UDC 669.15'28-198
DOI: 10.15587/1729-4061.2018.121615

A STUDY OF ENVIRONMENTALLY FRIENDLY RECYCLING OF TECHNOGENIC CHROMIUM AND NICKEL CONTAINING WASTE BY THE METHOD OF SOLID PHASE EXTRACTION

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Визначено закономірності впливу параметрів шихти на вміст Cr та Ni в продуктах відновлення. Досягнуто межі вмісту відповідних елементів: 15,1–17,1 % мас. та 0,2–7,0 % мас. Встановлено, що продукти металізації в основному складалися з твердого розчину легуючих елементів в α-Fe. Також виявлено оксид Fe_3O_4 і карбіди – Fe_3C, Fe_2C. Мікроструктура губчаста розупорядкована. Мікрочастки спечені, з різним вмістом Cr та Ni

Ключові слова: переробка відходів, корозійностійка сталь, вуглецевотремічне відновлення, фазовий аналіз, мікроструктура, ресурсозбереження

Определены закономерности влияния параметров шихты на содержание Cr и Ni в продуктах восстановления. Достигнуты пределы содержания соответствующих элементов: 15,1–17,1 % мас. и 0,2–7,0 % мас. Установлено, что продукты металлизации в основном состояли из твердого раствора легирующих элементов в α-Fe. Также выявлены оксид Fe_3O_4 и карбиды – Fe_3C, Fe_2C. Микроструктура губчатая разупорядоченная. Микрочастицы спеченные, с различным содержанием Cr и Ni

Ключевые слова: переработка отходов, коррозионностойкая сталь, углеродотермическое восстановление, фазовый анализ, микроструктура, ресурсосбережение

1. Introduction

Large volumes of industrial waste and secondary raw materials are hardly utilized effectively. They mainly belong to oxide and finely dispersed wastes (scale, cyclone dust) containing high value elements such as Ni and Cr. This issue is especially important for the production of welding and surfacing materials, where the lack of alloyed powders is traditionally offset with crushed ferroalloys. This negatively affects the manufacturability and the cost of production.

Consequently, it is essential to solve the problem of reducing losses of Cr and Ni in the processing of corrosion-resistant steels waste. This requires studying the mechanism for the extraction of oxide nickel and chromium containing raw materials. Environmental safety can be improved by replacing the reduction smelting with solid phase metallization. This treatment requires lower temperatures and energy resources, providing a relatively lower environmental release of gaseous reaction products.

2. Literature review and problem statement

The current conditions of metallurgical production are characterized by the formation of a significant amount of waste that accumulates in dumps, occupying the area of possibly cultivated land and contaminating adjacent areas [1]. The presence of heavy metals such as Cr and Ni, contaminating soils [2] and groundwater [3], is especially dangerous for the environment. Cr and Ni, according to the degree of danger to living organisms, belong to the 2nd class of danger (moderately hazardous) [4]. The maximum permissible concentrations of Cr and Ni in the soil in such a country of the European Union as Bulgaria in residential areas are 200 mg/kg and 100 mg/kg, respectively. In industrial areas, they are 300 mg/kg and 250 mg/kg, respectively [5]. In Germany, the situation is slightly different. In residential areas, the maximum permissible concentrations of Cr and Ni are 400 mg/kg and 140 mg/kg, and at industrial sites, they are 1,000 mg/kg and 900 mg/kg, respectively [4]. Getting into the human body, Cr and Ni cause poisoning. The toxicity of Cr depends on its valency. Trivalent Cr has a relatively low poisonous effect [6], whereas hexavalent Cr causes an acute toxic effect and is a carcinogen and a mutagen [7]. The poisonous carcinogenic effects of Ni and Cr are also mentioned by the authors of [8]. Moreover, it has been noted that Ni and Cr can cause the emergence of diseases of the cardiovascular and nervous systems in the human body. From the above, it follows that the utilization of chromium and nickel containing waste from metallurgical production helps prevent the pollution of land and water resources with the heavy poisonous elements, especially when there is a warning that people in contact with the contaminated environment can acquire diseases of the cardiovascular and nervous systems and also cancer.

Carbon thermal reduction is one of the technologically simple and economically attractive methods of solid phase extraction in the processing of industrial waste. However, the oxycarbide and carbide compounds may still contain residual carbon [9], which is confirmed in [10, 11] in the case of Fe and Cr. In welding powders and surfacing materials, some carbon content may provide additional protection from high temperature oxidation.

The authors of [12] performed a thermodynamic modeling of chemical and phase transformations in the Fe_2O_3–NiO–CoO–C system in the range of 573–1773 K. It has been determined that Fe from the oxide is basically converted to α-Fe. The degree of extracting Fe increases from 28.9 % at 1173 K to 99.05 % at 1773 K. The rate of recovering Ni while extracting it from oxides in metal phases approaches 100 % in the range of 573–1273 K. The increase in temperature to 1773 K causes an increase in Ni losses with sublimation in the gas phase. The results of [12] are well compliant with the data of [13], where thermodynamic regeneration laws in the Ni–O–C system in the range of 300–2000 K have been investigated. The study has determined the thermodynamic probability of extracting Ni oxides, which can be present as scale components of corrosion-resistant steels.

The extraction of Ni and Fe by carbon from the oxide component of nickel containing slags was investigated by the authors of [14]. The increase in the processing temperature from 1373 K to 1523 K provided an increase in the rate (%) of extracting Ni from 66 to 90 and Fe from 20 to 43. The optimum treatment was noted at 1473 K for 20 minutes with a carbon content of 5 mass%, which needs to be taken into account when developing parameters for recycling waste products from manufacturing corrosion-resistant steels.

In [15], an analysis of thermodynamic regularities of Cr_2O_3 reduction with carbon was performed and it proved the possibility of extracting Cr from oxides by solid-phase carbon-thermal reduction. It means that it is possible to replace smelting [16] with more resource-intensive and energy-efficient processes.

Studies [17, 18] deal with carbon thermal reduction of Cr_2O_3 in the temperature range of 1273–1773 K. It has been found that iron and chromium ligatures can be obtained with limited carbon content, with the leading role of CO and CO_2, which carry out the connection between solid reagents. That is, it is necessary to provide a certain level of porosity of the restorative material.

The extraction of $Fe_2O_3{\cdot}Cr_2O_3$ oxides at various C/Fe ratios in the range of 1373–1523 K was investigated in [19]. It was determined that with increasing C/Fe from 0.8 to 1.4 the degree of chromium extraction increased from 9.6 % to 74.3 %. The increase in temperature to 1523 K led to an increase in the formation of carbides. At C/Fe below 0.8, a significant reduction was observed in the degree of chromium extraction and a decrease in carbidation. It turns out that in order to achieve an increase in the degree of extracting Cr in the reduction of the charge, some excess of C is required relative to O according to stoichiometry.

The analysis of the sources of information points to the significant results of the studies on the extraction of Fe, Cr, and Ni by carbon on the basis of the particular selected oxides. However, the mechanism of extracting multiply alloyed raw materials, which are a mixture of oxide wastes from corrosion-resistant steels, has been studied insufficiently. Multiple alloying can significantly affect the extraction process and the final chemical and phase compositions, the microstructure of the target product. Research in this direction can reduce the losses of Cr and Ni by sublimation of oxide compounds during the receipt and use of the metallized material.

Therefore, it is expedient to study the patterns of the influence of charge parameters on the contents of elements in products of metallization. This will open the possibilities to adjust the composition of the target product and to extend its scope. It is also advisable to study the phase composition and the microstructure of extraction products to determine the nature of the elements present in the material.

3. The aim and objects of the study

The aim of the study is to explore the physicochemical characteristics of processing chrome and nickel containing wastes of corrosion-resistant steels by the method of carbon thermal reduction. This is necessary to determine the parameters that reduce the loss of Cr and Ni in the receipt and use of the metallized product in the manufacturing of welding and surfacing materials.

To achieve this aim, the following tasks are set:

– to study the patterns of the influence of the charge parameters on the contents of the elements in the products of metalizing chromium and nickel containing waste while manufacturing corrosion-resistant steels;

– to determine the phase composition and the microstructure of the products of metalizing chromium and nickel containing waste from manufacturing corrosion-resistant steels, in order to define the nature of the present elements;

– to carry out industrial testing of electrodes based on the obtained powders of the products of metalizing chromium and nickel containing waste while manufacturing corrosion-resistant steels, in the repair and welding of industrial equipment.

4. Materials and methods of research on the products of metalizing chromium and nickel containing waste from manufacturing corrosion-resistant steels

4. 1. Materials tested and equipment used in the experiment

In the tests, the raw materials were scales of steels 95Cr18 and 12Cr18Ni10Ti (Table 1). The reducers were carbon in the form of ultrafine dust (4.5–6.0 mass %) and waste of silicon carbide production of heating elements (6.0–10.5 mass %). The latter also served as the source of deoxidizing the welding joint in the composition of the resulting powder for manufacturing welding materials. The chemical composition of the waste of silicon carbide production, mass %, was the following: C – 3.8–4.2; SiC – 65–80; and SiO2 – 17–22.

To intensify the heating of the briquettes and the extraction processes, to provide additional alloying, as well as to prevent excessive sintering, cyclone dust of steel 13Cr13Mo1NiV was added to the charge.

Table 1

The chemical structures of the scales of the tested steels: 1 – 95Cr18; 2 – 12Cr18Ni10Ti

Steel scale	The content of the elements, mass%									
	C	Si	Mn	Cr	Ni	Ti	S	P	O_2	Fe
1	0.18	0.26	0.28	13.50	0.33	0.10	0.018	0.021	24	remainder
2	0.09	0.44	1.48	13.12	7.80	0.36	0.016	0.022	26	remainder

The briquettes were obtained in industrial conditions at a pressure of 12–16 MPa with a guaranteed density in the range of 2.64 and 3.55 g/cm^3. As a binder, carbon organic compounds of heavy fractions of petroleum distillation were used. The parameters of the briquettes were the following: diameter – 0.245 m; height – 0.250–0.350 m; and mass – 18–25 kg.

The total heat treatment time was 4 hours in the isothermal mode at 1180 °C. The resulting spongy material was ground by powder metallurgy methods to the required degree of grinding.

The X-ray structural phase analysis of the samples was carried out on the diffractometer DRON-6 (Russia).

Photographs of the microstructure of the samples were obtained on the raster electron microscope REM-106I (Ukraine). This type of microscope is equipped with a system of X-ray microanalysis with determining the chemical composition of individual sections of the surface of the samples.

4. 2. Methods of conducting experiments and determining the properties of the samples

The phase composition of the samples was determined by X-ray diffraction analysis using monochromatic radiation of Co K_α (λ=0.178897 Å) with the Fe filter. The measurements were carried out in a tube at a voltage of U=30 kV and an anode current of I=10 mA. The phase composition was determined using the PDWin 2.0 software package (Russia).

The microstructure of the samples was studied at an accelerating voltage of 20 kV and an electron probe current of 52–96 μA. The working distance to the investigated surface was 10.5 mm. The composition of the phases was determined by the non-reference method of calculating the fundamental parameters.

5. Results of researching the products of carbon thermal reduction of oxide wastes of producing chrome and nickel containing steels

The studied interval of the obtained indices (Fig. 1 and Fig. 2) has revealed relatively low levels of concentration, mass %, of S (0.019–0.029) and P (0.022–0.031). An increase in the content of 12Cr18Ni10Ti steel scale from 5 to 75 mass % provided an increase in the concentration of Ni in the powder from 0.8 to 7.0 mass %. The Cr content was in the range of 15.9–17.1 mass % (Fig. 1). The content of 95Cr18 steel scale in the charge in an amount from 5 to 55 mass % provided the Cr content in the powder in the range of 16.1–17.1 mass %. In this case, the concentration of Ni decreased from 6.9 to 0.2 mass % (Fig. 2). The residual C content in the investigated range was 0.52–0.62 mass %, and the Si content was 2.8–4.5 mass %.

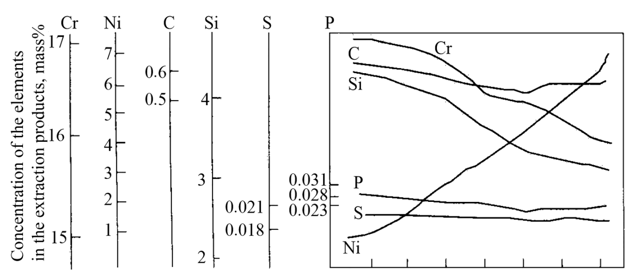

Fig. 1. Dependence of the chemical structure of the extraction products on the content of 12Cr18Ni10Ti steel scale in the charge

An increase in the content of 13Cr13Mo1NiV steel cyclonic dust up to 15 % leads to an increase up to 17 mass% in the concentration of Cr in the extraction products (Fig. 3).

With a content of cyclone dust of 20 mass %, the Cr concentration is reduced to 15.1 mass %. Increasing the content of cyclone dust provides more intense heating of the charge in the central part of the briquettes. Additives in an amount of up to 20 mass % increase the heating rate to 6 °C/min. The phase composition of the extraction products (Fig. 4) is predominantly α-Fe.

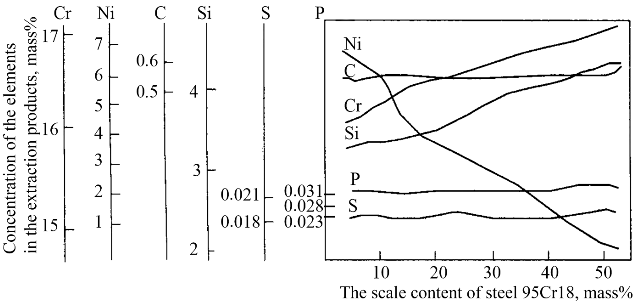

Fig. 2. Dependence of the chemical structure of the extraction products on the content of 95Cr18 steel scale in the charge

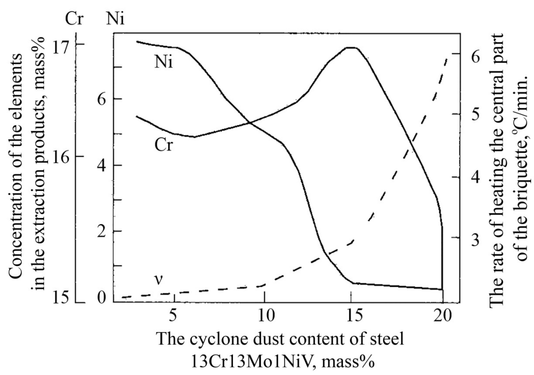

Fig. 3. Dependence of the chemical structure of the extraction products and the increase of the heating rate of the central part of the briquette on the content of 13Cr13Mo1NiV steel cyclone dust in the charge

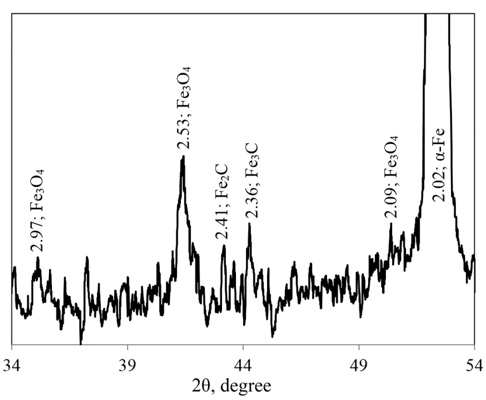

Fig. 4. A fragment of a diffractogram of metallization products with a degree of extraction of 97 % with a content of 50 mass % of 12Cr18Ni10Ti steel scale in the charge as to Fig. 1

Significantly lower intensity than of α-Fe was observed in the diffraction peaks of Fe_3O_4, indicating the residual nature of its presence. Fe_2C and Fe_3C were detected in carbides. No compound of alloying elements was identified separately. This indicates the predominant presence of the alloying elements as substitution atoms in the solid α-Fe

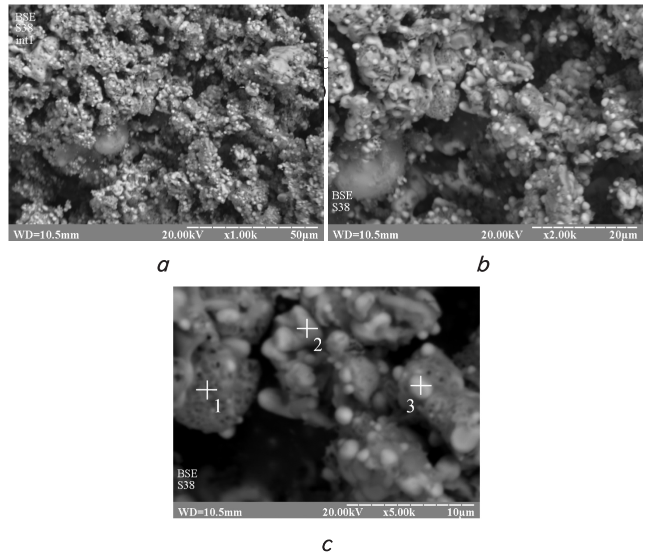

Fig. 5. The microstructure of the metallization products with an extraction degree of 97 % with a content of 50 mass % of 12Cr18Ni10Ti steel scale in the charge as to Fig. 1, zoomed in as follows: *a* — ×1000, *b* — ×2000, and *c* — ×5000

There is a manifestation of sintering of particles. The chemical composition of separate points is heterogeneous (Table 2, Fig. 6).

Table 2

The results of the X-ray microanalysis of the extraction products as to Fig. 5, *c*

Points	The content of the elements, mass%.							Total
	C	Si	Cr	Fe	Ni	Mo	W	
1	0.57	3.16	18.03	74.70	2.97	0.35	0.22	100.00
2	0.54	2.93	9.89	80.88	5.61	0.00	0.15	100.00
3	0.61	4.06	7.47	76.79	10.40	0.49	0.18	100.00

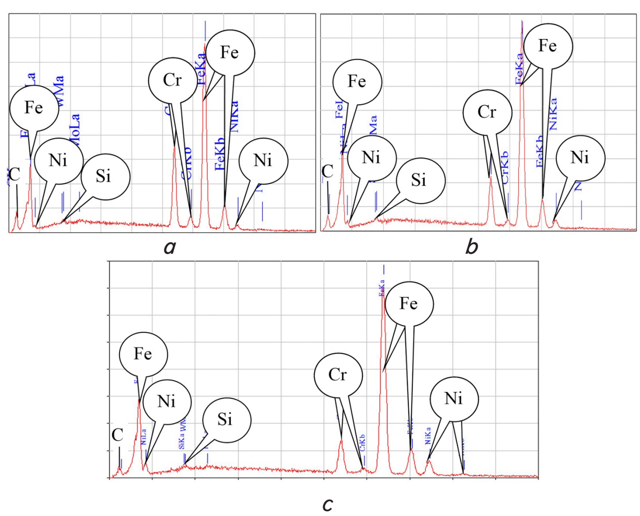

Fig. 6. Spectrographs of some investigated points as to Fig. 5: *a* — 1, *b* — 2, and *c* — 3

The contents of Cr and Ni in various proportions were in the range of 7.47–18.03 mass % and 2.97–10.40 mass %, respectively (Table 2, Fig. 5, 6).

6. Discussion of the results of researching the products of carbon thermal reduction of oxide wastes of producing chrome and nickel containing steels

The conducted tests indicate that the selected heat treatment parameters of 1180 °C in the isothermal mode for 4 hours provided the required extraction rate of 97 %. This, respectively, ensured conversion of the predominant part of the oxides into α-Fe with the dissolution of the alloying elements, as has been confirmed by the phase tests (Fig. 4). It also agrees well with the results of the microstructural tests and X-ray analysis (Table 2, Fig. 5, 6). They show the presence of particles with a relatively high content of Ni and Cr together with Fe in the extraction products. The obtained results coincide well with the studies of the authors of [14, 19]. There, the most suitable indicators for the extraction and removal of Ni, Cr and Fe from oxides were achieved by processing at temperatures close to 1200 °C. The presence of Fe_3C and Fe_2C in the extraction products is in good agreement with the results of [9–11]. These studies disclosed the occurrence of parallel processes of carbide formation along with the extraction under carbon thermal reduction. The results of the studies indicate that the phases are not subject to sublimation, which leads to an increase in the degree of using alloying elements.

The performed tests are in good agreement with the results of [17, 18]. The receipt of iron, chrome and nickel containing materials was implemented in energy-saving conditions at relatively low temperatures with the achievement of the intensification of heating the briquettes by adding cyclone dust of steel 13Cr13Mo1NiV to the charge. The complex was provided with a relatively small total processing time at moderate temperatures, with energy savings and, consequently, a reduction in the level of environmental pollution.

The resulting chromium and nickel containing powders have significantly lower S (0.018...0.020 mass %) and P (0.019...0.033 mass %) than the corresponding standard ferroalloys. In standard ferrochromium and ferronickel, in some grades of steel, the contents of S and P can reach 0.1 mass % and 0.05 mass %, respectively. That is, the use of the obtained chromium and nickel containing powders as alloying elements in the welding and surfacing materials helps achieve the highest quality of the steel in the welding joint than when using the corresponding standard ferroalloys.

The alloyability of the resulting products can be regulated by changing the quantity of components in the charge with the corresponding alloying elements in its composition. The optimum content of scale in chromium and/or chromium containing steels is 60...76 mass %, and the optimum content of cyclone dust is 6.0...14.5 mass %. Within the above-mentioned optimal parameters, paired dependencies of the contents of Cr and Ni in the metallization products were constructed on the content of the alloyed components of the charge. The approximation was carried out using the least squares method. As a nonlinear regression equation, the following model was chosen:

$$\hat{y} = ax^2 + bx + c, \qquad (1)$$

where $\hat{y}$ is the element content in the extraction products, mass %; x is the content of a component of the charge, mass %; a, b, and c are coefficients of regression the values of which are summarized in Table 3 for each dependence respectively.

Table 3

The combined results of the values of the regression coefficients *a*, *b*, and *c* for each dependence

$\hat{y}$	X	a	b	c	r	F_{kr}
Cr	Scale of steel 12Cr18Ni10Ti	−0.00006	−0.0117	17.043	0.99	394.82
Cr	Scale of steel 95Cr18	−0.0001	0.0282	15.833	0.98	358.40
Cr	Cyclone dust of steel 13Cr13Mo1NiV	0.0103	−0.0768	15.975	0.96	105.55
Ni	Scale of steel 12Cr18Ni10Ti	0.0005	0.0553	0.4754	0.99	1,283.70
Ni	Scale of steel 95Cr18	0.0011	−0.1807	7.5437	0.99	915.61
Ni	Cyclone dust of steel 13Cr13Mo1NiV	−0.0398	0.0147	8.6859	0.97	129.37

The coefficients of correlation r of linearized models, as can be seen from Table 3, are quite close to 1. This indicates a tight dependence between the indicator and the factor in each case. The adequacy of the models is confirmed by the calculated values of Fisher's criterion (Table 3), which exceed the Table value F_{kr}=5.32 with the chosen level of significance α=5 %.

A prospect of further research is to expand the range of steel grades the waste of producing which will be involved in recycling. One of the most promising high-alloyed grades is high-speed steel.

The resulting powder, recovered from different Cr and Ni ratios is 15.90–17.00 mass % and 0.49–7.90 mass %, respectively, was tested in the production of welding electrodes. It was used as an alloying and deoxidizing additive in electrode coatings. The experimental batches of electrodes underwent industrial testing in the welding of chromic and chromium and nickel steels. The tests were carried out at *JSC Arkhangelsk Pulp and Paper Mill*, Novodvinsk, Russia during repairing and welding of boilers sized as follows: height – 54 m, diameter – 9 m. Owing to the proposed solution, an increase in the quality of powders and welding joints relative to standard materials was achieved due to the use of the adjacent impurities S and P of the charge components. The assimilation of the alloying elements by the metal welding joint increased from 86–92 % to 98–100 % compared with the use of standard materials. This was due to the excessive content of deoxidizers at the normal level in the steels. Moreover, it is possible to reduce the costs of the powder and the welding materials as well as to increase the environmental safety while utilizing waste by the resource-saving and energy-saving solid phase extraction method.

The economic efficiency that is achieved by using the powders from metallized industrial wastes in welding and surfacing materials depends on the following factors:

1) consumption coefficients of the components of the charge composition for obtaining the metallized product and in the charge composition of the electrode coating;

2) prices of standard and research electrodes;

3) the volume of the standard and experimental electrodes used.

The actual savings were calculated per 1 ton of the welding and surfacing materials when using them in surfacing works with steel grade "18–10". Continuous reduction of the cost price, based on the calculation, can range from 21 % to 33 % or (at least) 3,150–4,950 USD.

7. Conclusion

1. The study has determined the regularities of the influence of the charge parameters on the Cr and Ni contents in the extraction products, mass%, with their provision in the amounts of 15.1–17.1 and 0.2–7.0, respectively. The investigated intervals of the charge contents of scales of steels 12Cr18Ni10Ti and 95Cr18 and cyclone dust of steel 13X13M1NF, mass %, had the ranges of 5–75, 5–55, and 2–20, respectively.

2. It has been found that the products of metallization mainly consist of a solid solution of alloying elements in α-Fe. Also, the tests have revealed certain proportions of underextracted Fe_3O_4 as well as Fe_3C and Fe_2C carbides. The microstructure of the extraction products is spongy and disordered. The particles are sintered, with varying Cr and Ni contents in the ranges of 7.47 to 18.03 mass % and 2.97–10.40 mass %, respectively.

3. The industrial testing of electrodes has been carried out on the basis of the powder obtained from the products of metallizing chromium and nickel containing waste from manufacturing corrosion-resistant steels, in the repair and welding of boilers for pulp and paper production. The quality of the welding joint and the increase in the absorption of alloying elements by the metal welding joint from 86–92 % to 98–100 % have been achieved in comparison with the use of standard materials.

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