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# THE STUDY OF PHYSICAL-CHEMICAL PATTERNS OF RESOURCE-SAVING RECYCLING OF TUNGSTEN-CONTAINING ORE RAW MATERIALS BY SOLID-PHASE REDUCTION

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*Визначено, що оксидний вольфрамовий концентрат представлений в основному  $\text{CaWO}_4$ . Мікроструктура розупорядкована. Проведення металізації вольфрамового концентрату при температурі теплової обробки 1350 К та 1450 К забезпечило ступінь відновлення 69 % та 87 % відповідно. Фазовий склад переважно представлений  $\text{WC}$  та  $\text{W}_2\text{C}$  з деякою часткою  $\text{CaWO}_4$ . Мікроструктура неоднорідна з проявом процесів спікання. Відсутність фаз схильних до сублимації забезпечує зменшення втрат  $W$  під час легування*

*Ключові слова: вольфрамовий концентрат, вуглецевотермічне відновлення, металізація, сублимація, фазовий аналіз, мікроструктура, ресурсозбереження*

*Определено, что оксидный вольфрамовый концентрат представлен в основном  $\text{CaWO}_4$ . Микроструктура разупорядоченная. Проведение металлизации вольфрамового концентрата при температуре тепловой обработки 1350 К и 1450 К обеспечило степень восстановления 69 % и 87 % соответственно. Фазовый состав преимущественно представлен  $\text{WC}$  и  $\text{W}_2\text{C}$  с некоторой долей  $\text{CaWO}_4$ . Микроструктура неоднородная с проявлением процессов спекания. Отсутствие фаз склонных к сублимации обеспечивает снижение потерь  $W$  во время легирования*

*Ключевые слова: вольфрамовый концентрат, углеродотермическое восстановление, металлизация, сублимация, фазовый анализ, микроструктура, ресурсозбережения*

## 1. Introduction

In recent years, demand for steel alloyed by rare-earth and refractory elements, specifically tungsten, has been

growing. At the same time, prices for tungsten in the world market tend to increase. Conventional technologies (carbon-silicon and aluminothermic melting processes) for obtaining tungsten-containing alloys are characterized by

high temperatures and long processing time. Accordingly, these processes are accompanied by a rather high pollution of the environment by gaseous reaction products and solid waste and are characterized by considerable resource and energy costs.

Therefore, the problem of resource and energy saving at lower tungsten losses in processing and use of tungsten-containing ores in steelmaking is very relevant. To that end, study of the mechanism of reduction of oxidic tungsten-containing raw materials is necessary. Improvement of environmental safety can be achieved with the help of the latest methods of powder metallurgy using solid-state reduction instead of reduction melting.

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## 2. Literature review and problem statement

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Advantages of tungsten-containing alloying materials obtained by the methods of powder metallurgy over those obtained by melting are mentioned in [1]. The main positive feature is the ability to achieve a considerably higher dissolution rate and the degree of assimilation of the target element by the metal melt. As a way of processing oxide ore and technogenic raw materials, the solid-phase recovery by carbon has a positive effect in practice [2]. The choice of a solid-phase recovery method instead of reduction melting in the processes of production of tungsten-containing alloys [3] is environmentally safer in terms of pollution by wastes and reaction products. This process requires lower temperatures, less energy resources and is accompanied by significantly lower losses of the target element [4].

Thermodynamic calculations of reactions of  $\text{WO}_3$  carbonothermia were carried out by the authors of work [5]. Transition of  $\text{WO}_3$  to  $\text{W}_2\text{C}$  and  $\text{WC}$  and then to  $\text{W}$  was most likely in the temperature range of 1,500–3,500 K. The probability of the presence of residual carbon bound in oxycarbide and carbide compounds of reduction products is also confirmed by authors in [6]. The study of the carbothermic reduction of tungsten oxides carried out by the authors of work [7] showed that this process passes through the stages of transition of  $\text{WO}_3$  to  $\text{WO}_{2.72}$ ,  $\text{WO}_2$  and  $\text{W}$ . The formed oxides are reduced to tungsten at 950 °C. At the same time, processes of carbide formation take place. Susceptibility to carbide formation along with reduction during carbonothermia is also confirmed by the authors of paper [8]. But it should be noted that in addition to tungsten compounds, the oxidic tungsten-containing raw material contains accompanying ore impurities. In this case, the form of presence of tungsten-containing compounds in ore materials may be more complex and differ from separately taken pure oxides. This can significantly affect the reduction processes and the phase and structural features of the products obtained.

The starting tungsten-containing raw material for processing and obtaining a dopant is a scheelite concentrate [9]. The tungsten-containing component is represented by  $\text{CaWO}_4$ . The authors of paper [10] have studied the problem of processing scheelite concentrate in order to reduce tungsten losses in transition of the tungsten-containing component to  $\text{WO}_3$ . In view of the tangible susceptibility to sublimation of oxidic compounds of tungsten, it is necessary to find measures to reduce the number of operations involving heat treatment and their temperature indices.

Investigations of carbonothermia of scheelite concentrate in a complex with scale of fast-speed steel were per-

formed by the authors of work [11]. The reduction degree was found to grow from 68 % to 88 % when the processing temperature increased from 1,373 K to 1,573 K. Reduction proceeded through the formation of  $(\text{Fe}, \text{W})\text{C}$ ,  $\text{WC}$ ,  $\text{W}_2\text{C}$ ,  $\text{W}$ , as well as a solid solution of tungsten in  $\alpha\text{-Fe}$  [12]. Reduction of the scheelite concentrate by carbon was investigated by the authors of studies [13, 14]. In the products with varying degrees of reduction after their treatment at 1,523 K,  $\text{W}_2\text{C}$  and  $\text{W}$  were found. In addition,  $\text{WO}_3$ ,  $\text{W}_{20}\text{O}_{58}$ ,  $\text{W}_4\text{O}_{11}$ ,  $\text{W}_{12}\text{O}_{49}$ ,  $\text{WO}_2$  have also manifested themselves at various stages. However, it should be noted that the share of  $\text{W}_4\text{O}_{11}$  and  $\text{WO}_3$  in the target product (papers [13, 14]) has a significantly greater susceptibility to sublimation than tungsten and carbides. This may cause additional tungsten losses when using a dopant. At the same time, diffractograms in works [12–14] have no phase manifestations involving the elements of the accompanying ore impurities. This makes it impossible to visually follow dynamics of the presence of such phases in the products with varying degrees of reduction. In addition, the absence of studies into content of chemical elements with the use of X-ray microanalysis of the sites in microstructure photographs significantly reduces significance and obviousness in terms of determining nature of the phases.

As it follows from the considered information sources, there are significant results of research into the mechanism of carbothermic tungsten reduction on the example of individual oxides. There is also an achievement in the direction of reduction of tungsten-containing raw materials. However, the influence of the accompanying ore impurities on phase composition and microstructure of the reduction products is insufficiently studied. Regarding reduction of the scheelite concentrate, there is no use of the newest methods for determining chemical composition of individual microstructure sections using X-ray microanalysis. Investigations in this direction can ensure reduction in tungsten losses by sublimation of oxide compounds during heat treatment of the scheelite concentrate and the subsequent use of a metallized dopant. Based on the above, it is expedient to carry out a comprehensive study of the phase composition and microstructure of the scheelite concentrate and the products of its carbonothermia at various heat treatment temperatures. Application of raster electron microscopy with X-ray microanalysis will make it possible to broaden the idea of structure and composition of individual microstructure sites in the materials under study.

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## 3. The aim and objectives of the study

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This work objective was to study physicochemical features of carbothermic reduction of the oxidic tungsten concentrate. This is necessary to determine the parameters that reduce loss of tungsten by sublimation of oxides during processing of ore concentrates and the use of metallized tungsten-containing dopants.

To achieve this objective, the following tasks were set:

- determine features of the phase composition and microstructure of oxidic tungsten concentrate as a raw material for metallization;
- investigate the phase composition and microstructure of metallized tungsten concentrate at various heat treatment temperatures in relation to the effect on the reduction of the target element loss by sublimation during doping.

**4. Materials and methods for studying the properties of products of metallization of oxidic tungsten concentrate**

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

The source material was an oxidic tungsten (scheelite) concentrate containing no less than 55 wt.% tungsten (GOST 213-83). The material was ground in a ball mill with a peripheral unloading of the ground matter. A sieve with a mesh size of 0.45 mm was used for screening. Reducer: dust of carbon production. The design O/C ratio was 1.33.

X-ray phase analysis of the samples was performed in a DRON-6 diffractometer (Russia).

Photographs of microstructure of the samples were obtained with the help of REM-106I raster electron microscope (Ukraine). The microscope was equipped with a system of X-ray microanalysis with determination of chemical composition of individual sites of the sample surface.

**4.2. Procedure for carrying out experiments and determination of the sample property indicators**

Heat treatment temperature range: 1,250–1,450 K; time of isothermal exposure: 60 min. Protective environment: argon atmosphere with a linear gas flow of  $2.5 \cdot 10^{-3}$  m/s. Weight of the samples under study before heat treatment: 80 g.

The phase composition was determined by X-ray diffraction analysis using monochromatic radiation of Cu K $\alpha$  ( $\lambda=1.54051$  Å). The measurements were carried out at a voltage  $U=40$  kV and an anode current  $I=20$  mA on the tube. The phase composition was determined using the PDWin 2.0 software complex (Russia).

Investigation of the sample microstructure was performed at an accelerating voltage of 20–25 kV and an electron probe current of 52–96  $\mu$ A. Working distance to the investigated surface was 10.1–29.8 mm. Phase composition was determined by the standard method for calculating fundamental parameters.

**5. Results obtained in the study of carbothermic reduction of oxidic tungsten concentrate**

The oxidic tungsten concentrate mainly consisted of CaWO $_4$  (Fig. 1). After treatment at 1,250 K, the degree of reduction was 21 % with a predominance of CaWO $_4$  in the phase composition. The processing temperature of 1,350 K and 1,450 K ensured reduction rate of 69 % and 87 %, respectively, and the phase composition was mainly WC and W $_2$ C. The presence of CaWO $_4$  in this case was of a residual nature.

Microstructure of the samples was heterogeneous with the presence of particles of various sizes (Fig. 2) and chemical composition (Table 1, Fig. 3). With the progress of reduction processes, manifestation of particle sintering was observed. In the sample of oxidic tungsten concentrate, particles with a relatively high content of tungsten, up to 47.55 wt. %, were observed. In addition, sites with increased content of Ca and Si up to 19.64 % and 26.31 wt. %, respectively, were found.

In addition to tungsten, molybdenum content was found to be in the range of 4.79–11.69 wt. %. It is an accompanying element and is present in many tungsten-containing ore concentrates. Oxygen content was within the range of 10.25 to 24.61 wt. % (Table 1).

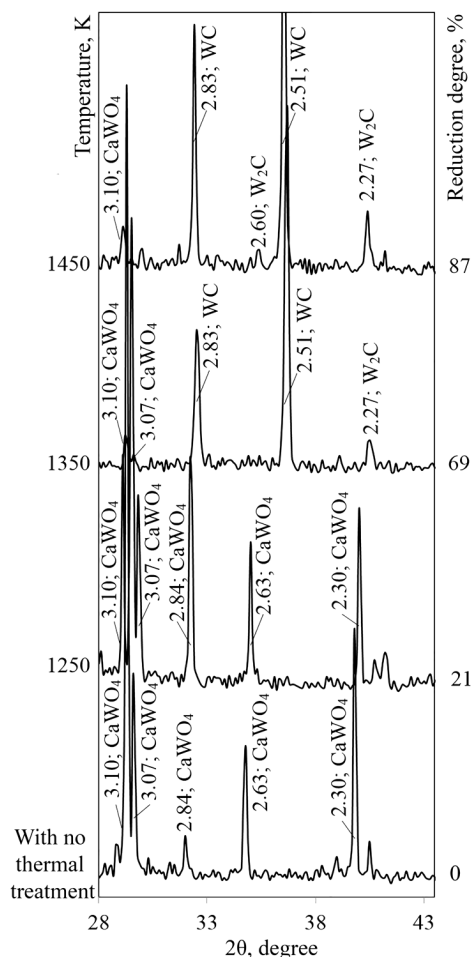


Fig. 1. Sections of diffractograms of oxidic raw materials and the products of tungsten concentrate metallization after treatment at various temperatures. The values near the diffraction maxima correspond to parameters of the crystalline lattice

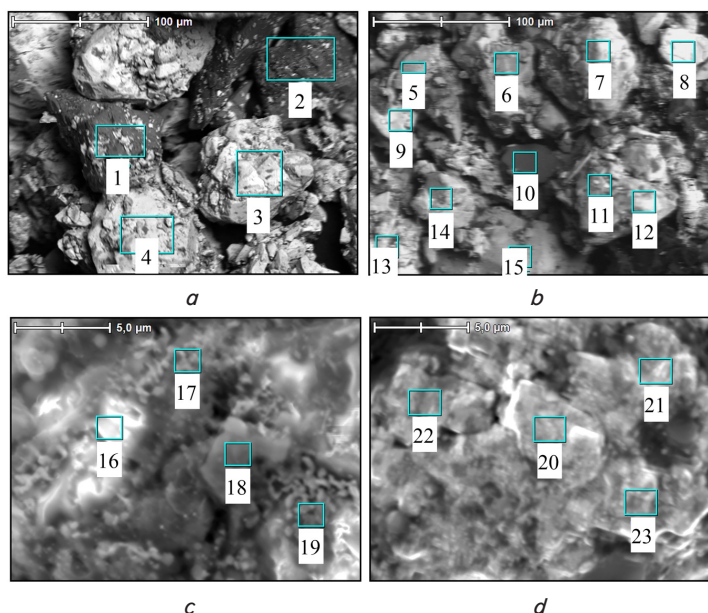


Fig. 2. Microstructure of oxidic and metallized tungsten concentrate according to Fig. 1 after treatment at various temperatures shown at various magnifications: without heat treatment,  $\times 500$  (a); 1,250 K,  $\times 600$  (b); 1,350 K,  $\times 7000$  (c); 1,450 K,  $\times 7000$  (d)

Results of X-ray microanalysis of the reduction products according to Fig. 2

Sample sites	Element content, wt. %									Total
	C	O	F	Al	Si	Ca	Fe	Mo	W	
1	7.42	22.74	1.56	0.45	16.48	19.64	9.95	4.79	16.97	100.00
2	8.35	24.61	2.06	0.00	26.31	18.75	9.23	4.76	5.93	100.00
3	6.30	10.25	0.00	0.21	7.46	16.57	0.00	11.66	47.55	100.00
4	7.49	11.35	1.70	0.00	6.47	19.22	0.00	11.69	42.08	100.00
5	1.23	7.36	0.00	0.00	9.33	24.10	0.00	2.17	55.81	100.00
6	0.00	7.40	1.10	0.00	9.80	23.30	0.00	4.22	54.18	100.00
7	2.13	8.51	0.00	0.39	7.80	24.60	0.00	3.80	52.77	100.00
8	1.76	10.20	0.00	0.00	7.40	20.60	0.00	8.54	51.5	100.00
9	1.69	9.46	0.00	0.40	7.11	23.40	0.00	2.57	55.37	100.00
10	2.46	10.70	4.75	0.00	9.07	31.90	0.00	4.00	37.12	100.00
11	2.51	5.21	0.00	0.35	10.00	21.70	0.00	7.74	52.49	100.00
12	3.14	11.40	0.00	0.00	8.04	21.30	0.00	6.50	49.62	100.00
13	4.02	8.30	1.97	0.39	9.19	21.40	0.00	5.21	49.52	100.00
14	2.25	4.98	5.34	0.00	7.77	32.30	0.00	4.47	42.89	100.00
15	9.82	10.50	3.34	0.00	9.50	21.90	0.00	4.33	40.61	100.00
16	1.16	9.15	2.03	0.00	8.96	28.10	0.00	5.88	44.72	100.00
17	5.65	4.42	1.97	0.00	12.20	19.20	0.00	8.06	48.5	100.00
18	2.81	3.57	0.75	0.00	2.18	9.63	5.54	68.90	6.62	100.00
19	0.94	2.77	0.80	0.00	13.80	13.20	0.00	6.79	61.7	100.00
20	1.60	1.66	0.00	0.47	14.10	1.73	0.00	7.74	72.7	100.00
21	1.20	1.90	0.00	0.33	14.00	1.90	0.00	9.44	71.23	100.00
22	0.81	1.53	0.00	0.41	14.80	1.48	0.00	7.99	72.98	100.00
23	1.66	2.19	0.00	0.53	13.80	2.78	1.77	6.54	70.73	100.00

In the temperature range of 1,250–1,450 K, oxygen content in reduction products was within 1.53–11.40 wt. %. Tungsten content in some particles amounted to 72.98 wt. % (Table 1, Fig. 3). Molybdenum content in most measurements was in the range of 4.33–9.44 wt. %. In this case, a particle with a relatively high content of molybdenum (68.90 %) was found (Fig. 2, c, site 18).

Along with calcium and silicon, contents of accompanying ore impurities such as iron, aluminum, fluorine and carbon were found at some investigated sites in various amounts.

## 6. Discussion of the results obtained in the study of carbothermic reduction of oxidic tungsten concentrate

It was found that oxidic tungsten concentrate is represented mainly by  $\text{CaWO}_4$  (Fig. 1) which is consistent with the data of work [10]. Presence of such ore impurities as molybdenum, calcium, silicon, iron, aluminum, fluorine (Fig. 2, 3, Table 1) detected by X-ray microanalysis can have a substantial effect on the reduction processes. These elements can be found in both individual particles of impurities and in chemical tungsten compounds.

It was determined that treatment at 1,250 K did not provide a sufficiently high reduction (21 %) with  $\text{CaWO}_4$  prevailing in the phase composition (Fig. 1). A significant increase in reduction degree was enabled after treatment at 1,350 K and 1,450 K: 69 % and 87 %, respectively. This agrees well with the results of works [11, 14] and causes significant changes in the phase composition (Fig. 1). Under these conditions, predominance of WC and  $\text{W}_2\text{C}$  relative to  $\text{CaWO}_4$  has been achieved. This is in good agreement with the results of paper [5] where, under similar conditions, a high probability of formation of WC and  $\text{W}_2\text{C}$  was confirmed, and their formation was found in [12]. The absence of a clear manifestation of the tungsten diffraction peaks is because of a greater predisposition to carbide formation than to metallization as indicated in [5] that is consistent with the

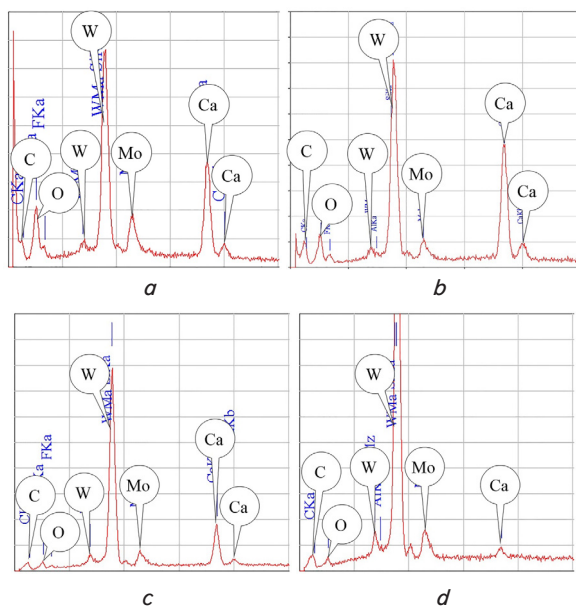


Fig. 3. Spectrograms of X-ray microanalysis of some sites in the samples of oxidic and metallized tungsten concentrate according to Fig. 2: 4 (a); 13 (b); 19 (c); 22 (d)

results of work [6]. The results of phase studies are in a good agreement with the data of works [13, 14] but in distinction from them, no presence of WC in the reduction products was found there. At the same time, the presence of tungsten and  $WO_3$ ,  $W_4O_{11}$ ,  $W_{12}O_{49}$  oxides was observed, which can be explained by different compositions of tungsten concentrates, carbon reducing agents and experimental conditions.

According to results of microstructure studies (Fig. 2), the presence of elements of ore impurities was found almost at all investigated sites of the samples. This indicates the inevitable effect of the latter on the reduction processes. Relatively high calcium content at most of the studied sites is in a good agreement with phase studies. According to these studies, the main component of the starting concentrate is  $CaWO_4$ . Activation of reduction processes is also confirmed by a decrease in oxygen content in most of the studied sites of the samples of reduction products in relation to the oxidic concentrate.

The conducted studies have allowed us to obtain a tungsten-containing reduction product that did not contain phases and compounds with a relatively high tendency to sublimation. This reduces loss of tungsten by sublimation when using the resulting material as a dopant.

As a drawback, one can note lack of the study data concerning the dependence of phase composition and microstructure of metallization products on the content of a carbon reducing agent in the charge.

Development of this study is possible in the direction of implementation of regulation of the chemical and phase composition of the metallization products of a mixture of oxidic tungsten concentrate and technogenic alloyed raw materials. This will open the prospect of expanding parameters of alloying and branded assortment of steels for the use of a dopant with a simultaneous utilization of technogenic waste. One of the difficulties faced in trying to develop this study was the lack of a sufficient base of experimental data

on the physicochemical laws of carbothermic reduction in the systems of complex alloying. This indicates the need for additional experiments to determine interaction of tungsten and a complex of alloying elements with a reducing agent and decreasing their losses during heat treatment.

The use of the resulting metallized tungsten-containing material is expedient for alloying steels at an absence of strict limitations for carbon. These include tungsten high-speed steel grades R6M5, R18, R18F2, R6M5K5, R12M3K5F2 and other grades smelted in electric arc furnaces. The sponge structure and the increased ability of the metallized material because of excess carbon provide a significantly higher dissolution rate and the degree of tungsten assimilation compared to standard ferroalloys. Along with reduction of the melting time, reduction of energy consumption and technogenic emissions into environment are ensured which results in more environmentally safe production conditions.

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## 7. Conclusions

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1. It was determined that oxidic tungsten concentrate is represented mainly by  $CaWO_4$ . Its microstructure is heterogeneous and disordered. The X-ray microanalysis revealed particles containing accompanying such ore impurities as molybdenum, calcium, silicon, iron, aluminum, fluorine and carbon.

2. It was determined that the metallized tungsten concentrate subjected to heat treatment at 1,250 K had a reduction degree of 21 % with  $CaWO_4$  predominance in the phase composition. An increase in temperature to 1,350 K and 1,450 K provided a reduction degree of 69 % and 87 %, respectively. The phase composition consisted of WC and  $W_2C$  and a portion of non-reduced  $CaWO_4$ . Microstructure was heterogeneous with a presence of particles of various size and chemical composition showing sintering processes.

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## References

1. Tarasov A. V. Mineral'noe syr'e, novye tekhnologii i razvitie proizvodstva tugoplavkikh redkikh metallov v Rossii i stranah SNG // Tsvetnye metally. 2011. Issue 6. P. 57–66.
2. Jung W.-G. Recovery of tungsten carbide from hard material sludge by oxidation and carbothermal reduction process // Journal of Industrial and Engineering Chemistry. 2014. Vol. 20, Issue 4. P. 2384–2388. doi: 10.1016/j.jiec.2013.10.017
3. Issledovanie alyuminotermicheskogo vosstanovleniya vol'framitovykh kontsentratorov / Pashkeev K. Yu., Pashkeev I. Yu., Mihaylov G. G., Sudarikov M. V., Tarasov P. A. // Vestnik Yuzhno-ural'skogo gosudarstvennogo universiteta. Seriya: Metallurgiya. 2015. Vol. 15, Issue 2. P. 13–19.
4. Leont'ev L. I., Grigorovich K. V., Kostina M. V. The development of new metallurgical materials and technologies. Part 1 // Steel in Translation. 2016. Vol. 46, Issue 1. P. 6–15. doi: 10.3103/s096709121601006x
5. Termodinamika reaktsiy vosstanovleniya  $WO_3$  uglerodom / Kozyrev N. A., Bendre Yu. V., Goryushkin V. F., Shurupov V. M., Kozyreva O. E. // Vestnik Sibirskogo gosudarstvennogo industrial'nogo universiteta. 2016. Issue 2 (16). P. 15–17.
6. Ryabchikov I. V., Belov B. F., Mizin V. G. Reactions of metal oxides with carbon // Steel in Translation. 2014. Vol. 44, Issue 5. P. 368–373. doi: 10.3103/s0967091214050118
7. Shveikin G. P., Kedin N. A. Products of carbothermal reduction of tungsten oxides in argon flow // Russian journal of inorganic chemistry. 2014. Vol. 59, Issue 3. P. 153–158. doi: 10.1134/s0036023614030206
8. Thermodynamic modeling of the formation of borides and carbides of tungsten, synthesis, structure and phase composition of the coatings based on them, formed by electron-beam treatment in vacuum / Smirnyagina N. N., Khaltanova V. M., Kim T. B., Milonov A. S. // Izvestiya vysshih uchebnykh zavedeniy. Fizika. 2012. Vol. 55, Issue 12 (3). P. 159–163.
9. Kuz'michev E. N., Nikolenko S. V., Balahonov D. I. Poluchenie karbida vol'frama iz sheelitovogo kontsentrata kontsentriruyannymi potokami energii // Himicheskaya tekhnologiya. 2017. Issue 3. P. 113–118.
10. Bel'skiy S. S. Pererabotka sheelitovogo kontsentrata s polucheniem trioksida vol'frama // Vestnik Irkutskogo gosudarstvennogo tekhnicheskogo universiteta. 2015. Issue 12 (107). P. 204–208.

11. Grigor'ev D. S. Nekotorye kineticheskie zakonomernosti uglerodotermicheskogo vosstanovleniya smesi okaliny bystrorezhushchey stali s dobavkami sheelitovogo kontsentrata // Metall i lit'e Ukrainy. 2010. Issue 9-10. P. 57–61.
12. Tsvirko E. I., Grigor'ev D. S. Nekotorye fazovye i strukturnye prevrashcheniya pri uglerodotermicheskom vosstanovlenii smesi okaliny bystrorezhushchih staley s dobavkami sheelitovogo kontsentrata // Novi materialy i tekhnologii v metalurhii ta mashynobuduvanni. 2010. Issue 2. P. 90–94.
13. Grigor'ev D. S. Nekotorye fazovye i veshchestvennye prevrashcheniya pri uglerodotermicheskom vosstanovdenii sheelitovogo kontsentrata // Stal'. 2011. Issue 11. P. 60–63.
14. Grigor'ev D. S. Sovershenstvovanie metoda opredeleniya stepeni vosstanovleniya vol'framovogo kontsentrata // Novi materialy i tekhnolohiyi v metalurhii ta mashynobuduvanni. 2010. Issue 2. P. 72–75.

*Розроблена автоматизована система вимірювань для визначення крайових кутів змочування та розрахунку компонентів вільної поверхневої енергії (ВПЕ) твердих поверхонь методом Ван Осса-Чодері-Гуда. Визначені крайові кути змочування і значення складових ВПЕ наповнених епоксидних полімерних композитів, сталі і скла. Показано, що вміст рутилу (TiO<sub>2</sub>) впливає на структуру і властивості епоксидних композитів і це найбільш яскраво відображається зміною кислотної та основної компонентів ВПЕ. Встановлено, що структурні перетворення пов'язані з кислотно-основним механізмом міжмолекулярних і між фазних взаємодій*

*Ключові слова: вільна поверхнева енергія, автоматизована система вимірювань, епоксидний композит, рутил*

*Разработана автоматизированная система измерений для определения краевых углов смачивания и расчета компонентов свободной поверхностной энергии (СПЭ) твердых поверхностей методом Ван Осса-Чодери-Гуда. Определены краевые углы смачивания и значения составляющих СПЭ наполненных эпоксидных полимерных композитов, стали и стекла. Показано, что содержание рутила (TiO<sub>2</sub>) влияет на структуру и свойства эпоксидных композитов и это наиболее ярко отражается изменением кислотно и основной компонентов СПЭ. Установлено, что структурные преобразования связаны с кислотно-основным механизмом межмолекулярных и межфазных взаимодействий*

*Ключевые слова: свободная поверхностная энергия, автоматизированная система измерений, эпоксидный композит, рутил, структура*

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# STUDY OF THE FREE SURFACE ENERGY OF EPOXY COMPOSITES USING AN AUTOMATED MEASUREMENT SYSTEM

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## 1. Introduction

Free surface energy (FSE), which characterizes energy state of a solid surface, can be a criterion for the evaluation of protective and operational properties of polymeric com-

posite materials. In some cases, FSE is an essential characteristic for studying the properties of polymeric coatings and films, adhesive contacts and adsorption of polymers. There are many studies focusing on determining FSE using different methods and correlating the properties of different