DETERMINING THE PATTERNS OF PHASE AND STRUCTURAL TRANSFORMATIONS AT CARBON-THERMAL REDUCTION OF MOLYBDENUM CONCENTRATE

Визначено вплив O/C шихти на склад металізованого молібденового концентрату після обробки при 1223–1423 K. Найбільш вигідним є O/C в межах 1,75–2,00, забезпечуючи відносно низькі залишкові C, O_2 і переважання Mo у фазовому складі. Структура неоднорідна із спечених мікрочасток. Не виявлено з'єднань, схильних до сублімації. Це обумовлює зниження втрат Mo при використанні легуючої добавки, що підтверджено в дослідно-промислових умовах

Ключові слова: молібденовий концентрат, вуглецевотермічне відновлення, фазовий аналіз, мікроскопічне дослідження, карбідоутворення, легування

Определено влияние O/C шихты на состав металлизованного молибденового концентрата после обработки при 1223–1423 K. Наиболее выгодным является O/C в пределах 1,75–2,00, обеспечивая относительно низкие остаточные C, O_2 и преобладание Mo в фазовом составе. Структура неоднородная из спеченных микрочастиц. Не выявлено соединений, склонных к сублимации. Это обуславливает снижение потерь Mo при использовании легирующей добавки, что подтверждено в опытно-промышленных условиях

Ключевые слова: молибденовый концентрат, углеродотермическое восстановление, фазовый анализ, микроскопическое исследование, карбидообразование, легирование

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1. Introduction

Recent years have witnessed a growing demand for steel, alloyed with rare and refractory elements such as Mo. At the same time, prices for respective alloying materials in the world market demonstrate a trend to increase. Traditional technologies (carbon silicone and aluminothermic melting) for obtaining the alloying materials based on Mo are characterized by considerable temperatures and duration of treatment. Accordingly, these processes are accompanied by

relatively high pollution of the environment with gaseous reaction products [1], as well as solid waste, along with considerable resource- and energy expenditures.

Therefore, it is an important task to bring down resource- and energy costs at lower Mo losses when processing and utilization of the ore molybdenum-containing materials in steelmaking. That necessitates studying the mechanism of reduction of the oxide molybdenum-containing raw materials. Improving the environmental safety is possible through the replacement of the reducing melting with the newest methods of powder metallurgy that employs a solid-phase reduction with a decrease in the pollution of the environment with wastes and products of reactions.

2. Literature review and problem statement

The techniques for processing oxide ore and anthropogenic raw materials that have demonstrated positive results include a solid-phase reduction of C or H_2. Study into hydrogen reduction of MoO_3, as the basic component of oxide molybdenum concentrate, to MoO_2, is reported in paper [2]. Formation of the intermediate Mo_4O_{11} oxide and parallel reduction reactions to Mo_4O_{11} and MoO_2 were experimentally confirmed. Hydrogen reduction of MoO_3 at 1,323 K was accompanied by the formation of the intermediate product MoO_2 and subsequent obtaining of Mo [3]. In other words, papers [2, 3] confirmed the stage character of reactions with a transition of higher oxides to lower oxides with subsequent reduction to Mo. Such a pattern is also shown by authors of paper [4], which also indicates a possible significant effect of the presence of impurities of other components in the system on the character and indicators of reduction. In this case, impurities may enter reactions with a reducing agent and molybdenum-containing compounds, forming joint bonds [4]. This can also manifest itself while reducing the oxide molybdenum concentrate, because it contains, along with the oxide compounds of molybdenum, related ore impurities. However, the studies reported in papers [2–4] failed to reveal the impact of the related ore impurities that are present in molybdenum concentrate on the processes of reduction, phase and structural transformations.

Authors of work [5] investigated reduction in the system Mo–O–C and Ca–Mo–O–C, which corresponds to the processes of carbon-thermal reduction of oxide molybdenum concentrate. They identified the formation of MoO_2 as an intermediate product that subsequently passed to Mo and carbides. The authors proposed a conditional division of the process into a primary interaction between MoO_3 and C with a progress of gasification reaction of C and subsequent course of MoO_2 reduction involving CO. However, results of research work [5] do not elucidate the impact of related ore impurities that are present in the oxide ore concentrate on the reduction process. This, in turn, can significantly affect the phase composition and structure of the reduction products.

The products of reactions, obtained in paper [5], are not susceptible to the sublimation in contrast to MoO_3 [6]. The specified property of MoO_3 is the reason for significant irreversible losses of Mo when obtaining and using molybdenum-containing alloying materials. Given this, when developing technological parameters for the reduction of oxide molybdenum concentrate, one should focus on the relatively low temperature. But it is necessary that the temperature

indicators of heat treatment should provide for the transition of MoO_3 into phases and compounds with a relatively low tendency to sublimation.

Conditions for lower Mo losses at sublimation were implemented by authors of paper [7] when reducing a MoO_3 powder using a two-stage regime of thermal treatment. The first stage occurred at 400–600 °C with the reduction of MoO_3 to MoO_2. The second stage – at 800–1,000 °C, enabling the post-reduction of MoO_2 to Mo. The specified temperature intervals may be indicative when determining the most favorable parameters for the molybdenum oxide concentrate reduction.

A confirmation for the susceptibility of primary conversion of MoO_3 to MoO_2, which has a lower susceptibility to sublimation, is given in paper [8]. In this case, the interaction between a MoO_3 powder and CO is observed at relatively low temperatures, starting from 200 °C [9]. In other words, there is a confirmed possibility to reduce molybdenum oxides from oxide concentrate, as well as to form carbides [10], at relatively low temperature of metallization. However, the existence of related ore impurities that are present in the oxide molybdenum concentrate can significantly affect gas exchange in the zone of reaction during reduction. This is not revealed in the research. In this case, a change in the possibility of CO access to molybdenum oxides, due to the presence of ore impurities, may affect the phase composition and structure of the reduction products.

Positive results of the application of carbothermal reduction was obtained at the disposal of Mo from molybdenum-containing slags formed in the production of copper [11]. Their Mo content was about 0.3 % by weight. The efficiency of extraction of Mo from used lubricating materials was examined by authors of paper [12]. They investigated the mechanism of carbothermal reduction in a range of temperatures from 1,073 K to 1,473 K, and at 1,773 K. They obtained the target iron-molybdenum-containing product with a content of Mo and C about 40 % by weight, and 4.3 % by weight, respectively. This is an additional confirmation to the fact that obtaining a carbon-free product by applying the carbon-thermal reduction of oxide molybdenum-containing raw materials is not possible. The data and temperature indicators of reduction, specified in papers [11, 12], should be considered when developing technological parameters for the oxide molybdenum concentrate reduction. However, the character of reduction and the resulting carbide phases in the systems investigated in papers [11, 12] and at carbon-thermal reduction of oxide molybdenum concentrate, may vary.

Using C as a reducing agent is technologically simpler and is more attractive economically than H_2. However, the products of reduction may contain residual C, bound in the oxycarbide and carbide compounds [13]. This predetermines certain limitations in the use of the resulting material without additional treatment when alloying steels and alloys with a limited C in the composition. However, a possibility of application of successful experience in treating with plasma eliminates the specified drawback [14, 15]. In paper [14], authors reported a possibility to obtain relatively pure Mo powders from oxides by using plasma. Treating the metallized molybdenum concentrate with a low-temperature plasma makes it possible to significantly reduce the content of S, P, As, Sn, Pb, Zn, Bi, Sb, and C [15].

There are important research results related to the mechanism of Mo reduction on the example of oxides, taken sepa-

rately, as well as certain types of industrial waste. However, still insufficiently studied are the patterns in carbon-thermal reduction of oxide molybdenum concentrates. They contain related ore impurities of Ca, Si, Al, Mg and others, which may significantly affect the process of reduction and the resulting composition of the product. In addition, still not deeply investigated are the regularities of influence of the content of C in charge on the composition of molybdenum-containing products. Research in this direction could provide a reduction in the consumption of Mo through the sublimation of oxide compounds. Determining the patterns that ensure relatively low residual C and O_2 opens the possibility for a wider scope of application of the alloying additive without additional treatment. In other words, it is a relevant task to study the regularities of influence of O/C in the charge on the content of C, O_2, and Mo in metallized molybdenum concentrate after different temperatures of thermal treatment. At the same time, it is necessary to investigate the phase composition and microstructure of metallization products at different ratio of O/C in the charge.

3. The aim and objectives of the study

The aim of present study was to examine physical-chemical patterns in the carbothermal reduction of oxide molybdenum concentrate. This is necessary to identify the parameters that reduce the loss of Mo by the sublimation of oxides when processing ore concentrates and using metallized molybdenum-containing alloying additives.

To accomplish the aim, the following tasks have been set:
– to explore patterns in the influence of O/C ratio in the charge on the concentrations of C, O_2, and Mo in metallized molybdenum concentrate after different temperatures of thermal treatment;
– to study the phase composition and microstructure of reduction products of oxide molybdenum concentrate at different ratios of O/C in the charge.

4. Materials and methods to study properties of the products of metallization of oxide molybdenum concentrate

4. 1. Examined materials and equipment used in the experiment

The starting material is oxide molybdenum concentrate of brand KMo-2 with a content of Mo not less than 55 % by weight. (TU 14-5-88-77). Reducing agent is the dust of coal-graphite production.

An X-ray phase analysis of the samples was carried out using the diffractometer "DRON-6" (Russia).

Photographs of the microstructure of samples were obtained from the raster electron microscope "REM-106I" (Ukraine). The microscope is equipped with a system of x-ray microanalysis that enables determining chemical composition of separate areas of the surface of samples.

4. 2. Procedure for conducting experiments and determining the indicators of properties of samples

Temperature interval of reduction study is 1,223–1,423 K. The examined ratio of O/C in the charge is 1.00–3.00. Duration is 60 min. Protective environment – argon. Mass of the samples is 80 g.

The approximation of dependence charts of the residual content of C, O_2, and Mo on O/C in the charge was performed by using the least squares method. The following models were chosen as nonlinear regression equations:

$$\hat{y}_1 = a \cdot x^3 + b \cdot x^2 + c \cdot x + d, \qquad (1)$$

$$\hat{y}_2 = m \cdot x^n, \qquad (2)$$

where $\hat{y}_1$ is the content of O_2, Mo, % by weight; $\hat{y}_2$ is the C content, % by weight; x is O/C in the charge; a, b, c, d, m, n are coefficients of regressions.

Correlation coefficients r of linearized models accepted values very close to 1 (not less than 0.98). Adequacy of the models was confirmed by the estimated values of the Fisher criterion, which exceeded tabular value $F_{kr}=5.32$, at the selected significance level $\alpha=5$ %.

Phase composition was determined by the method of X-ray diffraction analysis. Composition of the phases was determined using the software package PDWin 2.0 (Russia).

The microstructure of samples was determined at an accelerating voltage of 20–25 kW. We determined composition of the phases by a reference-free method for calculating fundamental parameters.

5. Results of research into carbothermal reduction of oxide molybdenum concentrate

Dependences of the O_2, C, Mo content, phase composition and structure of the metallized molybdenum concentrate on O/C in the charge are shown in Fig. 1, 2.
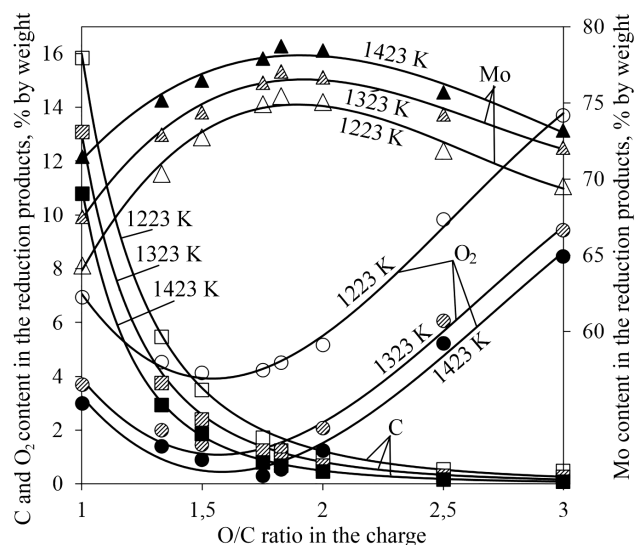

Fig. 1. Dependence of the O_2, C, and Mo content in metallized molybdenum concentrate on O/C in the charge

Values of regression coefficients for each dependence from Fig. 1 are given in Table 1.

We detected a decrease in O_2 and an increase in C at a decrease in O/C in the charge from 3.00 to 1.83–1.75 (Fig. 1). Further decrease in O/C led to a sharp increase in the content of C in the reduction products. An increase in the treatment temperature from 1,223 K to 1,423 K led to a relative decrease in O_2 and C and an increase in Mo.

Table 1

Summarized results of the values of regression coefficients *a, b, c, d, m, n* for dependences from with Fig. 1 according to formulae (1), (2)

$\hat{y}_1$	a	b	c	d
O_2 (1,223 K)	−2.98	22.84	−49.19	36.40
O_2 (1,323 K)	−2.28	18.13	−40.06	28.12
O_2 (1,423 K)	−2.08	16.89	−37.85	26.29
Mo (1,223 K)	4.46	−34.91	84.24	10.19
Mo (1,323 K)	3.43	−27.44	67.41	23.95
Mo (1,423 K)	2.07	−18.35	47.4	40.11
$\hat{y}_2$	m		n	
C (1,223 K)	16		−4	
C (1,323 K)	13		−4.5	
C (1,423 K)	11		−4.5	

Following heat treatment at 1,323 K at O/C in the charge 1.33, the products of reduction consisted of Mo and Mo_2C (Fig. 2). At O/C=1.83, only a phase of Mo clearly manifested itself. At O/C=2.50, along with Mo, we detected MoO_2. The microstructure of reduction products was disordered, heterogeneous, consisting of sintered microparticles.

The C content was within 0.18–4.14 % by weight, that of oxygen – 3.04–11.17 % by weight (Fig. 3, Table 2).

Fig. 3. Spectrograms of X-ray microanalysis of regions of the microstructure of molybdenum metallized concentrate according to Fig. 2 at O/C in the charge: *a* — 1.33, *b* — 1.83, *c* — 2.50

Table 2

Results of the X-ray microanalysis of regions of the microstructure of metallized molybdenum concentrate according to Fig. 3

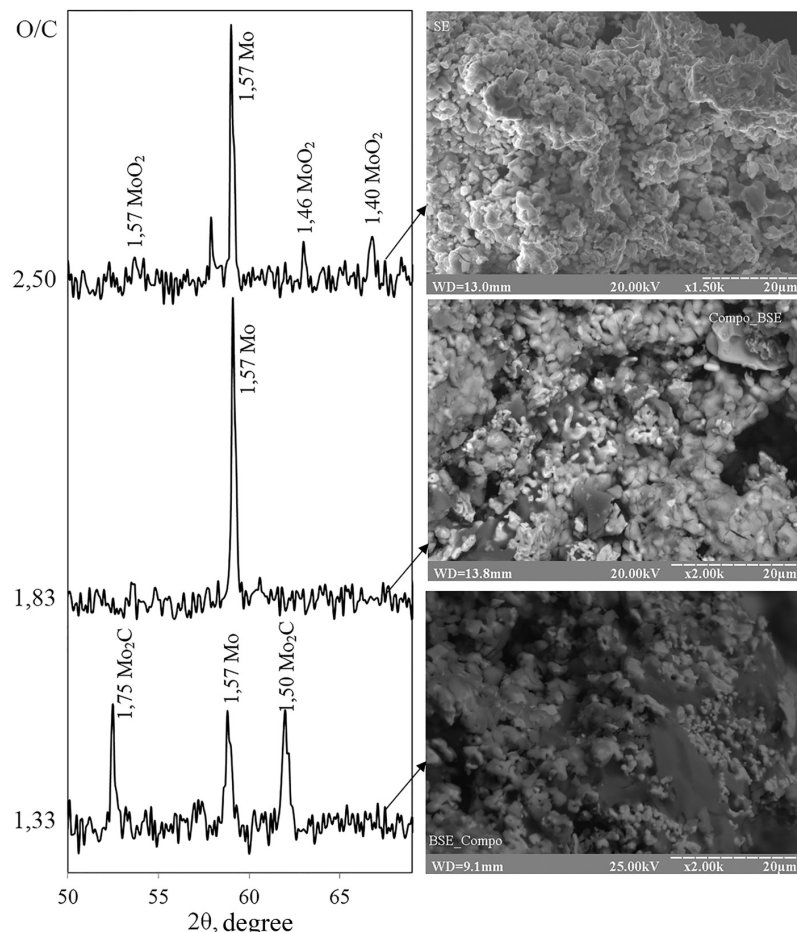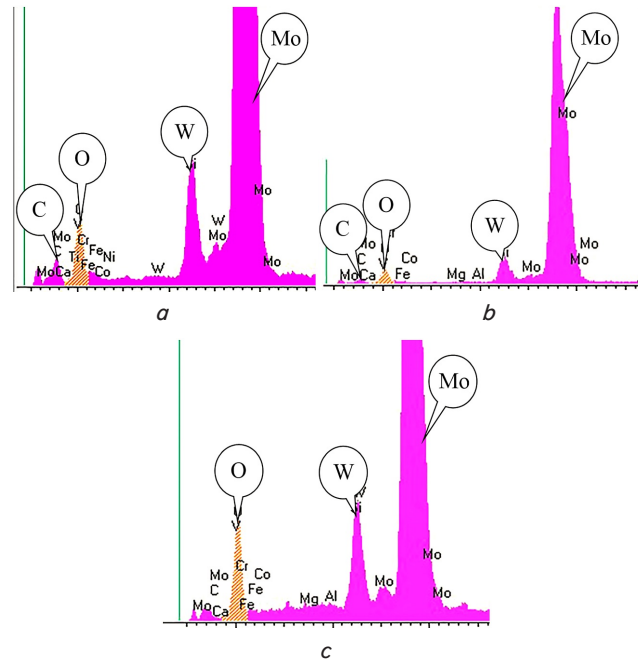| Element	Element content in the examined regions, % by weight		
	a	b	c
C	4.14	2.20	0.18
O	3.04	4.09	11.17
Mg	0.00	0.07	0.32
Al	0.00	0.05	0.27
Si	1.04	1.00	1.13
Ca	0.62	0.43	0.86
Ti	1.02	0.00	0.00
V	1.32	1.34	0.44
Cr	1.17	1.03	0.42
Fe	1.72	1.33	0.62
Co	1.65	1.05	0.21
Ni	1.80	0.00	0.00
Mo	78.61	82.99	77.60
W	3.87	4.42	6.78
Total	100	100	100

Fig. 2. Regions of diffractograms and the microstructure of metallized molybdenum concentrate, corresponding to them, after treatment at 1,323 K according to Fig. 1. Values near the diffraction maxima correspond to parameters of the crystal lattice

Along with Mo, we identified W and other related ore impurities of Mg, Al, Si, Ca, Ti, V, Cr, Fe, Co, Ni (Fig. 3, Table 2).

6. Discussion of results of research into carbothermal reduction of oxide molybdenum concentrate

We determined that the highest content of Mo (74.6–78.0 % by weight) was achieved at O/C in the charge within 1.75–2.00 (Fig. 1). In this case, C and O_2 are present in relatively small quantities, % by weight: 0.5–2.0 and 0.6–5.5, respectively. An increase in the treatment temperature from 1,223 K to 1,423 K ensured a relative increase in Mo at a reduction in C and O_2.

An increase in O_2 with decreasing O/C from 1.75 to 1.00 is due to the imperfect existing procedure for determining O_2 at a high content of C (Fig. 1). Determining O_2 was carried out by treating a material with dried H_2 at 1,173 K. It is known that at this temperature H_2 interacts with C to form methane. Given this, the product was depleted not only of O_2, but partially of C. Therefore, the loss of mass of the product, determined in a chemical analysis, belongs to the total loss of O_2 and C.

The process of transition of MoO_3 into MoO_2, described in papers [5, 7, 8], corresponds to the results of phase studies (Fig. 2). At O/C=2.5, following the reduction, we discovered Mo and MoO_2, indicating a non-complete reduction at a lack of C. Parallel metallization and carbide formation was identified at O/C=1.33, which agrees well with papers [5, 10, 13]. Mo dominated in the reduction products at O/C=1.83, indicating the balanced content of C in the charge.

Sintering of particles in the microstructure further indicates the occurrence of reduction processes (Fig. 3). Dark gray inclusions in samples at O/C=1.33 may indicate the unused reducing agent, at a relatively high content of C – 4.14 % by weight (Table 2). The relatively high content of oxygen, 11.17 % by weight, at O/C=2.50, indicates a certain lack of the reducing agent. This agrees well with the phase studies when identifying the non-fully-reduced MoO_2. We detected impurities of W, Mg, Al, Si, Ca, Ti, V, Cr, Fe, Co, Ni (Table 2, Fig. 4) that affect the reduction processes and their character.

With respect to the results of research, the most favorable conditions are the reduction conditions at 1,323 K or 1,423 K with O/C in the charge at 1.75–2.00. A variant for reducing the loss of Mo by sublimation is a two-stage mode of heating treatment, which was also implemented in paper [7]. Achieving relatively low residual C can make it possible to avoid additional treatment, as given in papers [14, 15], in order to extend the scope of application of the new material.

We consider a drawback of present research to be a missing dependence of phase composition and microstructure of the received material on the content of C in the charge at different reduction temperatures.

Further studies might address control over composition of the metallization products of the mixture of oxide molybdenum concentrate and anthropogenic alloyed raw materials. This would open up the prospect for expanding the parameters of alloying, as well as brand range of alloys, to use an alloying additive with the disposal of industrial waste in parallel. Difficulties that might arise at an attempt to develop such a study are due to the lack of a sufficient base of experimental data on the physical-chemical patterns of carbothermal reduction in complex-alloyed systems. This indicates the need to conduct further research in order to identify the interaction between Mo and a complex of the alloying elements and a reducing agent. as well as to reduce the loss of Mo during heat treatment.

The use of metallized molybdenum concentrate at the smelting of steel 38 HNM in 150-ton open-hearth furnaces did not cause any technological difficulties [16]. We have reached the degree of Mo assimilation at 70–90 % with an additive from metallized molybdenum concentrate of 100–150 kg and 92 % at 300...520 kg, respectively. The obtained results of Mo assimilation are 3–5 % higher compared to using standard ferromolybdenum [16].

7. Conclusions

1. It was determined that O/C in the charge at 1.75–2.00 after treatment at 1,223–1,423 K provides for the content of Mo at 74.6–78.0 % by weight. The content of C and O_2 was within, % by weight: 0.5–2.0 and 0.6–5.5, respectively. An increase in the reduction temperature from 1,223 K to 1,423 K provided for the relative growth of the Mo content at a decrease in C and O_2.

2. It was found that at O/C in the charge of 2.50 the products of reduction consisted of Mo and MoO_2. In the case of O/C=1.83, we clearly detected Mo only. At O/C==1.33 – Mo and Mo_2C. The structure is disordered, heterogeneous, consisting of sintered micro particles with the presence of ore impurities of Mg, Al, Si, Ca, Ti, V, Cr, Fe, Co, Ni. The lack of compounds susceptible to sublimation predetermines a reduction in the loss of Mo when using an alloying additive. A spongy microstructure ensures a relatively rapid dissolution and increases the degree of assimilation.

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