UDC 669.15′28-198
DOI: 10.15587/1729-4061.2024.313449

IDENTIFYING PATTERNS IN THE STRUCTURAL-PHASE TRANSFORMATIONS WHEN PROCESSING OXIDE DOPED WASTE WITH THE USE OF CARBON REDUCER

Anatolii Poliakov
PhD, Associate Professor*
Vadym Volokh
Corresponding author
PhD, Associate Professor
Department of Bridges, Structures and Construction Mechanics named after V. O. Rosiiskoho
Kharkiv National Automobile and Highway University
Yaroslava Mudroho str., 25, Kharkiv, Ukraine, 61002
E-mail: 69volokhv.o@gmail.com
Andrey Andreev
Doctor of Pedagogical Sciences, Professor, Head of Department
Department of General and Applied Physics
Zaporizhzhia National University
Zhukovskoho str., 66, Zaporizhzhia, Ukraine, 69600
Victor Rebenko
PhD, Associate Professor
Department of Labor Protection and Biotechnical Systems in Animal Husbandry
National University of Life and Environmental Sciences of Ukraine
Heroiv Oborony str., 15, Kyiv, Ukraine, 03041
Viacheslav Kurlov
Lecturer*
Mykhail Yamshinskij
Doctor of Technical Sciences, Professor, Head of Department**
Ivan Lukianenko
PhD**
Dmytro Ivanchenko
Assistant
Department of Foundry Production***
Dmytro Zhuravel
Doctor of Technical Sciences, Professor
Department of Machine Operation and Technical Service
Dmytro Motornyi Tavria State Agrotechnological University
Zhukovskoho str., 66, Zaporizhzhia, Ukraine, 69600
Iryna Kovalenko
PhD, Associate Professor
Department of General and Inorganic Chemistry***
*Cycle Commission of Technical Disciplines
Separate Structural Subdivision "Starobilsk Applied College of Volodymyr Dahl East Ukrainian National University"
Nauky ave., 72, Dnipro, Ukraine, 49010
Department of Foundry Production*
***National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
Beresteiskyi ave., 37, Kyiv, Ukraine, 03056

The object of this study is the structural and phase transformations during the carbon reduction of tungsten high-speed steel slag in order to obtain a resource-saving alloying additive. The problem is the loss of precious elements when obtaining and using alloying material from man-made raw materials. Solving the problem is related to the definition of technological parameters to enable the reduction of losses of the corresponding elements. As a result of increasing the degree of scale reduction from 33 % to 72 % and 85 %, the strengthening of the manifestation of the solid solution of carbon and alloying elements in α-Fe relative to $FeWO_4$, FeO and Fe_3O_4 was revealed. Fe_3C, WC, W_2C, FeW_3C, Fe_3W_3C, Fe_6W_6C, VC, V_2C, Cr_3C_2, Cr_7C_3 and $Cr_{23}C_6$ also appeared. Along with this, rounded and multifaceted particles with different chemical composition and the formation of a spongy microstructure were found. It was established that the most acceptable degree of recovery is 85 %. But achieving a recovery rate of 72 % is also sufficient. This is explained by the fact that the residual carbon in the carbides provides an increased reducing capacity, which is realized during the further reduction of oxides in the liquid metal during alloying. The spongy microstructure results in faster dissolution in contrast to standard ferroalloys, which provides a reduction in melting time while reducing spent resources. No phases with an increased tendency to sublimation were found in the obtained alloying material. That is, no additional conditions are needed that restrain the loss of alloying elements during evaporation with a gaseous phase, which provides an increase in the degree of extraction of the corresponding elements. The properties of the resulting alloying material make it possible to use it in metallurgical production when smelting alloyed steel grades in an electric arc furnace, the composition of which does not have strict restrictions on the carbon content

Keywords: oxide man-made waste, high-speed steel, slag, carbon reduction, structural-phase transformations

Received date 01.08.2024
Accepted date 11.10.2024
Published date

***How to Cite:** Poliakov, A., Volokh, V., Andreev, A., Rebenko, V., Kurlov, V., Yamshinskij, M., Lukianenko, I., Ivanchenko, D., Zhuravel, D., Kovalenko, I. (2024). Identifying patterns in the structural-phase transformations when processing oxide doped waste with the use of carbon reducer. Eastern-European Journal of Enterprise Technologies, 5 (12 (131)), 25–30. https://doi.org/10.15587/1729-4061.2024.313449*

1. Introduction

Waste from the production of tungsten high-speed steels contains such elements as tungsten, chromium, vanadium, the value of which tends to increase [1]. The complexity of processing oxide alloyed waste is due to the finely dispersed nature of the raw material and the uncertainty of interaction between the set of alloying elements [2]. The specified features indicate the difficulty of establishing manufacturability, ensuring the necessary quality and satisfactory production cost [3], and, as a result, the expected competitiveness.

The relevance of the problem follows from the above, related to reducing the loss of refractory alloying elements during the processing of the slag of tungsten high-speed steels with the provision of resource conservation when returning the obtained raw materials to the steelmaking industry. To solve this task, it is necessary to study the peculiarities of structural and phase transformations during the recovery of doped man-made raw materials.

2. Literature review and problem statement

Carbon steel slag contains FeO, Fe_2O_3, and Fe_3O_4, as shown by the authors of work [4]. At the same time, carbon reduction at 1023–1323 K was accompanied by the formation of Fe_3C together with a solid solution of carbon in α-Fe. But due to the lack of content of refractory alloying elements, the problem is the lack of data on the participation of the latter in the recovery process. In work [5], WO_2 and $W_2C{\cdot}Mo_2C$ were also found during the study of high-speed steel slag. However, no information is provided regarding the restoration of man-made raw materials, which does not provide an opportunity to follow the nature of transformations of compounds of alloying elements. The authors of paper [6], during the study of the carbonization of oxide waste with chromium and tungsten content, also found the formation of Fe_3C together with the presence of WC, W_2C, $W_2C{\cdot}Mo_2C$. But due to the lack of vanadium content, it is not possible to follow the participation of the latter compounds in reduction reactions. Carbide phases of refractory elements can manifest in the microstructure in the form of inclusions of different shapes and compositions [7]. But due to the lack of phase analysis results, it is not possible to determine the nature of the formed compounds. In work [8], Fe_3C, FeW_3C, Fe_3W_3C, WC, as well as a solid solution of carbon and alloying elements in α-Fe were detected during carbonization of high-speed steel slag. But there are still unsolved questions regarding the nature of the content of the main alloying elements in the phase formations of the slag reduction products of tungsten high-speed steels. Some unresolved aspects of the problem relate to the determination of the most acceptable parameters for the recovery of man-made raw materials in the Fe-W-Cr-V-O-C system. This may be due to objective difficulties associated with the need to conduct a series of experimental studies.

In [9], it was determined that WO_3 carbonation proceeds through the formation of W, W_2C, and WC. However, due to the presence of an iron-containing component, the nature of transformations of tungsten oxides during carbonization of the slag of tungsten high-speed steel may differ. Similar results, but with the formation of intermediate oxides, are reported in [10]. But taking into account the presence of several refractory elements in man-made raw materials at once, intermediate oxide compounds can have a complex character. The recovery of tungsten concentrate, studied by the authors of [11], was also accompanied by the appearance of WC and W_2C. But due to the content of ore impurities in the tungsten concentrate, phase transformations may have some difference in relation to man-made oxide raw materials. Also, a part of the problem related to determining the parameters of heat treatment of complex alloyed oxide raw materials when obtaining recovery products that do not contain phases and compounds prone to sublimation needs to be solved. The reason for this may be objective difficulties associated with the need to carry out relevant experiments.

In work [12], the carbothermic treatment of $FeO{\cdot}V_2O_3$ and $FeO{\cdot}Cr_2O_3$ at 1373–1523 K was investigated. When changing C:Fe in the charge from 0.8 to 1.4, an increase in the degree of extraction of V and Cr (%) from 10.0 to 45.3 and from 9.6 to 74.3, respectively, was found. At 1523 K, an increase in carbide formation was established. However, due to the content of a carbide-forming element such as tungsten in the oxide man-made raw material, there may be some differences in the phase composition of the reduction products. The authors of [13] studied the conditions of carbon reduction of FeV_2O_4 with the achievement of vanadium extraction at the level of 71.60 % at 1623 K. But due to the possibility of complex oxides of refractory elements being in the slag from the production of tungsten steels, there are possible differences in the recovery results. The unsolved part of the problem is related to the study of the structural and phase composition of the recovery products of complex doped man-made waste with the involvement of raster electron microscopy and X-ray phase analysis. The reason may be related to objective difficulties regarding the possibilities of using the appropriate set of research equipment.

One should note results from determining the composition of scale from carbon [4] and alloy steels [5]. The products from the latter's carbothermic treatment were determined by the content of iron carbides and alloying elements [6] in the form of individual inclusions of different shapes and compositions [7], which is especially strongly manifested in highly alloyed raw materials [8]. The carbonation of tungsten oxide compounds occurs due to the reduction of oxides [10], the formation of metallic tungsten [9] and carbides [11]. Processes in the Fe-Cr-V-O-C [12] and Fe-V-O-C [13] systems were also accompanied by carbide formation.

Our review of the literature [1–13] reveals the expediency of carrying out research on the identification of features of structural and phase transformations during carbonization of oxide doped with tungsten, chromium, and vanadium waste. The necessary properties of the resulting product can be provided by a given degree of recovery. Reducing the loss of precious alloying elements with the gas phase can be achieved through the determination of technological indicators that would enable the production of recovery products without phases with an increased tendency to sublimation.

3. The aim and objectives of the study

The purpose of our study was to determine the features of structural and phase transformations during carbonization of the slag of tungsten high-speed steel with an alloying additive. This is necessary to determine the most acceptable technological parameters for reducing the loss of alloying elements during the production and use of the alloying additive. This opens up the possibility of improving the technological parameters of resource-saving processing of alloyed metallurgical waste.

To achieve the goal, the following tasks were defined:

– to establish the features of phase composition of the products of carbonization of tungsten high-speed steel slag with different degrees of reduction in order to determine the processing parameters that exclude the formation of phases with an increased tendency to sublimation;

– to investigate the features of the microstructure of products of carbon-thermal reduction of slag of tungsten high-speed steel with different degrees of reduction to reveal the nature of the presence of elements in the formed structural components.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our research is structural and phase transformations during carbon reduction of tungsten high-speed steel slag in order to obtain a resource-saving alloying additive.

The research hypothesis assumes the possibility of obtaining a reduced product with the presence of carbides without the presence of phases with an increased tendency to sublimation.

The assumptions adopted in the research process are the possibility of the formation of complex compounds of iron and alloying elements.

The simplification accepted in the research process concerns the issue of possible interaction of the formed different carbide compounds with each other.

4. 2. Researched materials and equipment used in the experiment

Materials of the study are products of carbonization of slag of high-speed steel grade P9. The reducer is ultrafine dust from carbon graphite production, the addition of which provided for the ratio of oxygen to carbon in the charge at the level of 1.43. Ensuring the given degree of reduction was achieved due to isothermal exposure at 1423 K. The protective environment is an argon atmosphere.

X-ray phase analysis was carried out using the DRON-6 diffractometer.

Obtaining images of the microstructure and chemical composition of the investigated areas of surface of the samples was carried out using a scanning electron microscope "JSM 6360LA" with an X-ray microanalysis system "JED 2200" – JEOL (Japan).

4. 3. Methodology of conducting experiments and determining indicators of sample properties

The phase composition of the samples was determined using the X-ray phase analysis method under monochromatic Co Kα radiation with a tube voltage of 30 kV and an anode current of 20 mA. PDWin 2.0 software was used to determine the nature of the phases.

Microstructure images were obtained at an accelerating voltage of 15 kV with an electron probe diameter of 4 nm. Determination of the composition of phases was carried out by a standard-free method of calculating fundamental parameters: by calculating the correction coefficients of electron reflection of the probe, absorption of characteristic X-ray radiation and fluorescence.

5. Results of studying the properties of high-speed steel slag recovery products

5. 1. Determining features in the composition of the formed phases of high-speed steel scale reduction products

At the degree of reduction of 33 %, FeO and Fe_3O_4 were most intensively manifested in the phase composition, while the solid solution of carbon and alloying elements in α-Fe were relatively weak (Fig. 1). When the degree of reduction was changed to 73 % and 85 %, an increase in the manifestation of the solid solution of carbon and alloying elements in α-Fe relative to the oxide component was determined.

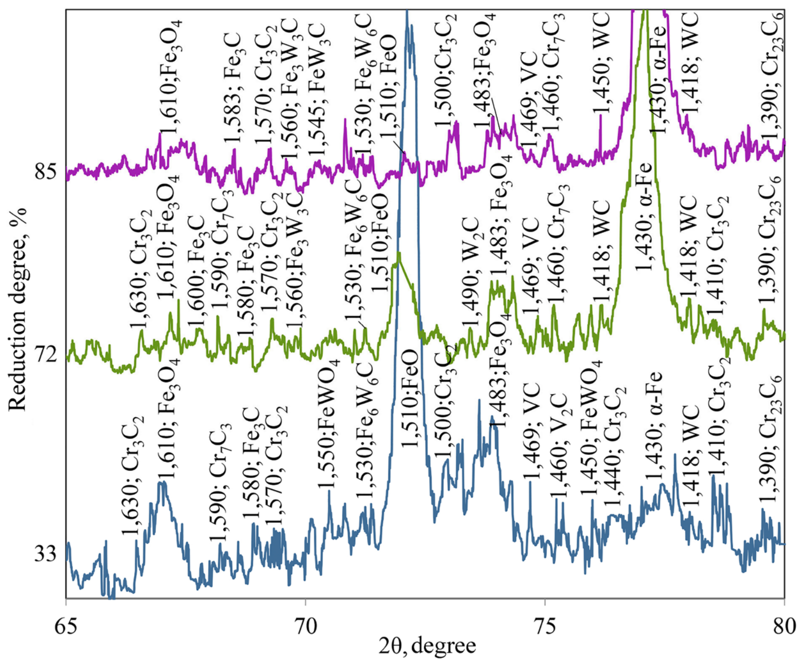


Fig. 1. X-ray phase studies of scale reduction products

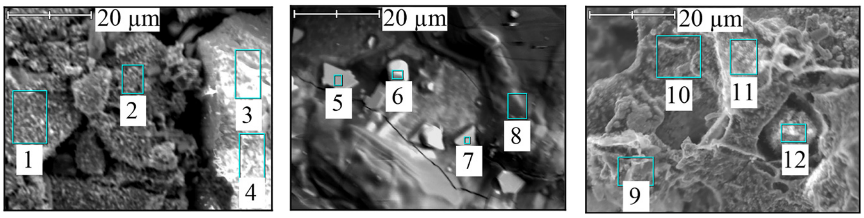
When the degree of reduction changed from 33 % to 72 % and 85 %, $FeWO_4$, Fe_3C, WC, W_2C, FeW_3C, Fe_3W_3C, Fe_6W_6C, VC, V_2C, Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$ phases were detected in the obtained products.

5. 2. Studying the microstructure of products from reduction of scale of high-speed steel

It was determined that the microstructure of the reduced material is heterogeneous and has phase formations with different content of elements (Fig. 2, 3, Table 1). An increase in the degree of recovery from 33 % to 72 % led to transformations in the microstructure with the appearance of rounded and multifaceted particles with different chemical compositions. At a degree of recovery of 85 %, the formation of a spongy microstructure was detected.

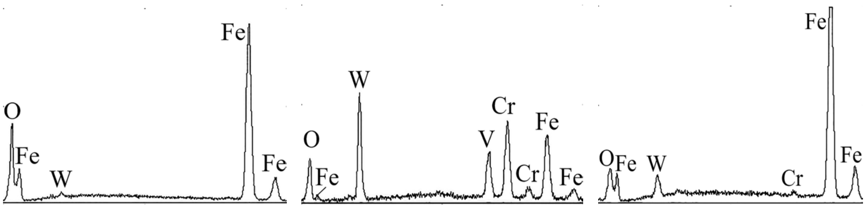
The research areas were chosen with a view to ensuring the representativeness of the obtained results with the definition and presentation of the characteristics of the existing formations in the recovery products. Choosing areas in another location has no effect on changing the result.

An increase in the degree of reduction from 33 % to 72 % and 85 % led to a decrease in the content of residual oxygen in the studied areas (% by mass) from 9.47–13.78 to 5.29–8.12 and 3.05–5.86, respectively. At the same time, the content of tungsten, chromium, and vanadium was in the range (% by mass) of 1.15–27.37, 0.00–8.10, and 0.00–6.39, respectively.



a *b* *c*

Fig. 2. Microstructure of scale reduction products with a magnification of ×2000 with different degrees of reduction: *a* – 33 %; *b* – 72 %; *c* – 85 %; 1–12 – sections for determining the content of elements



a *b* *c*

Fig. 3. Spectrograms of X-ray microanalysis of some studied areas of reduced raw materials according to Fig. 2: *a* – 2; *b* – 5; *c* – 10

Table 1

Results of X-ray microanalysis of reduced raw materials according to Fig. 2

No. of entry	Element content, wt%					Total
	O	V	Cr	Fe	W	
1	12.44	0.00	0.12	83.17	4.27	100.00
2	13.78	0.00	0.00	85.07	1.15	100.00
3	11.16	3.62	4.88	71.63	8.71	100.00
4	9.47	1.36	1.73	74.80	12.64	100.00
5	7.05	6.39	8.10	68.04	10.42	100.00
6	5.29	0.00	0.00	67.34	27.37	100.00
7	7.78	5.72	7.36	69.39	9.75	100.00
8	8.12	0.42	0.66	88.87	1.93	100.00
9	5.86	0.00	0.00	92.33	1.81	100.00
10	5.02	0.00	1.14	89.46	4.38	100.00
11	4.13	2.55	3.89	80.78	8.65	100.00
12	3.05	0.00	0.00	75.77	21.18	100.00

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

Upon reaching the degree of reduction of 72 % and 85 %, the manifestation of a solid solution of carbon and alloying elements in α-Fe prevailed in the material (Fig. 1). The residual character was the presence of Fe_3O_4 and FeO, which were transferred from the original scale, being the main components, which is consistent with the results of work [4]. In contrast to the results reported in [6], a greater manifestation of the carbide component of tungsten, as well as the presence of carbides of chromium and vanadium, was revealed. In comparison with work [8], $FeWO_4$, W_2C, Fe_6W_6C, VC, V_2C, Cr_3C_2, Cr_7C_3 $Cr_{23}C_6$ were additionally detected (Fig. 1). According to work [5], part of the carbides may change from the composition of the original scale. Compared to paper [8], residual oxides had a smaller manifestation.

Areas of the microstructure with an increased content of alloying elements were identified (Fig. 2, areas 3–7, 11, 12), including formations with an increased content of tungsten (up to 27.37 % by mass). The manifestation of the latter is consistent with the results reported in [7] and may be due to the formation of tungsten-containing carbides. This corresponds to the performed X-ray phase analysis (Fig. 1) and is consistent with the results from [10]. At the same time, in [11], as well as in our studies, the formation of two tungsten carbides, WC and W_2C, was revealed. As a difference, the detection of metallic tungsten in [9] can be explained by the predominance of tungsten in the raw material. The identified formation with a tungsten content of 21.18 % by mass (Fig. 2, *c*, section 12, Table 1) may indicate the presence of Fe_3W_3C, Fe_6W_6C, FeW_3C, WC there, according to the results of X-ray phase analysis (Fig. 1).

Some of the studied formations in the microstructure (Fig. 2, sections 3, 5, 7, 11) had a relatively high content of chromium and vanadium (3.89–8.10 wt% and 2.55–6.39 wt%, respectively). In such formations, carbides of the corresponding alloying elements may be present, the existence of which is consistent with work [12] and corresponds to the results of X-ray phase analysis (Fig. 1). The possible processes of carbide formation with the participation of chromium, vanadium, and iron also agree with the data from [13]. As a difference, according to our research, there is a possibility of the presence of part of the corresponding alloying elements as substitution atoms in the α-Fe solid solution.

The change in the degree of reduction from 33 % to 72 % and 85 % led to a decrease in residual oxygen in the studied areas (% by mass) from 9.47–13.78 to 5.29–8.12 and 3.05–5.86, respectively (Fig. 2, Table 2). The most acceptable can be considered the degree of reduction at the level of 85 % with the smallest manifestation of the residual oxide phase. But a reduction rate of 72 % can also be sufficient. This is due to a significant increase in the appearance of solid solution of carbon and alloying elements in α-Fe along with a decrease in the appearance of oxides, relative to the case with a degree of reduction of 33 %. A significant level of manifestation of iron carbides and alloying elements is also observed, the residual carbon of which provides increased reducing power and the degree of extraction of alloying elements. The final reduction of residual oxides will take place during alloying in liquid metal. Compared to standard ferroalloys, the spongy microstructure of the obtained alloying additive contributes to relatively fast dissolution, which affects the reduction of melting time and spent resources.

The field of application of the resulting alloying material belongs to metallurgy in the smelting of alloyed steels. The conditions of use correspond to the possibility of using an alloying material to replace a part of standard ferroalloys in the smelting of steel grades without strict restrictions on carbon content. High-speed steels of brands P9, P12, P18, and others, melted in an electric arc furnace, are promising in this case. Addition of an alloying additive is possible together with the metal charge during backfilling. The expected consumption coefficients of the alloying material can be at the level of 100–200 kg/t of steel, depending on the grade of steel obtained. Potentially expected effects from the practical use of the obtained results, taking into account the accumulated experience, can enable the degree of extraction of alloying elements at a level above 90 %. Such values are determined by the absence of phases with an increased tendency to sublimation. At the same time, there is no need to provide additional conditions that restrain the loss of alloying elements with the gas phase. The proposed technique for extracting alloying elements from oxide waste in production can provide a significant reduction in the costs of standard ferroalloys.

Some limitations that should be taken into account when trying to apply the results of the research in practice relate to the complex doping of the reduced material. Such cases refer to restrictions on the quantitative content of one or more alloying additive components in the composition of the target product, which may lead to exceeding the relevant indicators. In order to take into account the specified limitations and prevent the occurrence of such problems while ensuring efficiency and relatively high utilization rates, it is necessary to be guided by the proximity of the composition of the elements of the alloying additive to the target product. Limitations in our results in the field of reduction of man-made waste with a given ratio of elements can be taken into account in the following theoretical studies. As part of further development, it is possible to carry out thermodynamic calculations and equilibrium analysis in the system of reactions with the participation of a carbon reducing agent with a wider list of refractory elements.

The lack of images of the microstructure with different magnification values can be considered a disadvantage. This would enable a higher level of research visibility.

The development of this area can be realized by using oxide man-made waste from the production of other classes of alloy steels for processing. Difficulties in attempts to advance our research were in the lack of a sufficient volume of experimental base.

7. Conclusions

1. It has been found that increasing the degree of scale reduction from 33 % to 72 % and 85 % enabled an increase in the manifestation of a solid solution of carbon and alloying elements in α-Fe. At the same time, the intensity of the diffraction maxima of $FeWO_4$, FeO and Fe_3O_4 decreased. Fe_3C, WC, W_2C, FeW_3C, Fe_3W_3C, Fe_6W_6C, VC, V_2C, Cr_3C_2, Cr_7C_3 $Cr_{23}C_6$ were also detected in the reduced material.

2. It was established that with an increase in the degree of slag reduction from 33 % to 72 %, the presence of rounded and multifaceted particles with different content of alloying elements was noted in the microstructure. In the case of reduction to the degree of 85 %, the microstructure had a spongy structure with the presence of relatively rounded particles. A successive increase in the degree of reduction from 33 % to 72 % and 85 % led to a relative decrease in the content of residual oxygen in the studied areas. An increase in the degree of reduction from 32 % to 69 % and 77 % provided a relative decrease in the content of residual oxygen in the studied areas (% by mass) from 9.47–13.78 to 5.29–8.12 and 3.05–5.86, respectively. At the same time, the content of tungsten, chromium, and vanadium (% by mass) was in the range of 1.15–27.37, 0.00–8.10, and 0.00–6.39, respectively.

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, as well as the results reported in this paper.

Funding

The study was conducted without financial support.

Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

References

1. Henckens, M. L. C. M., van Ierland, E. C., Driessen, P. P. J., Worrell, E. (2016). Mineral resources: Geological scarcity, market price trends, and future generations. Resources Policy, 49, 102–111. https://doi.org/10.1016/j.resourpol.2016.04.012
2. Petryshchev, A., Milko, D., Borysov, V., Tsymbal, B., Hevko, I., Borysova, S., Semenchuk, A. (2019). Studying the physicalchemical transformations at resourcesaving reduction melting of chrome–nickelcontaining metallurgical waste. Eastern-European Journal of Enterprise Technologies, 2 (12 (98)), 59–64. https://doi.org/10.15587/1729-4061.2019.160755
3. Sekiguchi, N. (2017). Trade specialisation patterns in major steelmaking economies: the role of advanced economies and the implications for rapid growth in emerging market and developing economies in the global steel market. Mineral Economics, 30 (3), 207–227. https://doi.org/10.1007/s13563-017-0110-2
4. 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. Available at: https://www.ijser.org/researchpaper/Preparation-of-Iron-Powders-by-Reduction-Rolling-Mill-Scale.pdf
5. Grigor'ev, S. M., Petrishchev, A. S. (2012). Assessing the phase and structural features of the scale on Р6М5Ф3 and Р12М3К5Ф2 steel. Steel in Translation, 42 (3), 272–275. https://doi.org/10.3103/s0967091212030059

6. Smirnov, A., Petryshchev, A., Bilko, T., Andreev, A., Semenko, A., Skorobagatko, Y. (2023). Development of the Recycling of Alloyed Metallurgical Waste: Features of Phase and Structural Transformations. Minerals, 13 (9), 1171. https://doi.org/10.3390/min13091171
7. Tsymbal, B., Petryshchev, A., Anrieieva, L., Sharovatova, O. (2022). Improving Occupational Safety and Health in the Processing of Metallurgical Waste and Features of their Microstructure Transformation. Key Engineering Materials, 925, 187–196. https://doi.org/10.4028/p-f9x0w1
8. Borysov, V., Torubara, O., Volokh, V., Poliakov, A., Yamshinskij, M., Lukianenko, I. et al. (2022). Identifying features in the structural and phase composition of the products of recycling of the scale of high-speed cutting steel by carbon thermal reduction. Eastern-European Journal of Enterprise Technologies, 6 (12 (120)), 46–51. https://doi.org/10.15587/1729-4061.2022.269507
9. Kozyrev, N. A., Galevsky, G. V., Valuev, D. V., Shurupov, V. M., Kozyreva, O. E. (2015). Surfacing With Tungsten-containing Ores. IOP Conference Series: Materials Science and Engineering, 91, 012009. https://doi.org/10.1088/1757-899x/91/1/012009
10. Islam, M., Martinez-Duarte, R. (2017). A sustainable approach for tungsten carbide synthesis using renewable biopolymers. Ceramics International, 43 (13), 10546–10553. https://doi.org/10.1016/j.ceramint.2017.05.118
11. Hryhoriev, S., Petryshchev, A., Sergienko, O., Milko, D., Stepanenko, A., Kozhemiakin, G. et al. (2018). The study of physical-chemical patterns of resourcesaving recycling of tungstencontaining ore raw materials by solidphase reduction. Eastern-European Journal of Enterprise Technologies, 1 (12 (91)), 4–9. https://doi.org/10.15587/1729-4061.2018.122743
12. 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. https://doi.org/10.1016/s1003-6326(15)63731-1
13. Chen, S. Y., Chu, M. S. (2014). A new process for the recovery of iron, vanadium, and titanium from vanadium titanomagnetite. The Journal of the Southern African Institute of Mining and Metallurgy, 114, 481–487. Available at: https://www.scielo.org.za/pdf/jsaimm/v114n6/14.pdf