

This paper reports a study into the phase composition and microstructure of tungsten ore concentrate after carbon-thermal reduction at different O:C ratios in the charge. This is required for determining those indicators that reduce tungsten loss through the sublimation of oxide compounds when processing ore concentrates, as well as when using reduced tungsten-containing doping additives. The study results have established that the reduced tungsten concentrate at the O:C ratio in the charge within the interval of 1.33–2.30 contained the phases of W, W₂C, C, WO₂. The microstructure demonstrated a spongy and disordered character. Together with W, the Mo, Si, Ca, Al impurities were present in the reduced products. The main elements identified at the sites studied had the following limiting content, % by weight: O – 5.01–17.32; C – 0.84–4.23; W – 61.21–86.78; Mo – 1.57–7.51; Si – 2.07–9.06; Ca – 1.34–11.30; Al – 0.27–0.40. The micro-inclusions at the examined surface areas acquired different complex shapes. There were traces of the process of caking between the particles. The analysis of the resulting data has shown that the most preferred ratio of O:C in the charge was 1.65. In this case, there is no lack of carbon and there is a predominance of W in the phase composition with a relatively little manifestation of the W₂C phases, carbon, as well as the residual part of WO₂. The post-reduction of the oxide component would occur during the doping process. The sponge structure contributes to a higher dissolution rate compared to standard tungsten ferroalloys. Lack of compounds with a relatively high propensity for sublimation does not require any special conditions to prevent the loss of tungsten in the gas phase, which increases the degree of assimilation of the target element

Keywords: oxide tungsten concentrate, oxide, phase analysis, carbon-thermal reduction, carbide, doping

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ESTABLISHING PATTERNS OF THE STRUCTURAL-PHASE TRANSFORMATIONS DURING THE REDUCTION OF TUNGSTEN-CONTAINING ORE CONCENTRATE WITH CARBON

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1. Introduction

The increased demand for steel, doped with refractory elements, corresponds to modern trends of the steel industry. Given that the raw materials deposits are gradually depleted,

prices in the world market for refractory elements tend to grow [1]. These elements include tungsten.

The quality and cost of production determine the main indicators of competitiveness in the domestic and global markets [2]. Conventional technologies of aluminum-ther-

mal and carbon-silicon-thermal smelting are being replaced by powder technologies for obtaining doping materials through direct reduction of ore concentrates, including carbonaceous reducers. At the same time, the possibilities of improving the technological parameters are far from exhausted, which makes it appropriate and relevant to conduct further research.

The relevance of work in this area is to determine the manufacturing parameters required to increase the degree of assimilation of tungsten and to contribute to resource-saving in the processing and utilization of tungsten ore concentrates. To resolve a given issue, it is necessary to study the features of the processes of tungsten ore concentrate reduction at different charge composition while investigating the accompanying phase and structural transformations.

2. Literature review and problem statement

Paper [4] reported the thermodynamics calculations and determined the equilibrium of WO_3 reduction reactions involving C and CO at 1,500–6,000 K. The resulting reaction characteristics showed that when WO_3 is reduced, W and, subsequently, W_2C and WC carbides are most likely to be obtained. Work [4] states that there are stages in the conversion of WO_3 through $\text{WO}_{2.72}$ and WO_2 to W. The reduction to W takes place at 950 °C. Study [5] provides data on that the WO_3 -C system mainly produces compounds of the WO_x type at temperatures below 880 °C. At temperatures above 960 °C, the products of the reduction reactions were WO_2 and W. It was shown in [6] that at a temperature of 900 °C, with a content of 20 % by volume CO (in an N_2 atmosphere), WO_3 begins to be reduced with the formation of intermediate oxides $\text{WO}_{2.9}$ and $\text{WO}_{2.83}$. WO_3 was then fully reduced to $\text{WO}_{2.72}$. The carbon-thermal reduction of WO_3 at different temperatures is reported by the authors of [7]. It was shown that after processing at 750 °C, the WO_3 and $\text{W}_{18}\text{O}_{49}$ ($\text{WO}_{2.72}$) phases were detected in the reduction products. At 900 °C, tungsten oxides were fully reduced to W. After treatment at 960 °C, W dominated with a slight WC and W_2C manifestation. A further increase in the processing temperature to 1,450 °C led to a predominance of WC in the phase composition. The propensity to form carbides, together with the reduction of oxide tungsten-containing compounds, is confirmed by the studies reported in papers [8, 9]. The limitations of the results from the cited papers are that the form of presence of tungsten-containing phases in oxidized tungsten concentrate may differ and be more complex than in individual oxides. The unresolved part of the issue is to determine the parameters of processing oxide tungsten-containing ore raw materials and to obtain a target product without the presence of phases with an increased propensity for sublimation. Such a result would eliminate the need to maintain additional conditions that suppress the loss of doping elements with a gaseous phase.

It should be noted that tungsten-containing oxide ore raw materials together with the highest oxide compounds of tungsten contain ore impurities [10, 11]. This indicates that the reduction process and the form of the target element's presence may be more complex, different from the case of individual oxides. This feature can significantly affect the structural and phase properties of the resulting reduction products. In this case, the highest oxide compounds of

tungsten have a palpable propensity to sublimate. As a result, there is a distinct need to find solutions to reduce the number of reprocessing of oxide tungsten raw materials. The studies of carbon-thermal reduction of oxide tungsten concentrate at 1,523 K and the O:C ratio in the charge of 1.33, are reported in works [12, 13]. W and W_2C were identified in the phase composition after processing. The oxides of W_4O_{11} , $\text{W}_{20}\text{O}_{58}$, $\text{W}_{12}\text{O}_{49}$ were found in products with varying degrees of reduction along with WO_3 and WO_2 . At the same time, WO_3 and W_4O_{11} , not fully reduced in the resulting raw materials, are more prone to sublimation than W and W_2C , which is a disadvantage. In addition, a drawback is the lack of data on the influence of charge composition on the reduction of oxides, the formation of carbide and metal phases, as well as on the content of elements in the phase compositions and inclusions in the microstructure of samples. The unresolved aspects of the issue are the development of perceptions about the nature of the presence of doping elements in the reduced material. Comprehensive use of raster electron microscopy, X-ray microanalysis, and X-ray phase analysis would enable the implementation of a solution to this aspect of the issue.

The authors of work [14] investigated the reduction of a mixture of oxide tungsten concentrate and the scale of fast-cutting steel. The study temperature range varied from 1,273 K to 1,423 K. The O:C ratio in the charge was 1.30. The tungsten-containing phases that were formed during the reduction stages: W, WC, W_2C , (Fe, W)C. When studying the reduction of ore tungsten concentrate at temperatures of 1,350 K and 1,450 K, and the O:C ratio in the charge of 1.33, the authors of [15] noted the formation of tungsten carbides WC and W_2C . The limitations include the lack of data on the properties of the materials received at different amounts of carbon in the charge. The unresolved aspects of the issue relate to determining the most preferable parameters of carbon thermal treatment when the O:C ratio in the charge changes.

Of special interest is a study into the thermodynamic equilibrium in the reduction of individual tungsten oxides by carbon reported in [3]. The possibility of reactions to form W_2C and WC carbides, along with the reduction to W, was confirmed. Similar results were obtained by the authors of works [8, 9] in the reduction of oxide tungsten-containing compounds. The formation of intermediate oxides such as WO_x during the reduction in the WO_3 -C system was established by the authors of paper [5]. Intermediate oxides $\text{WO}_{2.9}$, $\text{WO}_{2.83}$, and $\text{WO}_{2.72}$ were detected during the WO_3 carbon thermal treatment in work [6]. The progress of reduction in several stages with the formation of $\text{WO}_{2.72}$ and WO_2 and subsequent post-reduction is noted in work [4]. In this case, paper [7] shows that an increase in processing temperature from 750 °C to 1,450 °C led to the predominance of WC instead of tungsten and metallic tungsten oxides. The specificity of the reduction of oxide tungsten-containing ore raw materials is conditioned by the presence of ore impurities and an increased propensity to sublimate oxide tungsten-containing components, which is reported in works [10, 11]. The presence of part of the under-reduced oxide component in the form of WO_3 , W_4O_{11} , $\text{W}_{20}\text{O}_{58}$, $\text{W}_{12}\text{O}_{49}$ compounds, along with W and W_2C , was identified by the authors of papers [12, 13] following the carbon thermal treatment of oxide tungsten concentrate. Similar results were obtained by the authors of [14, 15]. In this

case, WC was also identified in the reduction products. Among the limitations of the cited studies is the lack of data on the effect of carbon content in the charge on the phase composition and microstructure of the products of the reduction of oxidized tungsten concentrate. Based on this, the issue of the most acceptable values of O:C ratios in the charge is unresolved. There is also a need to determine the conditions for receiving reduction products without phases with an increased propensity for sublimation. This would reduce the loss of the target element when tungsten compounds transfer into the gas phase when using the resulting doping supplement.

Therefore, to solve the outlined task, it is appropriate to study the reduction of oxide tungsten concentrate when the ratio of O:C in the charge is changed using X-ray phase analysis, raster electron microscopy, and X-ray microanalysis. This could improve the understanding of the physical and chemical features of the reduction mechanism, with the identification of the most preferred parameters of the process.

3. The aim and objectives of the study

The aim of this study is to identify the features of physical and chemical transformations in the reduction of tungsten oxide concentrate with carbon. This is necessary to determine the manufacturing parameters that could reduce the loss of tungsten through sublimation in the processing of oxide concentrates and the use of reduced tungsten-containing doping additives.

To achieve the set aim, the following tasks have been solved:

- to determine features of the phase composition of the reduced tungsten concentrate with a different ratio of O:C in the charge regarding the nature of the presence of the elements;
- to investigate the microstructure of the reduced tungsten concentrate to determine the chemical composition of individual inclusions and phases at different O:C ratios in the charge.

4. Materials and methods to study the properties of reduced oxide concentrate

4.1. The materials and equipment used in the experiment

The starting raw material is oxide tungsten concentrate corresponding to GOST 213-83. The share of tungsten anhydride in the concentrate was not less than 55 % by weight. The reducer was the carbonaceous ultra-disperse dust derived from coal-graphite production. Adjusting the amount of the carbonaceous reducer ensured a change in the O:C ratio in the charge within 1.33–2.30. The heat treatment temperature was 1,373 K; the duration of isothermal aging was 60 minutes; the protective environment was the atmosphere of argon.

The X-ray phase analysis was performed at the diffractometer “DRON-6” (Russia). The microstructure images and the indicators of the content of the chemical elements at individual sites were acquired from the JSM 6360LA (Japan) raster electron microscope, which was equipped with the JED 2200 X-ray microanalysis system (JEOL, Japan).

4.2. Procedure to determine the samples' properties indicators

The phase composition of the target samples was determined by X-ray phase analysis. The monochromatic radiation of Cu K α was used at the value $\lambda=1.54051$ Å. The tube voltage and anode current were 40 kV and 20 mA, respectively. PDWin 2.0 (Russia) apps were used to determine the composition of phases.

The images of the microstructure of samples were acquired at an accelerating voltage of 15 kV. The diameter of the electronic probe was 4 nm. The content percentage of chemical elements was determined by a reference-free method of calculating fundamental parameters.

5. Results of studying the properties of the reduced tungsten concentrate at different O:C ratios in the charge

5.1. Defining the features of the phase composition

The phase composition of the reduction products at the O:C ratio in the charge of 2.30 is mainly represented by WO₂ with the manifestation of W (Fig. 1, *a*). At the O:C ratio in the charge of 1.65, the WO₂ intensity decreased while that of W increased. W₂C and C were also identified. Changing the O:C ratio in the charge to 1.33 led to an increase in the manifestation of W₂C and C.

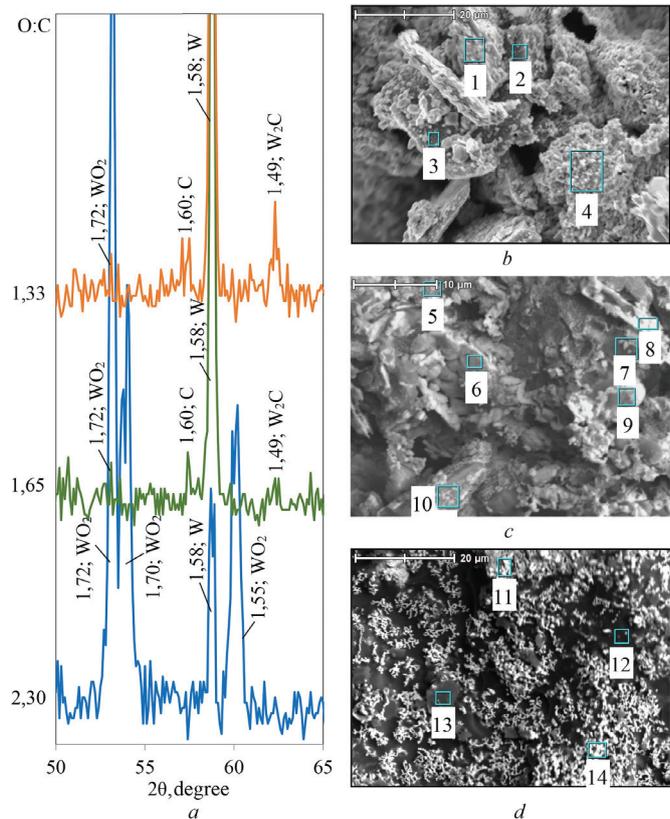


Fig. 1. X-ray phase study of tungsten concentrate after heat treatment at 1,373 K with different O:C ratios in the charge and the corresponding images of the microstructure at different magnification: *a* – sites of diffractograms; *b* – O:C ratio in the charge is 2.30 (magnification $\times 2,000$); *c* – O:C ratio in the charge is 1.65 (magnification $\times 3,000$); *d* – O:C ratio in the charge is 1.33 (magnification $\times 2,000$); 1–14 – sections of the X-ray microanalysis of samples

At the O:C ratio in the charge of 1.65 and 1.33 the W phase had the prevailing intensity indicators while the manifestation of WO_2 was residual. The compounds of oxide ore impurities in the reduced material had a fragmented nature of the manifestation of diffraction highs at a relatively low intensity.

5. 2. Studying features of the microstructure

The microstructure of reduction products was disordered and composed of particles of different shapes and sizes. This can be seen from the images at varying magnification providing a clear representation of the resulting microstructure (Fig. 1, *b–d*). There was some caking of the microparticles. The W content in the sites studied was within 61.21–86.78 % by weight (Table 1, Fig. 2).

Table 1

The results of X-ray microanalysis of reduction products corresponding to Fig. 1

Examined site	Element content, % by weight								
	C	O	Al	Si	Ca	Cl	Mo	W	Total
1	1.02	16.52	0.32	3.37	7.55	0	5.79	65.43	100.00
2	0.84	14.42	0	2.93	1.42	0	2.87	77.52	100.00
3	0.91	13.98	0.35	3.11	1.34	0	2.70	77.61	100.00
4	1.06	17.32	0	5.48	4.64	0.15	4.14	67.21	100.00
5	2.69	8.77	0.4	5.11	2.43	0	1.57	81.03	100.00
6	2.03	9.15	0	4.33	3.11	0	3.17	78.21	100.00
7	1.94	8.44	0	4.29	2.66	0	2.50	80.17	100.00
8	1.45	5.01	0	2.07	1.94	0	2.75	86.78	100.00
9	1.82	7.32	0	3.80	2.37	0	2.83	81.86	100.00
10	2.41	8.91	0	4.22	3.62	0	3.24	77.60	100.00
11	4.23	5.05	0.27	2.77	1.36	0	7.47	78.85	100.00
12	3.25	14.67	0	9.06	6.70	0	1.74	64.58	100.00
13	3.14	14.63	0	8.04	11.30	0	1.68	61.21	100.00
14	4.02	5.81	0.39	2.19	4.18	0	7.51	75.90	100.00

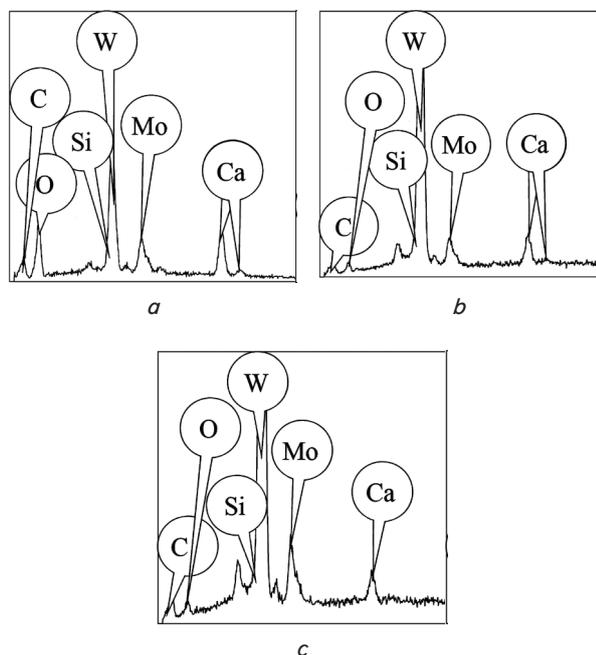


Fig. 2. Spectrograms of X-ray microanalysis of some areas of the samples corresponding to Fig. 1: *a* – 1; *b* – 10; *c* – 14

The Mo content of 1.57–7.51 % by weight was also revealed. The content of the accompanying ore impurities of Si, Ca, and Al was in the range of 2.07–9.06 % by weight, 1.34–11.30 % by weight, 0.27–0.40 % by weight, respectively. When the O:C ratio in the charge changed from 2.30 to 1.33, we observed a decrease in the residual oxygen content at the sites studied, from 13.98–17.32 % by weight to 5.05–14.67 % by weight. In this case, the carbon content changed from 0.84–1.06 % by weight to 3.14–4.23 % by weight.

6. Discussion of results of studying the properties of the reduced tungsten concentrate

The phase composition of the reduction products at the O:C ratio in the charge of 2.30 indicates the transition of the highest tungsten oxides to WO_2 along with the formation of W. This is consistent with the results reported in works [4–6], which describe the stages in the reduction process with the formation of tungsten oxides as intermediate components of the reactions. At the O:C ratios in the charge of 1.65 and 1.33, along with the reduction to W, there are the reactions of W_2C formation. This is consistent with the results reported in papers [3, 7, 8], which show the course of carbide formation along with the reduction processes. The residual nature of the WO_2 manifestation was noted, which is different from the results given in [12, 13], where the reduction products additionally contained WO_3 , W_4O_{11} , $W_{20}O_{58}$, $W_{12}O_{49}$. A fragmentary nature of the manifestation with a relatively low intensity of compounds of the accompanying ore impurities on the diffractograms cannot indicate the complete absence of these impurities in the reduction products. Apparently, the number of such impurities is relatively small for a clear display on diffractograms relative to the background level. The identified set of phases in the reduction products is close to that reported by the authors of works [14, 15] but W_2C was present there together with W_2C . In that case, as given in [15], the reduced product did not show a clear manifestation of W as an independent phase. The joint reduction of tungsten concentrate and the scale of fast-cutting steel in work [14], in contrast to our research, seems to have also led to the identification of the complex compound (Fe, W)C.

The microstructure of reduction products had a spongy and disordered structure (Fig. 1, *b–d*). The microparticles had different complex shapes with the manifestation of caking processes. The use of X-ray microanalysis showed the presence, together with W, of Mo, as well as other related ore impurities (Fig. 1, 2, Table 1), the nature of whose presence was considered by the authors of works [10, 11]. This feature can influence the course of reactions and the nature of reduction processes in the processing of raw materials. In this case, possible oxide ore impurities of Si, Ca, Al, without directly reacting, can affect the gas exchange inside the material and the caking of microparticles, changing the rate of processes.

The relatively high residual oxygen content in the reduction products at the O:C ratio in the charge of 2.30 (Fig. 1, *b–d*; Table 1) indicates a lack of the reducer to ensure the completeness of the reactions. This is consistent with the X-ray phase studies where the main phase, in this case, was WO_2 with some manifestation of the W pha-

se (Fig. 1, *a*). At the ratio of O:C in the charge of 1.33, there is a relatively high residual carbon content in the reduction products (Fig. 1, *b–d*, Table 1). Accordingly, in the studies of the phase composition, this was expressed in the form of the C and W₂C phases. The microstructure image showed particles with a relatively high W content (Fig. 1, *d*; sections 11, 14), which may appear to be a phase of W or W₂C. Excessively high residual carbon content has a negative impact on the technology of the doping supplement. Possible utilization expense factors for doping are reduced due to carbon restrictions. Based on our set of studies, the most preferred ratio of O:C in the charge is 1.65. In this case, there is no lack of carbon in the charge and there is a predominance in the phase composition of W. Some residual carbon in the form of W₂C and the undeveloped carbon reducer could subsequently ensure the post-reduction of residual WO₂ in the process of doping when the doping additive enters the liquid metal.

The limitations include the absence of multiple microstructure images with varying magnification for each of the reduction options studied, which could give greater visibility when studying the properties of reduction products.

The current research could be advanced towards studying the physical and chemical features of the reduction of a wider range of oxide ore concentrates. The most significant, in this case, are the ore concentrates of refractory elements. The difficulties that may emerge in the way of developing our study are due to the insufficient scope of available experimental base.

Some restrictions in the use of the resulting doping supplement are due to part of the residual carbon in the composition. Problems may arise if carbon from a doping additive leads to excess of the allowable carbon content in the melted steel. To prevent such issues, the use of the doping additive is preferable to replace some of the tungsten ferroalloys when smelting steels that do not have strict carbon limits. In this case, instrumental doped and tungsten-containing fast-cutting steels of grades P18, P12M3K5F2, P18F2, P6M5 and others, which are smelted in an electric arc furnace, are suitable. At the same time, the absence of compounds with a relatively high

propensity for sublimation does not require any special conditions to prevent the loss of the target element in the gas phase, which increases the degree of assimilation. Briquetting before reducing heating makes it possible to achieve greater compactness of the reduced material, as well as the manufacturability of subsequent use. The spongy structure of the doping supplement promotes a higher dissolution rate, providing less prolonged aging and, therefore, less burnout of doping elements compared to standard tungsten ferroalloys. In other words, it becomes possible to relatively reduce the melting time together with a decrease in the energy resources used. As a result, the volume of anthropogenic emissions into the environment is decreased, thereby improving the environmental safety of industrial conditions.

7. Conclusions

1. It has been determined that the reduced tungsten concentrate at the O:C ratio in the charge in the interval of 1.33–2.30 contained the phases of W, W₂C, C, WO₂. At the O:C ratio in the charge of 2.30, the phase composition was represented by W and WO₂. At the O:C ratio in the charge of 1.65, the W manifestation increased along with the weakening of WO₂. The diffraction highs of W₂C and C were also identified. At the O:C ratio in the charge of 1.33, an increase in the intensity of W₂C and C manifestation relative to the W phase was noted.

2. The microstructure of the reduced tungsten concentrate at the ratio of O:C in the charge in the interval of 1.33–2.30 had a spongy and disordered structure. Together with tungsten, the examined sites demonstrated the manifestation of the impurity of Mo and the accompanying ore impurities of Si, Ca, Al. The main elements identified at the examined sites had the following limiting content, % by weight: O – 5.01–17.32; C – 0.84–4.23; W – 61.21–86.78; Mo – 1.57–7.51; Si – 2.07–9.06; Ca – 1.34–11.30; Al – 0.27–0.40. The micro-inclusions at the studied areas of the surface showed different complex shapes. There were traces of the process of particle caking.

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