

Виконаний рентгеноструктурний фазовий аналіз зразків на дифрактометрі «ДРОН-6» показав, що найбільшу ймовірність в інтервалі температур 1173–1473 К мають процеси переходу CaWO_4 в WC і W_2C . Кінцевий продукт вуглеродотермії CaWO_4 представлений вуглецем в оксикарбідних і карбідних фазах. Показані процеси відновлення вольфраму з його оксидів через фази утворення карбідних сполук вольфраму, кисневих сполук (вищих і нижчих), і тільки потім вольфраму металевого. Основні хімічні та фазові перетворення протікають в межах температурного інтервалу 300–1800 К. Це відкриває перспективу виробництва вольфраму як легуючого матеріалу без утворення рідких фаз в гетерогенній системі та дає можливість виробляти легуючий матеріал на основі вольфраму при відносно невисоких температурах, що значно скорочує енерговитрати. Наведено якісний й кількісний склад шихтових матеріалів для лабораторних досліджень та промислових випробувань брикетів для металізації вольфрамовмісних сполук у шахтній печі з індукційним нагрівом. Досліджено механізм фазових структурних перетворень за відновлення W із шеєлітового концентрату в діапазоні температур 1273–1473 К і мікроаналіз зразків хімічних перетворень. Схематично показаний пінний агрегат із індукційним нагрівом, у якому поетатно виконані промислові випробування.

Проведені випробування показали, що в процесі теплової обробки зразків на основі шеєлітового концентрату їх маса зменшується в 1,3 рази, а питома щільність знижується на 23 %.

Було вироблено партії губчастого вольфраму, який було випробувано під час виплавки швидкорізальних сталей взамін стандартного феровольфраму. Показані переваги нової технології металізації W із шеєлітового концентрату та позитивна ефективність використання нового матеріалу в спеціальній металургії

Ключові слова: вольфрамовий концентрат, вуглецевотермічне відновлення індукційним нагрівом, металізація, фазовий аналіз, мікроструктура, ресурсозбереження

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INTENSIFICATION OF THE PROCESS OF METALLIZING TUNGSTEN-CONTAINING ORE RAW MATERIALS BY THE POWDER METALLURGY METHOD

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1. Introduction

Targeted efficiency of manufacturing the specialty metallurgy products is not achieved because of a low degree of use of alloying metals based on refractory elements and insufficient reliability and efficiency of the alloying material technologies. This problem is especially urgent in the face of substantial growth of prices of alloying materials shortage of which is replenished by imports.

Powder metallurgy methods successfully solve a number of problems in metallurgy of special steels and ferroalloy production [1, 2], however, reserves for increasing efficiency of this method saving resources and energy have not been completely exhausted. Therefore, industrial production of new alloying materials based on the “strategic four” elements

at temperatures not exceeding 1900 K in heterogeneous systems with application of the powder metallurgy methods ensuring a 30–35 % lower energy consumption is relevant.

2. Literature review and problem statement

Advantages of tungsten-containing alloying materials obtained by the powder metallurgy method in comparison with thermal aluminum-silicon smelting of standard tungsten ferroalloys were presented in [3]. High rate of dissolution of elements in molten steel and high degree of its absorption by liquid metal is one of advantages of technological characteristics of the spongy tungsten. There is a positive likelihood of development of a direction of tungsten

reduction from oxide raw materials and technogenic wastes in a heterogeneous system in terms of cost-effectiveness and practically significant advantages of its technological properties as an alloying material [4, 5]. The process of tungsten metallization occurs at much lower temperatures, requires less energy and is accompanied by much smaller irreversible consumption of the target element [6]. The problem of shortening time tungsten metallization from concentrates was not solved. The tungsten reduction processes occur in the diffusion region. It is impossible to intensify this process in resistance furnaces.

Thermodynamic calculations of WO_3 carbothermal reactions were presented in [7–10]. There is no mathematical model of equilibrium in the W–O–C system. This reduces likelihood of a temperature interval in the reduction reaction. For example, carbothermal reduction of WO_3 occurring in the diffusion zone and the problem of tungsten reduction in a carbothermal manner was solved in [7] but it was not shown how this process can be intensified in practice. Reduction of metals from their oxygen compounds was studied in [8]. The reduction process proceeds with an indirect heat input which disables productivity growth. Reduction of tungsten from its oxygen compounds in a protective atmosphere was studied in [9]. Because of the lack of direct heating, the possibility of increasing manufacture productivity is reduced. Modeling of thermodynamic regularities of tungsten reduction gives a clear picture of phase and structural transformations, however, the issue of increasing productivity of industrial manufacture was not considered in [10].

Shaft muffle furnaces with indirect input of thermal energy have been used in industrial conditions for a long time for production of metallized molybdenum and/or tungsten-containing concentrate (spongy ferromolybdenum and/or ferro-tungsten) [11–16]. A variant of the method of metallization and production of tungsten carbide by concentrated energy flows was proposed in [11]. This does not exclude possibility of tungsten losses in a form of higher tungsten oxide compounds caused by their sublimation. Likelihood of gradual reduction and metallization in stages of formation of tungsten carbides due to direct heat supply is reduced. Processing of scheelite concentrates to obtain tungsten trioxide proposed in [12] does not allow the tungsten reduction process to be intensified by direct heat input to the reaction space. Kinetic regularities of reduction of high-speed steel scale with addition of scheelite concentrate were studied in [13, 14]. All processes were conducted with indirect heat input. Phase and structural transformations were proposed in [15] for carbothermal reduction of scheelite concentrate. All processes took place in a space with indirect heat input which eliminated possibility of the process intensification. A procedure for determining degree of reduction using X-ray phase analysis was proposed in [16]. The fact that all samples tested were obtained in the system of indirect heat input does not yet guarantee accuracy of the results obtained. Main disadvantages of this technology include the too long (16–17 hours) process of temperature raise to the required value (1,150–1,200 °C) and physicochemical transformations in the production of powder alloying materials. The process of element reduction that takes place in the heterogeneous system proceeds in the diffusion rather than kinetic region. This results in high power consumption and forms the basis for necessity of designing more advanced furnace units and process conditions of heat treatment of charge

materials [1, 2, 17–18]. A method for the production of molybdenum and tungsten concentrates was proposed in [17], however, the issue of improving efficiency of industrial production requires further studies. The studies conducted in [18] are the closest in technical sense to productivity improvement. They address the issues of direct heat supply into the reaction space but no deepening of studies in phase and structural transformations was shown. There is no substantiation of transformation or reduction processes at the level of microanalysis. This approach does not complement the picture of theoretical studies. The major disadvantage of these furnaces and the metallization technology consists in a failure of the heating elements caused by gas corrosion in 85–90 days. Their repair and replacement require stoppage of the production process for 7–8 days. There is no possibility of obtaining alloying materials with qualitatively new physicochemical properties: spongy structure, required density and chemical composition.

Therefore, based on the study of the published data, the unresolved problems of powder metallurgy of refractory elements include necessity of cutting costs, lack of a possibility of obtaining alloying materials with qualitatively new technological properties and standard ferroalloys applying the method of aluminum-silicon thermal melting. There are no studies on the possibility of intensification of the reduction process through direct (induction) heat input into the reaction space. This makes impossible alloying of steel melts by the out-of-furnace metallothermic method.

3. The aim and objectives of the study

This study objective consisted in investigation of physicochemical and technological regularities of carbothermal reduction of tungsten oxide concentrates. This is necessary to develop composition of a briquetted charge and temperature regime of heat treatment in the process of concentrate metallization.

To achieve this objective, the following tasks were set:

- provide composition of the charge materials for carbothermal reduction of the scheelite concentrate in a heterogeneous system;
- conduct laboratory and industrial tests of the briquetted charge of cheelite concentrate in a furnace with induction heating;
- bring out basic physicochemical properties of a new tungsten-based alloying material produced in industrial conditions and laboratory test samples.

4. Materials and methods used in the study of scheelite concentrate

The following materials and equipment were used in the experiment. Tungsten oxide (scheelite) concentrate with tungsten content not less than 55 wt. % (GOST 213-83) was used in the studies as the main material. All components of the charge had a form of pellets generally less than 0.45 mm in size. Concrete dimensions are given in Table 1.

The scheelite concentrate had the following chemical composition, wt. %: WO_3 : 60.3; CaO: 27.7; SiO_2 : 3.9; P: 0.069; S: 0.33; As: 0.02; Cu: 0.039; Sn: 0.08; Mo: 0.05. Ground cast iron chips, wt. %: Fe: 95.70; O_2 : 0; SiO_2 : 0; Ca: 2.50; Csol.: 0.72; P: 0.024; S: 0.03. Bulk weight: 2.9–3.5 g/cm³.

Table 1

Granulometric composition of initial components of the charge

Material	Fractional composition, wt. %						
	+0.45 mm	+0.25 mm	+0.16 mm	+0.10 mm	+0.063 mm	+0.056 mm	0.056 mm
Tungsten concentrate	25.5	23.0	8.5	17.5	8.0	6.5	11.0
Ground cast iron chips	–	18.0	36.0	31.0	7.0	4.0	4.0
Cyclone dust of carbon and graphite production	18.0	22.0	16.5	12.0	18.5	5.0	7.5

Cyclone dust of carbon and graphite production in a form of carbon and graphite waste was supplied from purification units of graphite electrode production.

X-ray structural analysis of the samples was performed using DRON-6 diffractometer (Burevestnik SPE, Russian Federation).

The first stage of industrial heat treatment tests of the briquetted charge were conducted in the IAT-0.4 induction furnace (Zaporizhia Aluminum Combine, Ukraine) and the second stage of tests was conducted in the shaft passage induction furnace of modernized design (Zaporizhia Aluminum Combine developed on the basis of the IAT-0.4 furnace).

Testing procedure. Temperature range of heat treatment: 973–1,723 K; isothermal holding time: 60 minutes. Protective medium: argon stream with linear velocity of $2.5 \cdot 10^3$ m/s. Weight of the raw pellets under study: 150 g.

X-ray structural analysis of samples was performed on the DRON-6 diffractometer using Cu K_α monochromatic radiation ($\lambda=1.54051$ Å). Measurements were performed at the tube voltage $U=12$ kV and anode current $I=20$ mA. Phase composition was determined using the PDWin 2.0 software package (Russian Federation).

Study of the sample microstructure was performed with the use of the REM-200 electron microscope at accelerating voltage of 20–25 kV and electron probe current of 52–96 μ A. Working distance to the studied surface was 10.1–29.8 mm.

Industrial testing of technological conditions of carbothermal reduction of tungsten-containing briquette charge in a passage shaft furnace with induction heating was performed within a spot processing temperature interval of 50 K in the range of 973–1,723 K.

5. Results obtained in the studies of carbothermal reduction of scheelite concentrate

5.1. Composition of the charge materials for carbothermal reduction of scheelite concentrate in a heterogeneous system

Studies of reduction processes were performed with a charge [17] consisting of the components given in Table 1. This charge has been improved in order to optimize its composition and obtain better economic indicators. It was proposed to use SPP resin as a binding component and carbon cyclone dust as a reducing agent. The charge composition is given in Table 2.

Cyclone dust of carbon and graphite production contained more than 99.0 wt. % carbon. SPP resin was used as a binder in making briquettes. It consisted of heavy fractions of oil refining wastes of CnHm type with trace amounts of S and P.

Table 2

Composition of the charge under study

The charge component	kg	%
Scheelite concentrate	117.5	80.81
Ground cast iron chips	8.4	5.78
SPP resin	10.3	7.08
Cyclone dust of carbon and graphite production	9.2	6.33
Total	145.5	100.0

5.2. Results obtained in laboratory and industrial tests of the briquetted charge of scheelite concentrate in a furnace with induction heating

The charge materials were dosaged on ETVK-1.5 electric dosing cart (designed by Zaporizhia Titanium and Magnesium Combine, Ukraine). Components were mixed in SMB-2000 vane mixer (designed by Institute of Titanium PJSC, Ukraine). The mixture was heated to 383–433 K in the mixer using an overheated steam heater (manufactured by Zaporizhia Aluminum Combine, Ukraine).

Seven 3,000 kg (on average) batches of charge materials were prepared. The following tasks were solved in the course of industrial tests.

1. Produce batches of metallized tungsten-containing material (spongy ferro-tungsten) for testing it as an alloying material in smelting of high-speed special steels.
2. Establish a possibility of using a passage shaft furnace with induction heating in production of a new tungsten-based alloying material.
3. Determine coefficients of materials consumption and other indicators required to calculate economic efficiency of production and use of the metallized tungsten-containing material.

Technological parameters of reduction of briquetted scheelite concentrate were tested in a specially designed furnace unit with induction charge heating. Its design is shown in Fig. 3 [18].

Reduction of briquettes was carried out in a counterflow of converted natural gas. The gas mixtures supplied to the furnace (item 3, Fig. 1) contained 77.5 % H_2 ; 13.5 % CO ; 9.2 % CO_2 , and 0.68 % CO_2/CO .

Total weight of the briquettes filling the furnace volume was 115 kg. Load of briquettes was 35 kg in the first zone (item 2, Fig. 1) and 75 kg in the second zone of the furnace (item 3, Fig. 1).

Chemical composition of the test batches of metallized tungsten concentrate was as follows: 56.4–56.9 wt. % W; 18.50–18.87 wt. % Fe; 0.60–0.67 wt. % C; 0.20–0.21 wt. % S; 0.064–0.065 wt. % P; 0.06–0.07 wt. % Sn; 0.04–0.05 wt. % Mo; 0.019–0.021 wt. % As; 0.030–0.031 wt. % Cu; 0.61–0.80 wt. % O_2 .

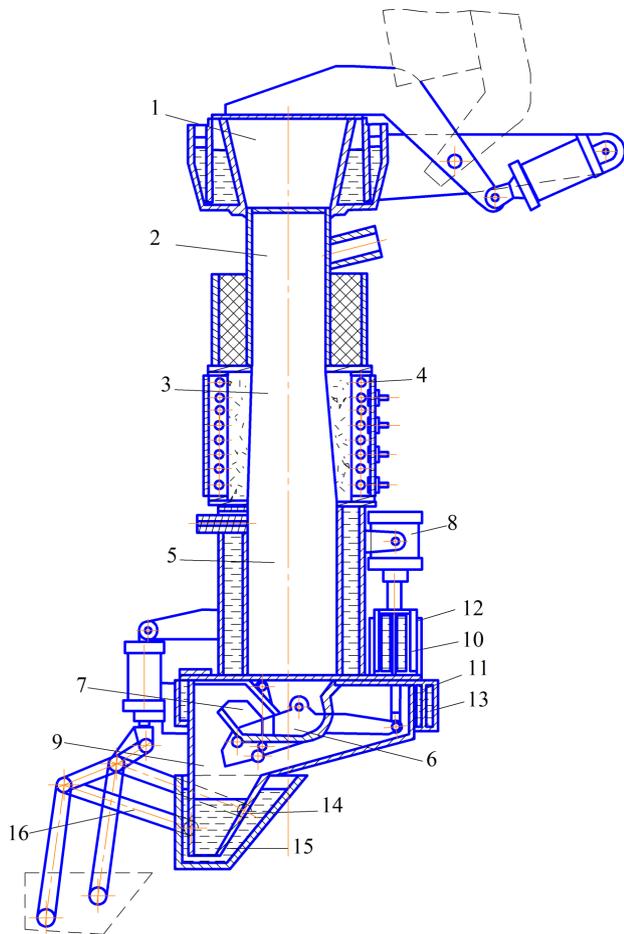


Fig. 1. Design of the passage shaft furnace with induction heating: 1 – loading chamber; 2 – pre-heated tubular muffle; 3 – chamber; 4 – inductor; 5 – water cooled refrigerator; 6, 7 – trays; 8 – pneumatic actuator; 9 – transfer chamber; 10 – first hydraulic gate; 11 – flange; 12 – cursor; 13 – second hydraulic gate; 14 – third hydraulic gate; 15 – loading nozzle; 16 – scissors-type mechanism

The products of reduction of the scheelite concentrate after its heat treatment at 1,273 K mainly included CaWO_4 which is an indicator of difficulty in passing of the processes of carbide formation and reduction to metallic tungsten in these conditions (Fig. 2).

With an increase in reduction temperature to 1,373 K and 1,473 K, domination of WC carbide was observed in the phase composition. W_2C carbide was also identified. In general, processes of CaWO_4 transition into WC and W_2C carbides without appearance of metal tungsten were activated with growth of the heat treatment temperature from 1,273 K to 1,473 K.

Fractographic and X-ray microanalysis of samples based on the scheelite concentrate was performed during its heat treatment in the temperature range from 1,173 K to 1,473 K. The results are presented in Fig. 3, 4 and Table 3.

Like in the case of initial scheelite concentrate, the samples heat treated at 1,273 K consisted of disordered particles of different sizes (Fig. 5). At the same time, traces of reduction with formation of sites with a spongy structure were revealed. These sites were in a form of incrustations (zone 3, Fig. 3).

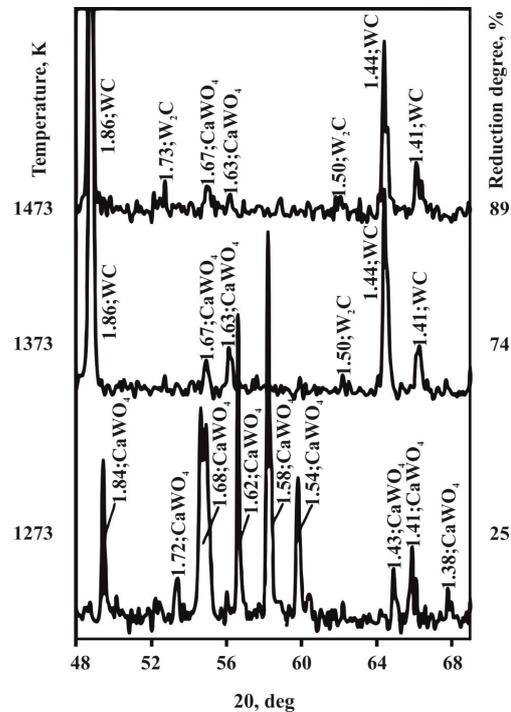


Fig. 2. A section of diffractograms of tungsten-containing tablets based on scheelite concentrate after carbothermal reduction ($\text{O}/\text{C}=1.33$)

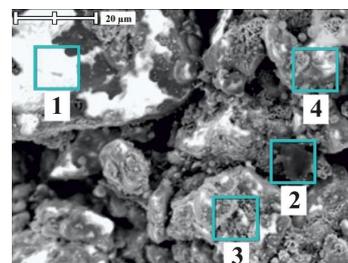


Fig. 3. A section of a diffraction pattern of a tungsten-containing tablet based on the scheelite concentrate after carbothermal reduction ($\text{O}/\text{C}=1.33$) at 1,273 K; magnification: $\times 1,500$

5. 3. Basic physicochemical properties of the samples of reduced scheelite concentrate with different degrees of reduction

Basic physicochemical properties of samples of the reduced scheelite concentrate with different degrees of reduction obtained in laboratory and industrial conditions are given in Table 3.

The results of reduction processes are clearly visible in Fig. 4. Zones 7 and 8 (Table 3) are highly likely to belong to WC and W_2C tungsten carbides with presence of a relatively small fraction of molybdenum carbides. Zones 5 and 6 indicate the sites of concentration of accompanying impurity calcium compounds formed as a result of CaWO_4 dissimilation.

Comparative technical and economic indicators for existing and proposed methods of reduction of the scheelite concentrate are presented in Table 3. The existing method was implemented in a shaft furnace with resistance elements. The proposed method was implemented in a passage shaft furnace with direct induction heating.

Table 3

Results of X-ray microanalysis of the samples based on the scheelite concentrate subjected to carbothermal reduction at various temperatures

Zone No.	Chemical composition, wt. %										Total
	C	O	F	Na	Al	Si	CCl	Ca	Mo	W	
1,273 K											
1	0	7.60	0	0	0	8.74	0	22.70	7.15	53.80	100
2	50.30	2.95	0	0	0	5.78	0	11.20	4.02	25.80	100
3	2.04	7.12	1.38	0	0.32	11.10	0	26.20	9.16	42.70	100
4	3.20	6.25	1.60	0	0.33	11.30	0	27.80	4.20	45.30	100
1,473 K											
5	0	0	0	0	0	0	0	91.70	0	8.29	100
6	0	0	0	0	0	0	0	95.00	0.76	4.29	100
7	0.62	0.46	0	0	0.37	14.30	0	0.63	9.32	74.30	100
8	2.07	1.48	0	0	0.49	13.20	0	2.75	10.80	69.20	100

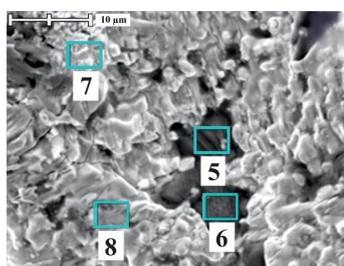


Fig. 4. A section of a diffraction pattern of a tungsten-containing tablet based on the scheelite concentrate after carbothermal reduction ($O/C=1.33$) at 1,473 K; magnification $\times 1,500$

The samples changed their physical characteristics during heat treatment. Relative change of specific density and weight reduction in the samples are given in Table 4.

Table 4

Change of physical characteristics of the samples based on the scheelite concentrate during heat treatment

The process temperature, K	1,173	1,273	1,373	1,473
Specific density, g/cm^3	2.6 ± 0.3	2.2 ± 0.3	2.4 ± 0.3	2.0 ± 0.4
Relative weight change, %	16 ± 1	18 ± 2	19 ± 3	21 ± 3

Analysis of the data presented in Table 4 has revealed that relative weight reduction in the heat treatment temperature range from 1,173 K to 1,473 K increased and specific density of the samples decreased by 23 %. This change of density indicates that the samples acquired a microporous spongy structure.

6. Discussion of the results obtained in the study of carbothermal reduction of the tungsten concentrate

The study of spectrograms of X-ray microanalysis of the ore concentrate and metallized tungsten-based product has revealed that the tungsten concentrate was mainly $CaWO_4$ calcium tungstate. This is completely consistent with the results of [12]. The accompanying impurities of Mo, Ca, Si, Fe, Al, F were present in the form of chemical compounds and mechanical inclusions which can significantly affect the reduction processes. However, from the point of view of irreversible costs, the $WO_3 \rightarrow WO_2 \rightarrow W$ transformations and

the carbide-forming processes taking place in the tungsten containing compounds [13–15] are of practical interest.

Technological parameters of obtaining metallized tungsten-containing concentrates in a shaft furnace with a direct (deep) heat input included briquetting of initial components with carbon-containing materials. This was characterized by oxide oxygen to carbon weight ratio of 1.46–1.78 and a metal powder with bulk weight of 2.9–3.5 g/cm^3 in an amount of 4.52–25.71 % of the charge weight and reduction in a counterflow of a protective gas and the briquetted charge. The reduction process occurred in two stages: the first at 973–1,273 K for 4–9 hours and the second at 1,373–1,723 K for 2–6 hours with subsequent cooling in a neutral gas to 333–363 K.

The procedure of calculation of effectiveness of the implemented measures is presented in [19]. Compared to the technology of metallization of such materials in shaft furnaces with resistance elements, there was a 1.3–1.5 times higher specific productivity and a 27–31 % lower specific power consumption.

When alloying steels and alloys, absorption of tungsten and molybdenum has increased by 6.20 and 7.52 %, respectively, and a 2–3-fold increase in chromium, vanadium and manganese absorption. Quality of the metallized tungsten concentrate was improved due to a 1.8–2.0 times reduction of impurities of non-ferrous metals and oxygen. In addition, specific energy consumption was reduced 1.9–2.2 times due to the direct heat input and elimination of temperature gradient in the neutral and surface part of the reaction space.

All results were obtained by using direct induction heating of the charge in the furnace instead of indirect heat input to the reaction space. Substantiation of the possibility of all processes during reduction was confirmed by the results of studies of phase and structural transformations and microanalysis of samples.

Further development of this study will be advisable in development and implementation of technologies for production of alloying materials based on chromium, niobium, vanadium and other heavy-metal elements by methods of powder metallurgy in a way similar to that used for molybdenum and tungsten.

7. Conclusions

1. Composition of charge materials for the production of raw briquettes of oxides of the charge components and

carbon reduction at O/C ratio of 1.46–1.78 was presented on the basis of the results obtained in the study of physico-chemical features of carbothermal reduction of the scheelite concentrate.

2. Laboratory and industrial studies of the technology of reduction of briquetted tungsten concentrate have shown fundamental and technological possibility of using a passage shaft furnace with direct (induction) heat input. Reaction space of the furnace of own design is reduced when new tungsten-based alloying material is produced.

Specific productivity of the new furnace unit was increased by 1.3–1.5 times in comparison with the known

shaft resistance furnaces. Yield of the main elements was close to 100 % due to optimization of thermal conditions of metallization in the furnace zones.

3. Physicochemical properties of metallized scheelite concentrate produced in industrial conditions and samples for laboratory tests coincided with high accuracy (chemical composition, phase and X-ray structure composition, microanalysis results) which confirms accuracy of the target results. No higher oxygen compounds of the WO_3 type were found in the samples which eliminates the possibility of their sublimation during intensification of the process of direct heat input.

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