to data from work [7], a different ratio of alloying elements, such as tungsten and other carbide-forming refractory elements, led to a more intense manifestation of iron carbides and alloying elements. The analysis of the results of studies of transformations in the Mo-O-C [8] and W-O-C [10] systems showed that the reduction proceeds through the formation of lower oxide compounds with subsequent transition to the metal [9] and carbide phases [11]. Parallel formation of carbides and reduction was also manifested in the process of carbothermic treatment in the Fe-V-O-C [12] and Fe-Cr-V-O-C [13] systems.

Our review of the literature [1–13] indicates the expediency of conducting research aimed at identifying the features of structural and phase transformations that occur during the recovery of carbon doped with tungsten, chromium, vanadium, and molybdenum oxide man-made material. The specified properties of the target product can be achieved by ensuring the required degree of reduction. Determining the technological parameters that will allow obtaining a material without components with a high tendency to sublimation will ensure a reduction in the loss of the alloying elements present together with the gas phase.

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

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The purpose of our research was to determine the features of phase and structural transformations during carbon reduction of the slag of tungsten-molybdenum-containing high-speed steel with an increased content of vanadium with the addition of an alloying additive. This is necessary to identify the most acceptable technological indicators for reducing losses of alloying elements in the process of obtaining and using alloying material for steel smelting. This will provide an opportunity to improve resource-saving technologies for the processing of alloyed oxide anthropogenic wastes of metallurgical production.

To achieve the goal, the following tasks were defined:

- to establish the features of the phase composition of products of carbonization of high-speed steel slag with different degrees of recovery to determine the processing conditions that exclude the formation of phases with a relatively high tendency to sublimation;
- to investigate the features of the microstructure of products of carbonization of high-speed steel slag with different degrees of recovery using X-ray microanalysis. This is necessary to determine the nature of the presence of elements in the identified structural components in order to clarify the characteristics of phase formations at different stages of reduction.

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### 4. The study materials and methods

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

The object of this study is the products of carbon-thermal reduction of scale of high-speed steel of the P12MF5-MP grade. Ultrafine dust from carbon graphite production was used as a reducing agent. The addition of

such a carbon reducing agent provided a ratio of oxygen to carbon in the charge at the level of 1.47. Achieving the appropriate degree of recovery was ensured by isothermal exposure at a temperature of 1493 K. An argon atmosphere was used as a protective medium.

X-ray phase analysis was carried out using the DRON-6 diffractometer (Russia), which is justified by the need to identify phases in multiphase substances, as well as the relatively high sensitivity of the method.

Images of the microstructure and the content of elements in certain areas of the examined surface of the samples were acquired using a scanning electron microscope “JSM 6360LA” with an X-ray microanalysis system “JED 2200”, manufactured by JEOL (Japan). The involvement of this research method is justified by the need to achieve relatively high magnification and resolution with the determination of the composition of elements in selected areas on the obtained images of the microstructure.

#### 4.2. Procedure for conducting experiments and determining the indicators of the properties of samples

To determine the phase composition of materials, the method of X-ray phase analysis was used with monochromatic Co K $\alpha$  radiation, tube voltage and anode current of 30 kV and 20 mA, respectively. The nature of the phases was determined using PDWin 2.0 software (Russia). Processing of experimental data of X-ray phase analysis was performed by decomposing the diffraction spectrum of the sample into the spectra of its phase components. Detection of phase components was carried out by comparing the previously known spectra of phase standards and the experimental spectrum of the sample.

To acquire images of the microstructure, the accelerating voltage was 15 kV with a diameter of the electron probe of 4 nm. Determination of the content of elements in the studied materials was carried out using a standard-free method of calculating fundamental parameters: calculation of correction coefficients for the reflection of probe electrons, absorption of characteristic X-ray radiation and fluorescence.

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### 5. Results of investigating the properties of scale reduction products of high-speed steel

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#### 5.1. Determination of the peculiarities of the composition of the formed phases of the scale reduction products of high-speed steel

Upon reaching the degree of reduction of 32 %, the phase composition had the most intense manifestation of FeWO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> with a relatively weak expression of the solid solution of alloying elements and carbon in the  $\alpha$ -Fe lattice (Fig. 1). A gradual change in the degree of reduction to 69 % and 77 % led to an increase in the appearance of a solid solution of alloying elements and carbon in the  $\alpha$ -Fe lattice relative to FeWO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>. In the case of FeWO<sub>4</sub>, this tendency is more pronounced.

With a gradual increase in the degree of reduction from 32 % to 69 % and 77 %, the presence of carbides Fe<sub>3</sub>C, FeW<sub>3</sub>C, WC, VC, V<sub>2</sub>C, and Cr<sub>3</sub>C<sub>2</sub> was determined in the obtained products. At the same time, the manifestation of FeW<sub>3</sub>C increased relative to Fe<sub>3</sub>C and WC.

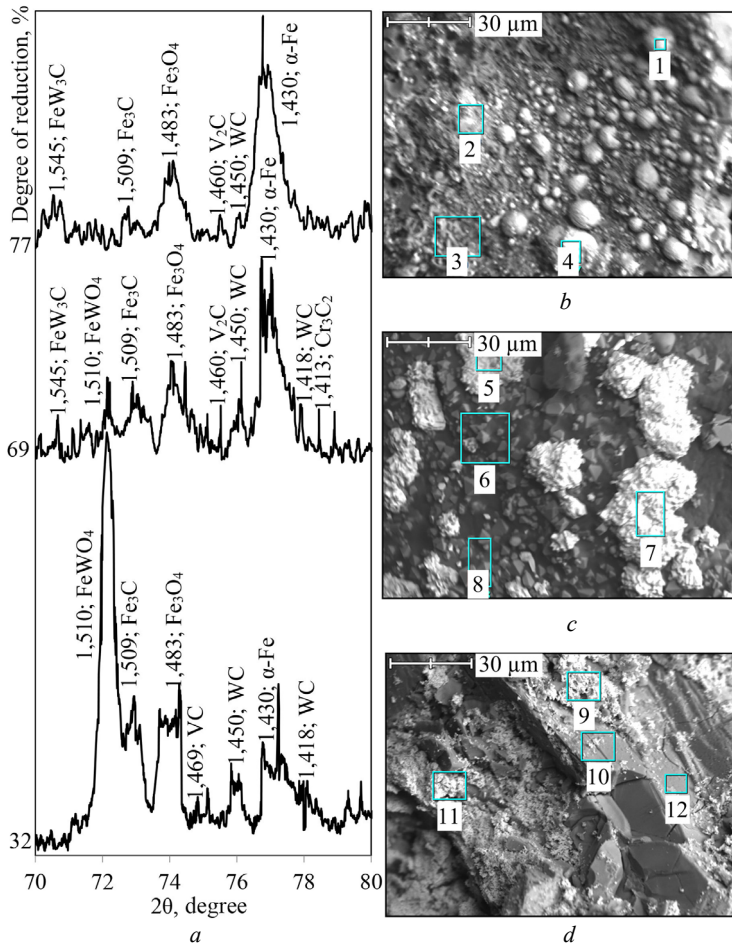


Fig. 1. X-ray phase and microstructural studies of scale reduction products with different degrees of reduction with a magnification of  $\times 1000$ : *a* – diffractograms; *b* – 77 %; *c* – 69 %; *d* – 32 %; 1–12 – sections for determining the content of elements

**5. 2. Investigation of the microstructure of scale reduction products of high-speed steel**

Studies have shown that the microstructure of the recovery products is heterogeneous and has several types of phase formations with different content of elements (Fig. 1, 2, Table 1). An increase in the degree of reduction from 32 % to 69 % led to changes in the microstructure with the formation

of polyhedral and rounded particles of different chemical composition. Achieving the degree of recovery at the level of 77 % ensured the formation of a spongy structure with rounded formations.

A gradual increase in the degree of reduction from 32 % to 69 % and 77 % provided a relative decrease in the residual oxygen content in the studied areas (% by weight) from 10.89–14.10 to 5.71–8.97 and 3.74–6.01, respectively. At the same time, the content of tungsten and molybdenum (% by weight) was in the range of 2.36–42.36 and 0.00–2.27, respectively. The content of vanadium and chromium in the areas of the studied samples ranged from 0.00 to 17.93 % by weight, and 0.00–24.41 % by weight, respectively.

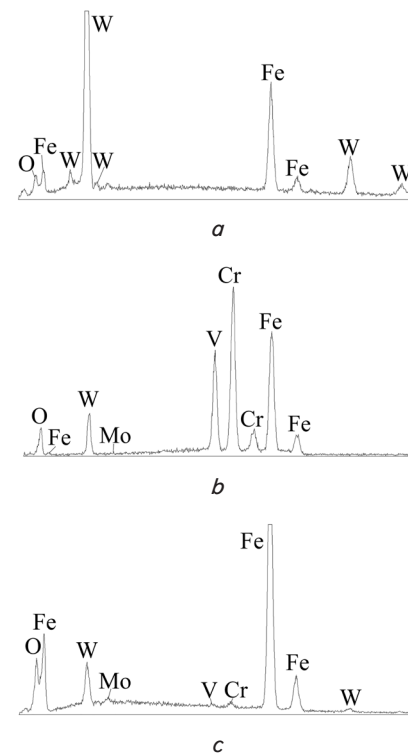


Fig. 2. Spectrograms of X-ray microanalysis of some studied areas of recovered raw materials in accordance with Fig. 1: *a* – 4; *b* – 8; *c* – 10

Table 1

Results of X-ray microanalysis of recovered raw materials in accordance with Fig. 1

No. of entry	Element content, % wt.						Total
	O	V	Cr	Fe	Mo	W	
1	6.01	0.00	0.00	91.63	0.00	2.36	100.00
2	3.74	5.80	0.27	75.18	1.42	13.59	100.00
3	5.08	4.03	5.21	75.56	0.36	9.76	100.00
4	4.67	0.00	0.00	52.97	0.00	42.36	100.00
5	5.96	6.94	0.38	52.12	0.78	33.82	100.00
6	8.97	14.66	16.23	55.77	1.09	3.28	100.00
7	5.71	0.00	0.00	54.78	0.00	39.51	100.00
8	6.42	17.93	24.41	44.54	1.73	4.97	100.00
9	10.89	2.31	2.16	66.94	2.27	15.43	100.00
10	12.64	1.16	1.62	77.53	0.56	6.49	100.00
11	11.33	8.85	7.54	60.70	0.00	11.58	100.00
12	14.10	0.22	2.07	81.08	0.00	2.53	100.00

## 6. Discussion of results of investigating the properties of high-speed steel scale reduction products

Our studies indicate that after heat treatment, the phase composition of the heat treatment products was dominated by  $\text{Fe}_3\text{O}_4$ ,  $\text{FeWO}_4$  and a solid solution of alloying elements and carbon in the  $\alpha$ -Fe lattice. The unreduced component in the form of iron oxides remained from the original scale, where such compounds were in the form of main phases, which is consistent with the results of work [4].

In the studies reported here, unlike the results from [6], it should be noted the manifestation in the phase composition of  $\text{Fe}_3\text{C}$ ,  $\text{FeW}_3\text{C}$ ,  $\text{WC}$ ,  $\text{VC}$ ,  $\text{V}_2\text{C}$  and  $\text{Cr}_3\text{C}_2$ , which makes it possible to obtain alloying elements without additional sublimation. Based on the results given in [5], part of the carbides in the recovered raw materials could have changed from the composition of the original scale. A relatively large proportion of refractory carbide-forming elements in the samples, as in the studies of the authors of work [7], determines the significant participation of the processes of interaction of alloying elements and carbon. One should note a clearer manifestation of individual carbide compounds of vanadium and tungsten, as well as an increase in the intensity of the manifestation of  $\text{FeW}_3\text{C}$ .

Based on the results of the microstructure study, it is possible to note areas with an increased content of alloying elements (Fig. 1, areas 4–8, 11). The relatively high content of tungsten in sections 4, 5, 7 (33.82–42.36 % by weight) may correspond to the presence of formed carbide or oxycarbide iron-tungsten-containing compounds. This is in good agreement with the performed X-ray phase analysis (Fig. 1, a), and also corresponds to the results from [11], where the processes of formation of tungsten carbides during the reduction of the corresponding oxides are given. The presence of identified free tungsten in the results of work [10], as a difference compared to our research, is explained by a higher content in the raw material. At the same time, sections 2, 5, 6, 8, 9 are characterized by a relatively high content of molybdenum in the range of 0.78–2.27 % by weight. At the same time, molybdenum, like tungsten, is prone to carbide formation during carbon-thermal reduction, which is consistent with the results reported in [8] and determines the possibility of the presence of complex carbide compounds of tungsten and molybdenum in the reduction products.

In the microstructure photographs, some of the studied formations (Fig. 1, b–d, Table 1) had a relatively high content of chromium (7.54–24.41 wt.%, sites 3, 6, 8, 11) and vanadium (2.71–21.14 % by weight, plots 2, 3, 5, 6, 8, 11). Such formations can probably consist of a complex of carbides of iron, chromium and vanadium, which is consistent with the results in [12]. But, as a drawback, one should note the smaller number of components in the investigated system of reactions, where other refractory elements did not participate. The possibility of the formation of iron-chromium-vanadium-containing carbide compounds is consistent with the results reported in [13]. However, as a difference, taking into account the performed X-ray phase and microstructural studies, some of the chromium atoms can be found as substitution atoms in the lattice of iron-based carbides. That is, in the recovery products, the residual carbon is to a greater extent in the composition of carbide compounds of iron and refractory elements.

A stepwise increase in the degree of reduction from 32 % to 69 % and 77 % ensured an increase in the intensity of the manifestation of the solid solution of alloying elements and carbon in the  $\alpha$ -Fe lattice in complex with carbides. At the same time, the manifestation of the oxide component decreased. At the same

time, residual oxygen in the studied areas of recovered raw materials decreased from 10.89–14.10 % by weight to 5.71–8.97 % by weight and 3.74–6.01 % by weight, respectively. Based on this, taking into account the set of studies performed, the most acceptable degree of recovery of alloyed tungsten-molybdenum-containing scale of high-speed steel with a relatively high content of vanadium with the subsequent use of the obtained material as an alloying additive is 77 %. At the same time, ensuring a recovery rate of 69 % is also sufficient. Because of the residual carbon in the form of carbides, which have an intensive manifestation in the results of our research, an increased regenerative capacity and level of assimilation of alloying elements are ensured. At the same time, the reduction of the remaining oxide component is carried out in the liquid metal during alloying. The spongy microstructure of the alloying additive provides relatively fast dissolution compared to standard ferroalloys. This gives a reduction in the total melting time, as a result of which a decrease in spent resources is ensured.

Certain limitations that should be taken into account when trying to apply the results of the research in practice are due to the complex doping of the products of high-speed steel slag recovery. The specified limitations refer to the case when some of the elements of the obtained alloying additive are strictly limited in the target product, which may lead to an excess of the corresponding content of elements in the composition. In order to prevent problems of this nature and to take into account the specified limitations with the provision of relatively high utilization rates in practice, it is necessary to observe the approximation of the content of the elements of the alloying additive relative to the target product. The limitations of our results in the framework of the recovery of oxide waste with a certain composition of alloying elements can be taken into account in further theoretical studies. In this direction, it is possible to perform calculations and analysis of the thermodynamic equilibrium of the system of carbon-thermal reduction reactions with the participation of a wider range of refractory elements.

The lack of images of the microstructure obtained with different magnifications can be noted as a drawback. This would increase the effectiveness of the conducted research.

The development of this direction is possible with the involvement of finely dispersed oxide waste from the production of other classes of steels for processing. Difficulties in attempts to advance our research consisted in the lack of the necessary volume of the experimental base.

The scope of application of the obtained alloying additive refers to special metallurgy, respectively, the smelting of alloyed steels. The conditions of use correspond to the possibility of involving an alloying additive to obtain grades of steels, the composition of which does not have strict restrictions on carbon, when replacing part of the standard alloying materials. Taking into account the above, high-speed steels of R12F3, R6M5F3, and other brands, which are smelted in an electric arc furnace, are promising in this case. Addition of the resulting alloying material is possible together with the metal charge during back-filling. At the same time, the expected consumption coefficients of the alloying additive can be at the level of 100–200 kg/t of steel, depending on the grade being smelted. Potentially expected effects from the practical use of our results, taking into account the accumulated experience, can determine the degree of extraction of refractory elements at a level above 90 %. No phases and compounds characterized by an increased tendency to sublimation were detected in the obtained alloying additive. That is, there is no need to provide additional conditions that prevent the loss of high-value elements during evaporation

with the gas phase, which causes an increase in the degree of extraction of alloying elements. The proposed technique for extracting alloying elements from the slag of high-speed steel in own production can provide a significant reduction in the costs of standard ferroalloys and metal alloying materials.

## 7. Conclusions

1. It was found that increasing the degree of reduction of high-speed steel scale from 32 % to 69 % and 77 % increases the manifestation of the solid solution of alloying elements and carbon in the  $\alpha$ -Fe lattice. At the same time, the intensity of the diffraction maxima of  $\text{FeWO}_4$  and  $\text{Fe}_3\text{O}_4$  decreased. The presence of  $\text{Fe}_3\text{C}$ ,  $\text{FeW}_3\text{C}$ , WC, VC,  $\text{V}_2\text{C}$ , and  $\text{Cr}_3\text{C}_2$  was observed in the reduction products. At the same time, the manifestation of  $\text{FeW}_3\text{C}$  increased relative to  $\text{Fe}_3\text{C}$  and WC.

2. It was found that when the degree of slag recovery increased from 32 % to 69 %, the formation of polyhedral and rounded particles with different composition of alloying elements was observed in the microstructure. In the case of a degree of recovery of 77 %, the microstructure had a spongy structure with the presence of rounded particles. A stepwise increase in the degree of recovery from 32 % to 69 % and 77 % provided a relative decrease in the content of residual oxygen

in the studied areas (% by weight) from 10.89–14.10 % by weight to 5.71–8.97 % by weight and 3.74–6.01 % by weight, accordingly. At the same time, the content of tungsten and molybdenum (% by weight) was in the range of 2.36–42.36 and 0.00–2.27, respectively. The content of vanadium and chromium in the studied areas of the samples was in the range of 0.00–17.93 % by weight and 0.00–24.41 % by weight, accordingly.

## Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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## Data availability

All data are available in the main text of the manuscript.

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