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Development of the Recycling of Alloyed Metallurgical Waste: Features of Phase and Structural Transformations

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Abstract: The features of structural and phase transformations during the processing of alloyed metallurgical wastes using reduction smelting are determined herein. This is necessary in order to determine the technological parameters of the melting process that ensure the reduction in the losses of alloying components. The use of X-ray phase analysis in combination with the methods of raster electron microscopy and X-ray microanalysis ensured the identification of the microstructure features and the chemical composition of individual phases and inclusions in the metal. Our study identified new technological aspects of high-alloyed technogenic waste processing using reduction smelting. The obtained parameters of the resource-saving alloying compound provide the possibility to replace parts of the standard ferroalloys in steelmaking processes.

Keywords: oxide metallurgical waste; alloy steel scale; reduction smelting; phase transformations; microstructure



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1. Introduction

The gradual depletion of the raw materials fields dictates the rising trend of the global market prices for refractory metal alloys [1]. One of the alternative sources of alloying materials is processing and returning to the production of alloyed technogenic wastes, large volumes of which are not used effectively in practice [2]. Wastes of alloyed, heat-resistant, corrosion-resistant, and other steel and alloy grades, the operation of which can be accompanied by the effects of aggressive atmospheres, temperatures, and mechanical factors, contain expensive chemical elements. These elements include Ni, Cr, W, Mo, and many others. A specific feature of wastes is the presence of alloying elements in the form of oxides and complex compounds. This requires consideration of the complexity of chemical–physical interactions of elements when developing the technological conditions of processing [3]. The major portion of the alloyed wastes contains oxide and fine-dispersed compounds (scale, power grinding chips, and grinding dust), the effective processing of which is complicated. The above characteristics present challenges in terms of implementing the competitive ability due to problems with production processes and the high price of the finished products, respectively [4].

Therefore, the problem with decreasing losses of expensive chemical elements in wastes processing resulting from the production of high-alloy steels and compounds still needs to be urgently addressed. To accomplish this, transformations during the processing of metallurgical oxide industrial wastes using reduction smelting should be studied.

In accordance with the paper cited in [5], 0.043 t of scale and slag accounts for 1 ton of produced rolled steel. Steel losses, when it is processed in scarfing machines, are 5%–15%. The particle size for stainless corrosion-resistant steels with a nickel content of 19 wt% is 240–450 μm . Based on the data from the work cited in [6], in the best case scenario, 12% of the manufactured product volume is lost with the scale when small commercial billets are made of high-alloy steel. The difficulties lie in the fact that pre-treatment of scale and other fine-dispersed wastes is required in order to increase the level of alloy element recovery by molten metal. Moreover, there are additional difficulties associated with “oily” (contaminated) scale [7]. This means that before adding to the charge, harmful admixtures must be treated off. Based on the data in [6], when finely-dispersed high-alloy steel waste is added to a liquid bath without pre-treatment, the loss of refractory elements reaches 40%.

Iron scale is composed of Fe_3O_4 , Fe_2O_3 , and FeO , as specified in [8], but [6] also identified WO_2 and $\text{W}_2\text{C}\cdot\text{Mo}_2\text{C}$ in the high-speed steel scale. The reason for this may be an increased level of steel alloying. Similar results to those for the iron carbide presence were shown in [9], when chromium-nickel steel oxide waste was reduced by the carbon. The authors of the study in [8] investigated the iron scale reduction by carbon within the range of 1023–1323 K, with the detection of Fe_3C and carbon along with the iron phase in the resultant products. Residual iron oxides appeared only after heat treatment at a temperature of 1023 K. In contrast, as indicated in [10], the additional presence of tungsten seems to have had an effect on the nature of carbide formations, which affected the microstructure’s features. Some particles, probably carbide ones, with high levels of carbon, tungsten, and other elements, were found. Among the shortcomings, insufficient research into the reduction products’ physical and chemical properties involving refractory elements—tungsten and niobium—can be noted. There is still a need to identify the most preferable conditions for reducing alloyed technogenic raw materials in the Fe-Ni-Cr-Mo-W-O-C system.

The reduction of oxides $\text{FeO}\text{--}\text{Cr}_2\text{O}_3$ at different C:Fe ratios and temperatures varying from 1373 K to 1523 K was studied by the authors of [11]. It was found that the increase in the C:Fe ratio from 0.8 to 1.4 caused the increase in the chromium extraction rate from 9.6% to 74.3%, respectively. The temperature rise to 1523 K caused the formation of a larger quantity of carbides, the residues of which could not be avoided in the products reduced by carbon [12]. If the C:Fe ratio was less than 0.8, there was a significant decrease in the chromium extraction rate and the carbide formation. The resulting chromium carbides dissolved in the iron phase [11]. The formation of metallic chromium and chromium carbides was also demonstrated by the authors of [13] during the reduction of chromium-containing ore raw materials. After heat treatment at a temperature of 1273 K and reaching the O:C ratio of 1.05–1.15 in the charge, the carbothermal reduction was accompanied by the occurrence of Cr_3C_2 and Cr_7C_3 . Thus, to increase the chromium extraction rate during the reduction, the charge must contain certain excessive carbon relative to oxygen. The study cited in [14] specifically researches Cr_2O_3 reduction with carbon within a range of 1273–1773 K. Parallel reduction and formation of Cr_3C_2 , Cr_7C_3 , and Cr_{23}C_6 carbides were found, and the possibility of obtaining iron–chromium ligatures with the limited carbon content was fixed. There is a possibility of obtaining products of carbon thermal reduction with relatively low residual carbon, which indicates the expanded scope of application. However, it is impossible to see the regularities of changes in the microstructure and composition of the phase formations in the obtained materials during the reduction of the chromium and iron oxides complex within the alloyed technogenic raw materials.

The study cited in [15] outlines the research into reduction reactions in the Fe–Ni–O system at a temperature of 1373 K. When the treatment temperature rose, the reduced products appeared 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, a relatively considerable tendency for nickel oxide reduction against iron oxides was observed. The formation processes of metallic nickel and iron were seen in separate stages. The possible presence of iron carbides and the iron-containing phase Fe_xNi_y , which can appear during the reduction of oxide alloyed waste, was indicated.

The disadvantage lies in the absence of data regarding the reduction of complex oxide compounds which can be present in technogenic raw materials. This may lead to potential differences during the reduction reactions. The unresolved parts of the problem lie in the expansion of our understanding of the elements' presence in reduced products, determined using scanning electron microscopy and X-ray microanalysis.

The authors of [16] studied the reduction in the Mo–O–C and Ca–Mo–O–C systems. The formation of molybdenum dioxide as an intermediate product was found; the latter was further transformed into molybdenum and carbides. The conditional division of the process into the primary interaction of MoO₃ with carbon occurred with the carbon gasification reaction, as did the further reduction of MoO₂ with the involvement of carbon monoxide. The authors of [17] made calculations using thermodynamics and determined the equilibrium of WO₃ reduction reactions with the involvement of carbon and carbon monoxide at a temperature of 1500–6000 K. The obtained characteristics of the reactions showed that the reduction of WO₃ most likely occurred to produce tungsten and then the carbides W₂C and WC. As was indicated in [18], there are stages of WO₃ transformation through WO_{2,72} and WO₂ to W. The tungsten reduction takes place at a temperature of 1223 K. The tendency to form carbides, along with the reduction of oxide tungsten-containing compounds, was confirmed by the studies contained in [19]. The disadvantage is that the form of the molybdenum- and tungsten-containing compounds present in the oxide wastes of high-alloy steels can be more complicated and differ from specific pure oxides.

Based on the above, the purpose of this work was formulated. It lies in the identification of features of phase and structural transformations in the processing of high-alloy wastes from metallurgical production using reduction smelting to obtain an alloy containing refractory elements such as Ni, Cr, Mo, and W. This is necessary to determine the parameters that reduce the losses of alloying elements by means of sublimation in the processing of oxide-alloying raw materials and use of the received alloying additive.

2. Materials and Methods

In this study, a mixture of chromium–nickel-containing steels, type 18–10 (grades 08H18N10, 04H18N10 and others, respectively, GOST 5632-2014) scale, and a grinding chip of nickel-based heat-resistant alloys (grades EI868 and EK171, respectively, GOST 5632-2014) formed under metallurgical production conditions, was used as a feedstock. The addition of metal chips ensured the intensification of heat exchange at the initial stages of charge heating and an additional alloying improvement. The reducing agent was carbon in the form of ultradispersed dust, which was the waste from the carbon–graphite production, the addition of which ensured the O:C ratio in the charge at the level of 1.56. The samples for the research were melted in an indirect heating furnace with coal lining in alundum crucibles. The melting temperature was 1873–1913 K. After melting, the alundum crucibles with the alloy were taken out of the furnace and cooled at ambient temperature.

To make a comparative assessment of the probability of reduction reactions in the Ni–Cr–Mo–W–O–C system at a temperature of 300–2000 K, the Gibbs energy change (ΔG) was calculated using the given thermodynamic values of the changes in enthalpy (ΔH), entropy (ΔS), and heat capacity (ΔC_p) [20–25]. In the calculations, we used the technique described in [21], along with the following equation:

$$\Delta G_T^0 = \Delta H_{T_1}^0 + T\Delta S_{T_1}^0 + \int_{T_1}^T \Delta C_p dT - T \int_{T_1}^T \frac{\Delta C_p}{T} dT \quad (1)$$

The effect of the heat capacity changes and polymorphic transformation progress in the initial components and reaction products at different temperatures was also taken into account.

X-ray phase analysis of the samples was performed with the help of a diffractometer, using monochromatic radiation Cu K α ($\lambda = 1.54051$ Å). Measurements were made at the tube voltage of $U = 40$ kV and anode current of $I = 20$ mA. Images of the sample's microstructure were obtained with the help of a JSM-IT300 scanning electron microscope

from JEOL (Tokyo, Japan). Equipping the microscope with a X-MAX80 attachment for X-ray microanalysis from Oxford Instruments (Abingdon, UK) allowed us to identify the contents of elements in individual phase formations, which can be seen on the microstructure images. The sample's microstructure was studied at an accelerating voltage of 10–25 kV and an electron probe current of 52–96 μA . The operating distance to the sample surface was 10.5–11.7 mm.

3. Results

As one can see in Figure 1, reaction 25, providing the reduction of molybdenum oxide MoO_3 to MoO_2 when reacting with carbon, had the highest probability in the Ni-Cr-Mo-W-O-C system within the studied temperature range of 300–2000 K. Curve 25 of this reaction is located in the negative part of the diagram.

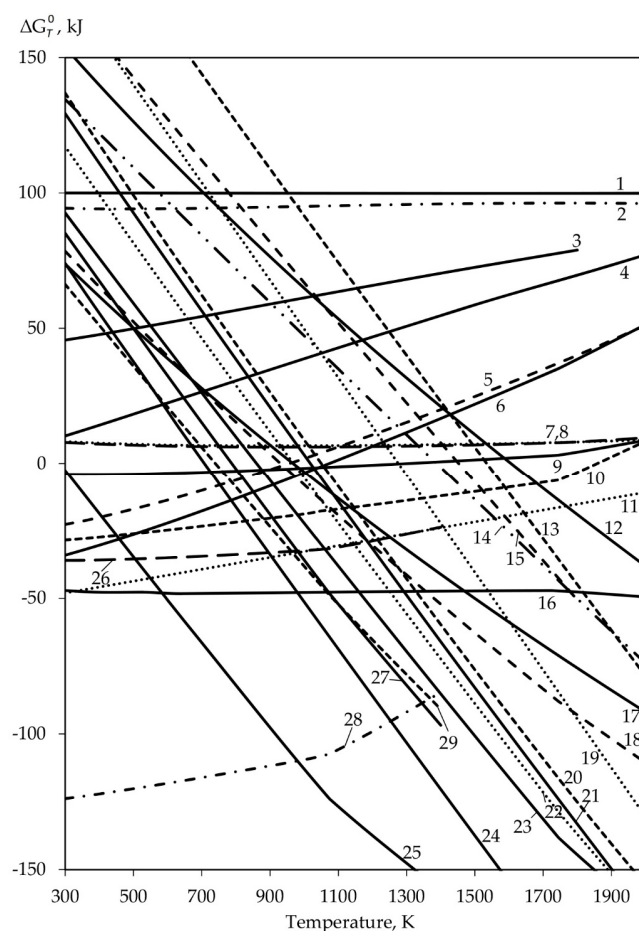


Figure 1. Dependence of the Gibbs free energy difference on the carbon reduction reaction temperature in the Ni-Cr-Mo-W-O-C system: 1— $7/33\text{Cr}_2\text{O}_3 + \text{CO} = 2/33\text{Cr}_7\text{C}_3 + 27/33\text{CO}_2$; 2— $1/3\text{Cr}_2\text{O}_3 + \text{CO} = 2/3\text{Cr} + \text{CO}_2$; 3— $23/93\text{Cr}_2\text{O}_3 + \text{CO} = 2/93\text{Cr}_{23}\text{C}_6 + 81/93\text{CO}_2$; 4— $3/17\text{Cr}_2\text{O}_3 + \text{CO} = 2/17\text{Cr}_3\text{C}_2 + 13/17\text{CO}_2$; 5— $1/3\text{MoO}_2 + \text{CO} = 1/6\text{Mo}_2\text{C} + 5/6\text{CO}_2$; 6— $1/5\text{WO}_3 + \text{CO} = 1/5\text{WC} + 4/5\text{CO}_2$; 7— $1/2\text{MoO}_2 + \text{CO} = 1/2\text{Mo} + \text{CO}_2$; 8— $1/2\text{WO}_2 + \text{CO} = 1/2\text{W} + \text{CO}_2$; 9— $1/3\text{WO}_3 + \text{CO} = 1/3\text{W} + \text{CO}_2$; 10— $\text{WO}_3 + \text{CO} = \text{WO}_2 + \text{CO}_2$; 11— $1/4\text{MoO}_3 + \text{CO} = 1/8\text{Mo}_2\text{C} + 7/8\text{CO}_2$; 12— $7/27\text{Cr}_2\text{O}_3 + \text{C} = 2/27\text{Cr}_7\text{C}_3 + 21/27\text{CO}$; 13— $1/3\text{Cr}_2\text{O}_3 + \text{C} = 2/3\text{Cr} + \text{CO}$; 14— $3/13\text{Cr}_2\text{O}_3 + \text{C} = 2/13\text{Cr}_3\text{C}_2 + 9/13\text{CO}$; 15— $23/81\text{Cr}_2\text{O}_3 + \text{C} = 2/81\text{Cr}_{23}\text{C}_6 + 69/81\text{CO}$; 16— $\text{NiO} + \text{CO} = \text{Ni} + \text{CO}_2$; 17— $1/3\text{WO}_2 + \text{C} = 1/3\text{WC} + 2/3\text{CO}$; 18— $1/4\text{WO}_3 + \text{C} = 1/4\text{WC} + 3/4\text{CO}$; 19— $2/5\text{MoO}_2 + \text{C} = 1/5\text{Mo}_2\text{C} + 4/5\text{CO}$; 20— $1/2\text{MoO}_2 + \text{C} = 1/2\text{Mo} + \text{CO}$; 21— $1/2\text{WO}_2 + \text{C} = 1/2\text{W} + \text{CO}$; 22— $1/3\text{WO}_3 + \text{C} = 1/3\text{W} + \text{CO}$; 23— $\text{WO}_3 + \text{C} = \text{WO}_2 + \text{CO}$; 24— $\text{NiO} + \text{C} = \text{Ni} + \text{CO}$; 25— $\text{MoO}_3 + \text{C} = \text{MoO}_2 + \text{CO}$; 26— $1/3\text{MoO}_3 + \text{CO} = 1/3\text{Mo} + \text{CO}_2$; 27— $1/3\text{MoO}_3 + \text{C} = 1/3\text{Mo} + \text{CO}$; 28— $\text{MoO}_3 + \text{CO} = \text{MoO}_2 + \text{CO}_2$; 29— $2/7\text{MoO}_3 + \text{C} = 1/7\text{Mo}_2\text{C} + 6/7\text{CO}$.

When the temperature rises above 700 K, the reduction reaction of nickel oxide NiO to Ni (curve 24) takes negative values of the Gibbs free energy difference. At a temperature above 950 K, the negative values of the Gibbs free energy difference are taken by the reaction of the molybdenum trioxide reduction to Mo₂C carbide, and above 800 K to Mo. Reaction 23, which is typical for the reduction of WO₃ to WO₂, which takes negative values of the Gibbs free energy difference at a temperature above 850 K. In the temperature range of 920–1050 K, the negative values of the Gibbs free energy difference are taken by the reactions of tungsten oxides WO₃ (reactions 18, 22) and WO₂ (reactions 17, 21) reductions to WC and W, respectively (Figure 1). In the case of MoO₂, one can observe reactions 20 and 19 with the formation of Mo₂C and Mo, respectively.

In the temperature range of 1400–1600 K, the reactions involving the carbonothermal reduction of chromium oxide Cr₂O₃ (reactions 12–15) take negative values of the Gibbs free energy difference. Reactions with the formation of Cr₃C₂ and Cr₂₃C₆ carbides can most likely be seen from the thermodynamic point of view (reactions 14 and 15, respectively). The reduction reaction of chromium oxide Cr₂O₃ to carbide Cr₇C₃ had the lowest thermodynamic probability; thus, the relevant curve is seen in the negative part of the diagram at a temperature of 1600 K.

The oxide reduction reaction curves of the discussed system with carbon monoxide show the lowest values of the Gibbs free energy difference in areas of relatively low temperatures. However, regarding the thermodynamic probability of an oxide reduction reaction, a clear analogy with the interaction with carbon can be seen. This means that the probability of the occurrence of a reduction reaction for the relevant oxides decreases in the following sequence: NiO, MoO₃, WO₃, MoO₂, WO₂, Cr₂O₃. It should also be noted that reactions 11, 16, 26, and 28 can be found in the negative part of the diagram, and reactions 9 and 10 fall within the positive part of the diagram only at temperatures of 1400 K and 1800 K, respectively. The curves of reactions 1–4, 7, and 8 occur in the positive part of the diagram. Reactions 1 and 2 of Cr₂O₃ reduction to Cr₇C₃ and Cr, respectively, have the highest value of Gibbs free energy difference.

Studies of the phase composition of the obtained alloying compound showed relatively active development of the FeNi phase, as well as FeCr (Figure 2). The carbide component was expressed as the development of Fe₃C, tungsten carbides WC and W₂C, and complex carbide W₂C·Mo₂C.

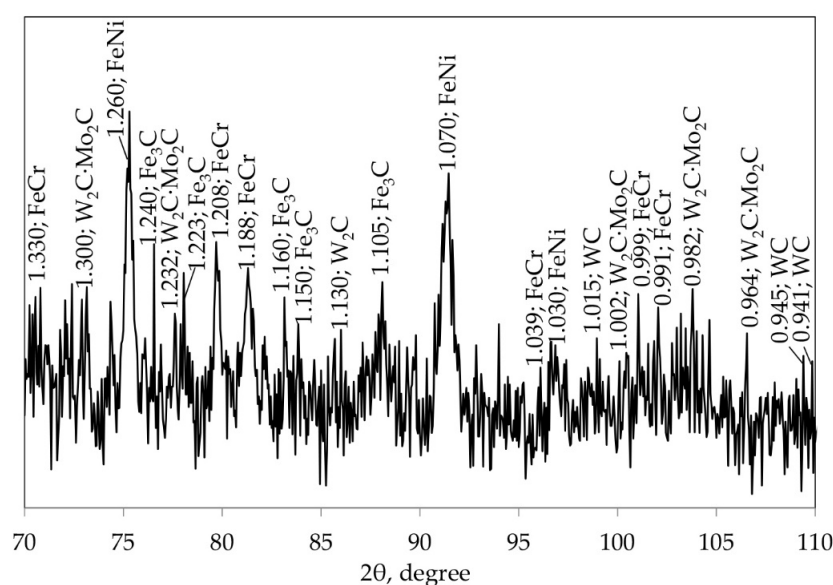


Figure 2. Diffractogram section related to the X-ray phase analysis of the alloying compound.

The alloy's microstructure was composed of several phases, with different shapes and sizes of particles (Figure 3a–d). The phases with relatively high contents of Ni (areas 3, 7,

9, and 15) and Cr (areas 5, 8, 11, 12, and 16), up to 44.33 wt% and 46.33 wt%, respectively, were identified in the studied areas (Figures 3 and 4, Table 1). Some particles had high contents of Mo and W (areas 2, 4, 10, 13), up to 14.17 wt% and 26.52 wt%, respectively. These particles also contained Nb up to 1.59 wt%. The carbon content in the above areas (Figures 3 and 4, Table 1) varied within a range of 0.45–2.26 wt%. Moreover, some phase formations with carbon contents up to 89.54 wt% were found, and they seemed to be the residual unreacted carbon-reducing agents.

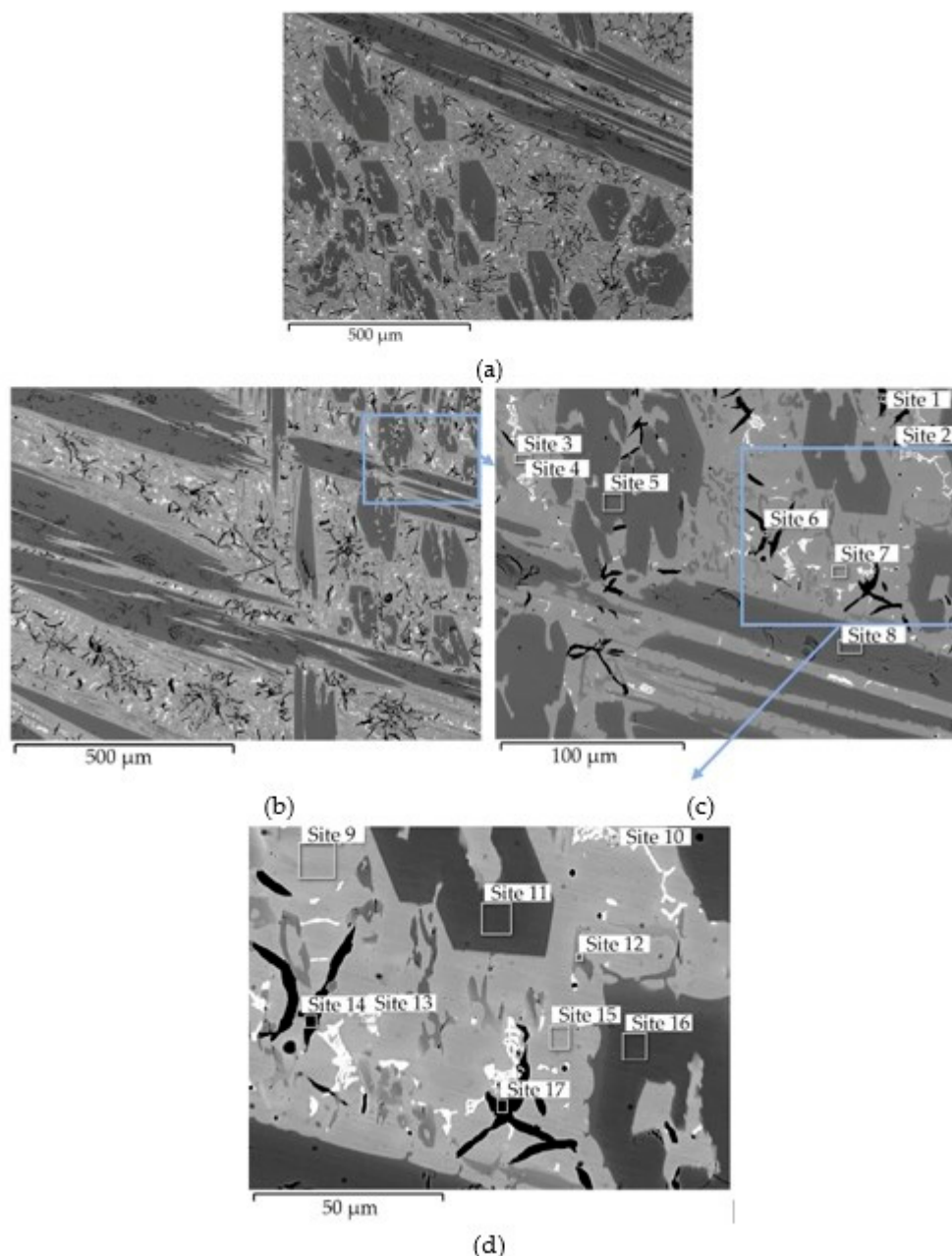


Figure 3. Images of the alloying compound's microstructure, with magnifications of: (a,b)— $\times 100$, (c)— $\times 500$, (d)— $\times 1000$, 1–17—X-ray microanalysis areas. Arrows indicate scaled points of microstructure.

The determination of element concentrations in the studied area of the sample surface showed a clear distribution between the phases with different contents of Cr and Ni (Figure 5c,d). The Fe content was relatively uniform throughout the studied area (Figure 5b), except for carbon inclusions and phases with high Mo and W contents. However, the highest concentration of iron was observed in the phase with a high nickel content, which

is evidenced in the figure by the corresponding more intensively colored areas. W and Mo, as well as Nb, were more concentrated in separate inclusions (Figure 5e–g).

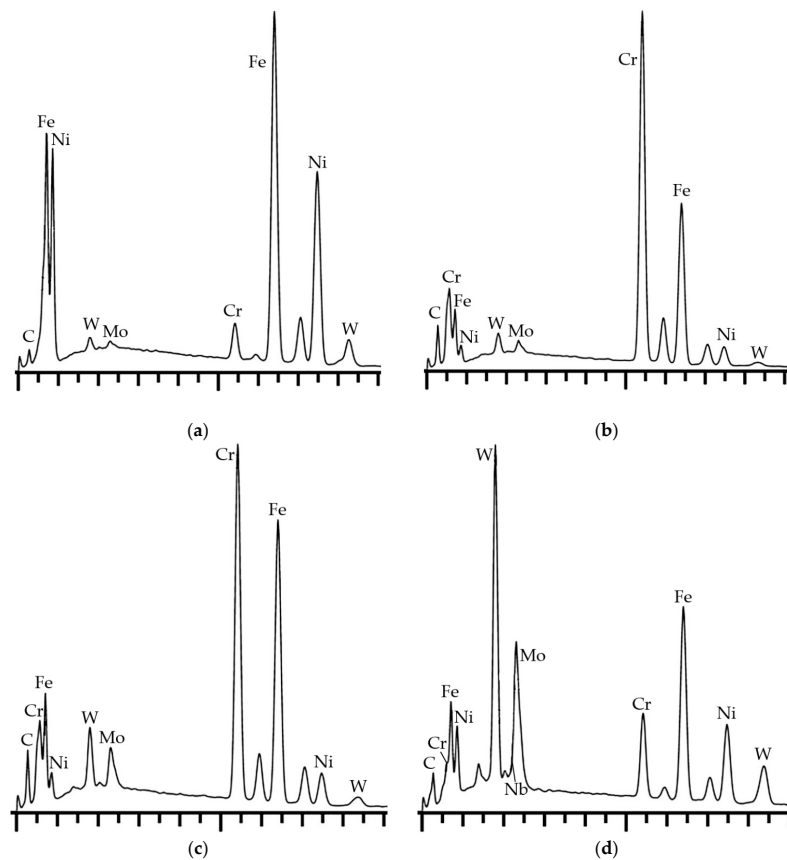


Figure 4. Spectrographs of the X-ray microanalysis of some studied areas of the alloy obtained in Figure 3, respectively: (a)—9; (b)—11; (c)—12; (d)—13.

Table 1. Results of the X-ray microanalysis of the alloying compound, based on Figure 3.

Areas Studied	Element Content, wt%									Total
	C	Al	Cr	Mn	Fe	Ni	Nb	Mo	W	
1	81.37	0.00	0.87	0.00	9.92	7.84	0.00	0.00	0.00	100
2	2.26	0.15	5.46	0.00	41.50	22.13	0.85	9.79	17.86	100
3	0.47	0.07	3.77	0.11	48.97	44.33	0.00	0.41	1.87	100
4	2.21	0.07	5.91	0.00	40.28	23.03	1.02	9.18	18.30	100
5	1.81	0.08	46.33	0.00	42.90	5.42	0.00	1.09	2.37	100
6	85.53	0.00	0.98	0.00	7.67	5.82	0.00	0.00	0.00	100
7	0.45	0.10	3.62	0.09	49.52	44.09	0.00	0.39	1.74	100
8	1.85	0.06	46.17	0.00	42.67	5.65	0.00	1.16	2.44	100
9	0.48	0.00	3.16	0.10	51.61	41.53	0.00	0.67	2.45	100
10	2.25	0.12	7.26	0.00	36.27	15.51	1.44	13.3	23.85	100
11	1.82	0.03	45.10	0.00	43.39	5.60	0.00	1.36	2.70	100
12	1.89	0.06	31.97	0.00	50.52	6.56	0.00	3.52	5.48	100
13	2.23	0.17	7.78	0.00	33.07	14.47	1.59	14.17	26.52	100
14	89.54	0.00	1.09	0.00	6.02	3.35	0.00	0.00	0.00	100
15	0.46	0.11	3.70	0.08	50.02	43.75	0.00	0.31	1.57	100
16	1.84	0.05	45.46	0.00	43.17	5.54	0.00	1.23	2.71	100
17	84.02	0.00	0.71	0.00	8.94	6.33	0.00	0.00	0.00	100

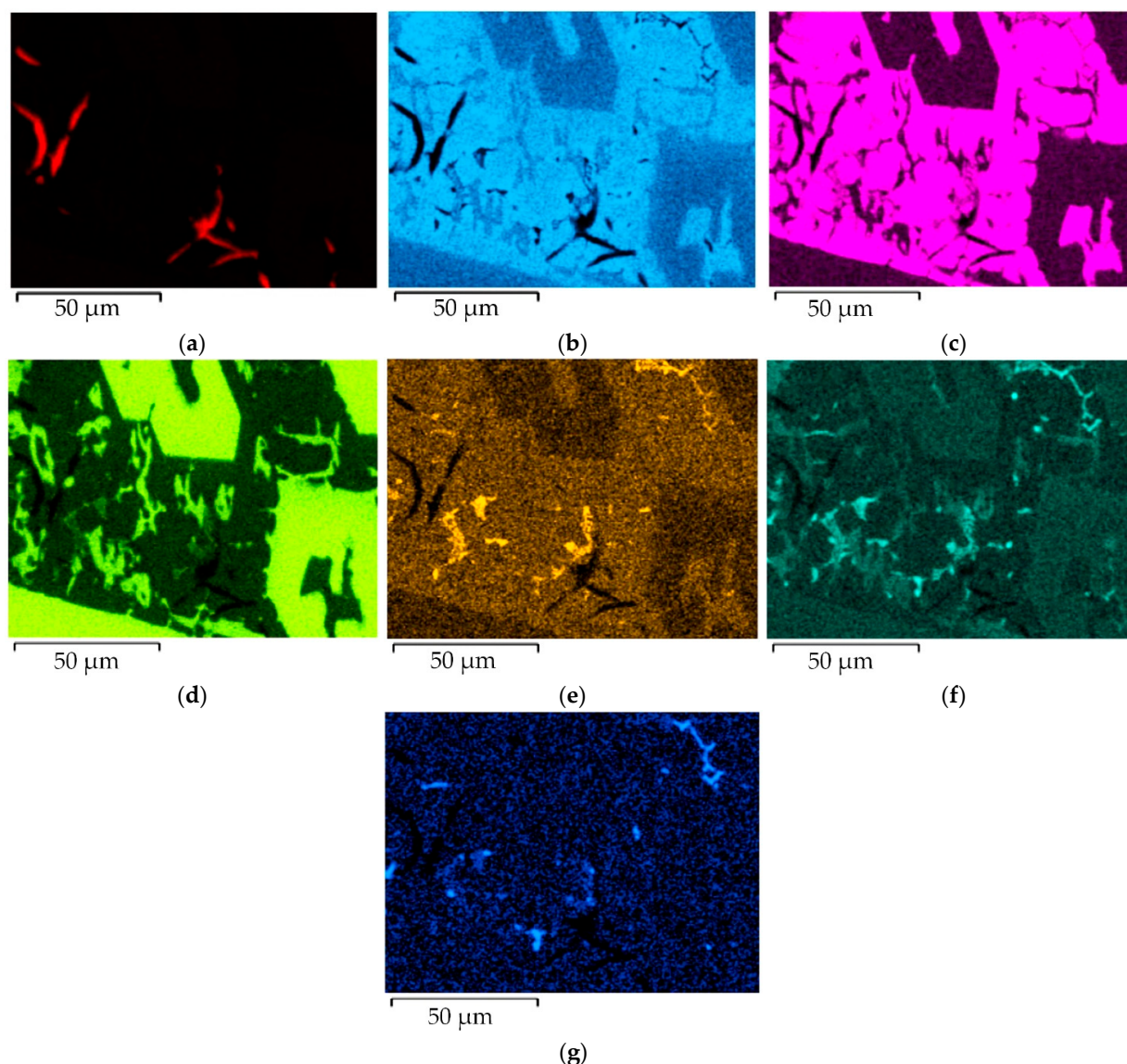


Figure 5. The results of X-ray microanalysis in the major elements distribution mode in the characteristic X-rays, according to Figure 3d (magnification $\times 1000$). The higher element contents correspond to more intense colors: (a)—C, (b)—Fe, (c)—Ni, (d)—Cr, (e)—Mo, (f)—W, (g)—Nb.

4. Discussion

It follows from the results obtained from thermodynamic analysis in the Ni-Cr-Mo-W-O-C system regarding the reduction of metal oxide technogenic raw materials that the stability of oxide compounds of refractory elements decreases as the temperature rises. From a thermodynamic point of view, higher oxide compounds have less stability than lower oxide ones. In the system which we studied, the formation of metal oxides and carbides, free metals, and CO and CO₂ are possible. The refractory metal oxides are reduced by carbon and carbon monoxide. A high probability of parallel carbide formation reactions, along with the reduction reactions at relatively low temperatures, has been discovered. As the temperature rises, the probability of metal reduction in a free state increases. This additionally dictates a negligible probability of obtaining a carbon-free product. The consideration of phase transitions and the change in the heat capacity of the reaction components along with the temperature increase allowed us to obtain more accurate results. The significant number of concerned reactions in a wide temperature range demonstrates a broader picture of possible transformations in the process of alloyed

technogenic waste reduction. Difficulties in the development of this area lie in the lack of a sufficiently large reference base to be used for calculations. There are possible prospects of studies in this direction for calculating, plotting, and updating the equilibrium reaction diagrams in the Ni-Cr-Mo-W-O-C system with the identification of the formed areas. In addition, it will be possible to establish the most acceptable conditions for the existence of phases depending on changes in the temperature and partial pressure of CO. The plotted diagram can be used in the technological field for the purpose of obtaining metallized materials from alloyed steel waste.

The X-ray phase analysis of the studied compound (Figure 2) shows that the alloying elements Cr and Ni mostly occurred in the form of intermetallic phases FeNi and FeCr, respectively. Some alloying elements could be found in the form of substitutional atoms in Fe_3C . This agrees with the results of the study cited in [9], where the diffractogram of the reduced alloyed product clearly showed only iron-containing compounds, which is also typical for unalloyed raw materials [8]. However, in contrast to the above study, the completed studies also showed some carbide compounds of the alloying elements, such as WC, W_2C , and $\text{W}_2\text{C}\cdot\text{Mo}_2\text{C}$. This agrees with the results of [12] regarding the parallel reduction and carbide formation and the practical impossibility of obtaining a completely carbon-free product, as well as with the results of [7]. In this case, the residual carbon in the form of carbides will further ensure a relatively high reducibility when the alloying element is used.

The studies of the microstructure, together with the X-ray microanalysis of the obtained alloy, further demonstrate the nature of the elements' presence within it. The inclusions with higher contents of nickel with iron (Figure 3c,d, areas 3, 7, 9, 15) appear to constitute the intermetallic phase of FeNi, which is evidenced by the completed X-ray phase analyses (Figure 2). This agrees well with the results of [15], where the relatively high efficiency of the carbon reduction of the iron–nickel oxide component was confirmed. At the same time, [15] showed that the iron-containing carbide component Fe (Fe_nC_m) was present together with Fe_xNi_y in the course of the reduction process. Some phases were characterized by the high content of Cr and Fe (Figure 3c,d, areas 5, 8, 11, 12, 16). These appear to be the intermetallic FeCr phases which were seen on the obtained diffractogram (Figure 2). Taking into account the results of the X-ray phase analyses, the above areas can contain Fe_3C carbide, where Fe atoms are partially substituted by Cr atoms. This agrees with the completed thermodynamic studies and the results of [11,13,14], which demonstrated the formation of chromium-containing carbides in parallel with the reduction reactions. However, in [13,14], the reduction was accompanied by the formation of separate chromium carbides of the Cr_nC_m type. The absence of chromium carbides in the diffractogram in these studies can be explained by the fact that some carbides can be dissolved in the intermetallic component FeCr when two phases come into contact. Similar processes are described in [11], where the formed chromium carbides were dissolved in γ -Fe. In turn, the thermodynamic studies (Figure 1) showed a lack of chromium carbides and metallic chromium, along with a relatively low probability of the corresponding reactions.

Some particles with higher contents of Mo, W, Nb, and C (Figure 3, areas 2, 4, 10, 13) can constitute the carbide phases. This corresponds to the results of the thermodynamic (Figure 1) and phase (Figure 2) studies, based on which we determined that the phases in the specified surface areas may contain carbides such as WC, W_2C , and $\text{W}_2\text{C}\cdot\text{Mo}_2\text{C}$. This also agrees with the results of studies regarding the reduction mechanisms of W [17–19] and Mo [16] oxides. It was also found that the metallic and carbide components were formed in parallel at the final stage of the reduction. Here, as a contrast, the assumed particles of the carbide phase in these studies were characterized by high contents of the alloying element complexes. This indicates a more complex nature of the refractory element compounds. Analysis of the study results indicates the predominance of intermetallic phase formations of iron with nickel and chromium in the phase composition. The fraction of residual carbon in the form of a carbide component had a relatively low presence, thus ensuring that the reducing ability is required when the alloy is used.

The limitations of the study's results encourage the use of the obtained alloying composite in relation to certain steel grades, based on the set of present elements. For example, the complex of elements Ni, Cr, Mo, and W in some heat-resistant steels identifies the required qualitative properties of the product. In contrast to Cr, Mo, and W, the Ni content in high-speed tool steels is highly limited to tenths of a percent. Therefore, the allowable limits of the element content can be exceeded in the target product. Similar problems cannot be excluded for other steel grades where there are severe limits on the content of one or more elements in the alloying compound. Thus, to avoid problems of this nature and to increase the use rates of raw materials, close ratios of the element contents in the alloying composite and in the target product should be followed.

The lack of results of X-ray analyses for several phase formations at once, which would have allowed us to obtain the averaged contents of the elements, should be noted as a disadvantage. This would make it possible to monitor the distribution of the major elements throughout the studied surface of the samples, which would characterize, to a greater degree, the nature of the phases and inclusions.

This study can be continued in order to expand the range of the steel grades, the oxide wastes of which can be involved in processing by reduction smelting. The difficulties in continuing this study are due to the lack of a sufficient experimental database. The most promising for prospective studies are wastes with high levels of alloying elements.

The completed studies determined new technological aspects involved in the processing of high-alloy technogenic waste to obtain compounds with relatively low residual carbon content. The resulting parameters of the resource-saving alloying compound can make it possible to replace some standard ferroalloys of those steel grades in the manufacturing process that place limitations on the carbon content. Heat-resistant austenitic steels that are melted in electric arc furnaces are promising in these terms. The obtained alloy did not contain compounds and phases with relatively high tendencies for sublimation. That is, there is no need to create special conditions to prevent evaporation and losses of alloying elements with the gas phase. This also leads to wider use of the alloying elements.

5. Conclusions

1. The features of thermodynamic equilibrium in the Ni-Cr-Mo-W-O-C system in relation to the reduction of oxide technogenic raw materials were determined. This provided a satisfactory notion of the possibility of the reactions, depending on the temperature. The thermal conditions that can ensure the high probability of reactions forming carbides and free elements during carbon and carbon monoxide reduction were clarified. The probability of reduction reactions of the corresponding oxides decreases in the following order: nickel oxide, trioxides, molybdenum and tungsten dioxides, and chromium oxide. The reduction reactions of higher oxides are more probable than those of lower oxides. Moreover, obtaining a reduced product without carbides is unlikely.

2. The features of the phase composition of the obtained alloying compound were determined. The intermetallic phases FeNi and FeCr were developed quite intensively. The phase of Fe₃C carbide clearly occurred. The fragmentary development of the carbides of the alloying elements WC, WC, W₂C, and W₂C·Mo₂C was found. The absence of compounds and phases with relatively high tendencies for sublimation was determined. That is, there is no need to create special conditions in order to prevent the evaporation and losses of alloying elements with the gas phase, which leads to the wider use of the alloying elements.

3. It was found that the alloy microstructure was composed of several phases with particles of different shapes and sizes. Inclusions with relatively high contents of iron and nickel (up to 44.33 wt%), as well as chromium (46.33 wt%), which were found in the studied areas appeared to be of intermetallic nature. Moreover, the phase formations with carbon contents up to 89.54 wt% were found, and they appeared to be the residual unreacted carbon-reducing agents. Some particles had higher contents of Mo and W, up to 14.17 wt% and 26.52 wt%, respectively, and of Nb, up to 1.59 wt%. Such inclusions were composed mainly of iron carbides and alloying elements.

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