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RESEARCH INTO RESOURCE-SAVING MOLYBDENUM-CONTAINING ALLOYING ADDITIVE, OBTAINED BY THE METALLIZATION OF OXIDE CONCENTRATE

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Досліджено фазовий склад, мікроструктуру оксидного молібденового концентрату і продуктів металізації, які отримані дослідно-промисловим шляхом. Виявлено губчасту структуру металізованого концентрату і надлишок вуглецю у вигляді карбідів. Це забезпечує зниження часу розчинення в рідкому металі, високу відновну здатність при легуванні, що призвело до зниження втрат молібдену від вторинного окиснення та сублімації

Ключові слова: молібденовий концентрат, вуглецевотермічне відновлення, металізація, сублімація, фазовий аналіз, мікроструктура, ресурсозбереження

Исследованы фазовый состав, микроструктура оксидного молибденового концентрата и продуктов металлизации, которые получены опытно-промышленным путем. Выявлена губчатая структура металлизованного концентрата и избыток углерода в виде карбидов. Это обеспечивает уменьшение времени растворения в жидком металле и высокую восстановительную способность при легировании, что привело к снижению потерь молибдена от вторичного окисления и сублимации

Ключевые слова: молибденовый концентрат, углеродотермическое восстановление, металлизация, сублимация, фазовый анализ, микроструктура, ресурсосбережение

1. Introduction

At present, indicators of energy- and material consumption of the final product in metallurgy are the basic ones during comprehensive planning of production output [1]. These trends have particularly manifested themselves in the metallurgy of rare metals and related alloying materials.

In recent years, there has been an increased demand for steel alloyed with rare and refractory elements such as Mo. At the same, price for the appropriate alloying materials has shown a trend to grow in the world market [2].

Traditional technologies (carbosilicon- and alumothermal smelting) for obtaining alloying metals based on Mo are transformed into modern methods of powder metallurgy and are further developed [3, 4]. Derived products possess qualitatively new consumer properties [5].

Therefore, there is a relevant problem of resource and energy saving with a reduction in Mo losses through the

sublimation of oxides, when processing and employing the ore and technogenic molybdenum-containing materials in steelmaking. Strategic direction in solving this problem is to develop understanding of the mechanism of restoration of oxide molybdenum-containing raw materials.

2. Literature review and problem statement

Study into kinetics and mechanism of hydrogen restoration of MoO_3, as the main component of oxide molybdenum concentrate, to MoO_2 is presented in article [6]. The formation of the intermediate oxide Mo_4O_{11} and parallel restoration reactions were experimentally confirmed:

1) MoO_3 to Mo_4O_{11};

2) Mo_4O_{11} to MoO_2.

Hydrogen restoration of MoO_3 at 1323 K was accompanied by the formation of the intermediate product MoO_2 and subsequent obtaining of superdispersed powder of metal Mo of high purity [7].

Authors of paper [8] outlined the possibility to obtain relatively pure powders of metal Mo from the molybdenum oxides using plasma. In addition, treating the metalized molybdenum concentrate by low-temperature plasma makes it possible to significantly reduce the content of S, P, As, Sn, Pb, Zn, Bi, Sb, and C [9].

Authors of article [10] have studied thermodynamics and kinetics of restoration in the system Mo–O–C and Ca–Mo–O–C, which matches the processes of carbon-thermal treatment of oxide molybdenum concentrate. They discovered formation of MoO_2 as the intermediate product, which was subsequently transformed to metal Mo and molybdenum carbides. These reaction products are not subject to sublimation in contrast to MoO_3 [9]. They represented conditional split of the process into two stages:

1) interaction between MoO_3 and C with a progress of gasification reaction of C;

2) interaction reaction between MoO_2 and CO.

A confirmation of susceptibility of the preferred conversion of MoO_3 to MoO_2, which has a lower susceptibility to the sublimation, is given in article [11]. In this case, interaction between molybdenum oxides and CO is observed even at relatively low temperatures [12], at which there is no significant increase in the elasticity of vapors of molybdenum-containing compounds. In other words, it is expedient to study the regularities of restoration and carbide-formation at relatively low temperatures of metallization of oxide molybdenum concentrate with the goal of reducing the losses of Mo with its oxides by sublimation. Positive results of the use of the carbon-thermal restoration were obtained during recycling of Mo from molybdenum-containing slag, formed during production of copper [13]. Their Mo content was about 0.3 % by weight. Authors in paper [14] reported the efficiency of extracting Mo from the used lubricating materials. They investigated the mechanism of carbon-thermal restoration in a range of temperatures from 1073 K to 1473 K and at 1773 K. They received the target iron-molybdenum-containing product with a content of Mo and C about 40 % by weight and 4.3 % by weight, respectively.

The use of carbon as a recovering agent is easier technologically and is more attractive economically than hydrogen. However, the products of restoration may contain residual carbon, bound in the oxy-carbide and carbide compounds [15]. This predetermines certain limitations in the use of resulting material without additional treatment for alloying the steels and alloys with limited carbon in their composition. Nevertheless, the possibility of applying successful experience in the treatment by low-temperature plasma, described above [9], eliminates the specified shortcoming.

It follows from the considered sources of information that there are significant results of studies into the processes of Mo restoration on the example of oxides taken separately, as well as certain kinds of technogenic waste. However, still not sufficiently investigated is the mechanism of progress of recovering and carbide-forming processes during carbon-thermal treatment of oxide molybdenum concentrates. They, in contrast to pure oxides of Mo, contain associated oxide ore impurities of Ca, Si, Al, Mg and others. They can significantly affect the flow of processes of metallization, the phase composition and microstructure of recovered products. Research in this direction could provide a reduction in the Mo losses by the sublimation of oxide compounds during thermal treatment of oxide molybdenum concentrates and subsequent use of a metallized alloying additive. Given the aforementioned, it is expedient to conduct a comprehensive study into phase composition and microstructure of oxide molybdenum concentrate, as a starting raw material, and the products of its metallization. The use of raster electron microscopy with an x-ray microanalysis would greatly expand our understanding of the nature of separate phases and inclusions in the examined materials.

3. The aim and objectives of the study

The goal of present work was to study the physical-chemical properties of oxide molybdenum concentrate and the products of carbon-thermal restoration obtained under experimental-industrial conditions. This is required to determine parameters that reduce the losses of Mo during processing of ore concentrates and use of metallized molybdenum-containing alloying additives in steelmaking. In addition, research in this field is necessary for the further development of understanding the mechanism of the course of recovering and carbide-forming processes at metallization.

To accomplish the set goal, the following tasks have been set:

– to determine the features of phase composition and microstructure of oxide molybdenum concentrate, as a starting raw material, for metallization;

– to examine phase composition and microstructure of metallized molybdenum concentrate received by experimental-industrial technique, in terms of the impact of the sublimation during alloying on reducing the losses of the target element.

4. Materials and methods for examining the properties of oxide molybdenum concentrate and the products of metallization

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

Starting material is oxide molybdenum concentrate of grade KMo-1 with Mo content not less than 55 % by weight (TU 14-5-88-77). Grinding was performed in a ball mill with peripheral unloading of the ground material. Sifting was carried out through a sieve with cell size of 0.45 mm.

Reducing agent is the dust of coal-graphite production. Cast iron shavings were used as a component that increases the intensity of heat-mass transfer and controls the density of restoration products. Crushing of cast iron shavings was carried out in the ball mill ShMA-1 with magnetic separation of the milling. Estimated ratio of O/C in the samples was 0.8–1.1, which is below stoichiometric, and ensures full restoration of molybdenum trioxide and the formation of molybdenum carbides and metal molybdenum. In order to adjust the required degree of restoration of oxide molybdenum concentrate, we determined the required curing time under isothermal mode, which is 2–4 hours when temperature of the furnace reaches 1453 K.

An X-ray structural phase analysis of the samples was performed in the diffractometer DRONE-6 (Russia).

Images of the microstructure of samples were obtained on a raster electron microscope REM-106 (Ukraine). The microscope is equipped with a system of x-ray microanalysis to determine chemical composition of separate areas of the surface of the samples.

4. 2. Procedure for determining the indicators of properties of the samples

In order to determine the phase composition in the diffractometer DRON-6, scanning was performed in the radiation of copper cathode with a nickel filter. Scan mode is 40 kV, 20 mA. The nature of the phases was defined using the software package PDWin 2.0 (Russia).

Scanning on the raster electron microscope SEM-106 was performed at accelerating voltage of 10–25 kV and current of electronic probe 52–96 mkA. Working distance to the examined surface equaled 10.5–11.6 mm.

Determining a phase composition was performed using the reference-free method of calculating fundamental parameters: computation of correction factors of reflection of probe electrons, absorption of characteristic x-ray radiation and fluorescence. Determining the chemical composition of phases was carried out in the areas marked in the images of the microstructure with relevant conditional signs.

5. Results of examining the indicators of properties of oxide and metallized molybdenum concentrates

Phase composition of oxide molybdenum concentrate is represented mainly by MoO_3, as well as by a relatively small amount of MoO_2, WO_3, Mo_2C and associated impurities Al_2O_3, CaO, SiO_2, MgO (Fig. 1).

The structure of oxide molybdenum concentrate is heterogeneous: in the form of plates, granules of rounded shape, thread-like formations (Fig. 2).

Attachment of micro particles of the concentrate relative to one another is achieved using a structure that is visually similar to a phase, which is formed in the process of sintering. According to results of x-ray microanalysis, in point 1 (Fig. 2, 3, Table 1), there may be present mainly oxide compounds of Mo with impurities of compounds of W. In point 3, we observed a nano-dimensional structure (probably, a combination of MoO_3 and WO_3 with impurities of carbon-containing compounds of molybdenum and tungsten). Chemical composition of point 4 is similar to the composition of point 2.

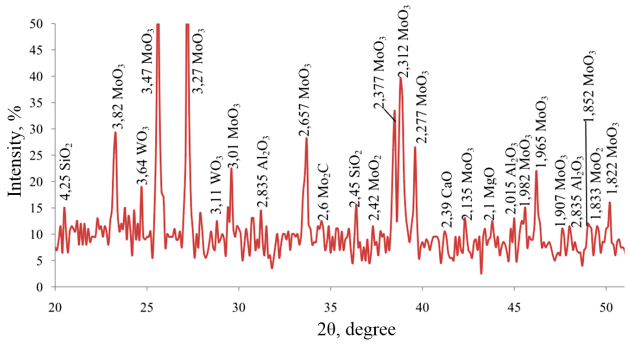

Fig. 1. Section of diffractogram of oxide molybdenum concentrate

Metal Mo dominates in the resulting metallized molybdenum concentrate (Fig. 4). Clearly observed is the presence of carbides Mo_2C and MoC. Unrecovered molybdenum-containing constituent is represented by an oxy-carbide compound (Mo, O, C) and lower molybdenum oxide MoO_2. We detected fragmented presence of Mo_8O_{23}. Diffraction peaks that characterize iron-containing compounds are introduced in briquettes by the cast-iron chips; combinations of ore impurities were not detected in the diffractogram. This might be explained by the presence of areas of local clusters of these compounds, which did not make it to the section of the sample that underwent x-ray imaging.

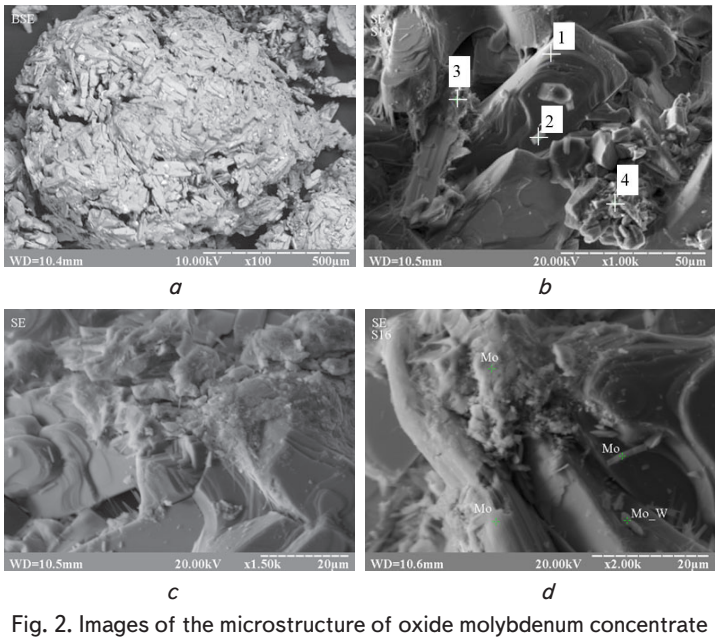

Fig. 2. Images of the microstructure of oxide molybdenum concentrate at magnification: *a* – ×100, *b* – ×1000, *c* – ×1500, *d* – ×2000

Metallized molybdenum concentrate possesses spongy structure (Fig. 5). Clearly observed are the areas where the molybdenum oxides restoration products dominate (Fig. 5, 6, Table 2, areas 1, 5, 6, 9, 10).

Residual oxygen indicates the possibility of a presence, along with metal Mo, unrecovered oxide or oxy-carbide compounds. In addition, the residual oxygen can be in the form of oxide ore impurities of Si, Al, Ca, Mg, K, Na, which were introduced along with the oxide molybdenum concentrate. This is confirmed by detection of the specified elements in the examined areas.

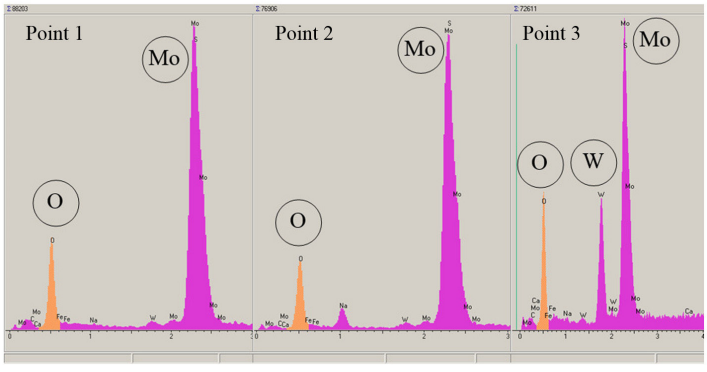

Fig. 3. Spectrograms of x-ray microanalysis of oxide molybdenum concentrate related to Fig. 2

Table 1

Results of x-ray microanalysis of the sample of oxide molybdenum concentrate related to Fig. 2

Area	Content of elements, % by weight									
	C	O	Na	S	K	Ca	Fe	Mo	W	Total
1	6.23	48.69	0.47	0.67	0.09	0.13	0.12	42.56	1.04	100
2	1.30	41.59	2.72	3.24	0.07	0.18	0.37	49.45	1.08	100
3	6.31	44.52	0.42	0.68	–	–	0.28	32.88	14.91	100

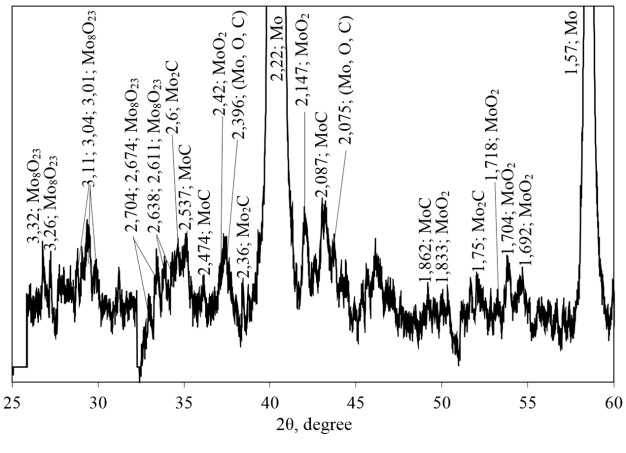

Fig. 4. Snippet of diffractogram of the sample of metallized molybdenum concentrate

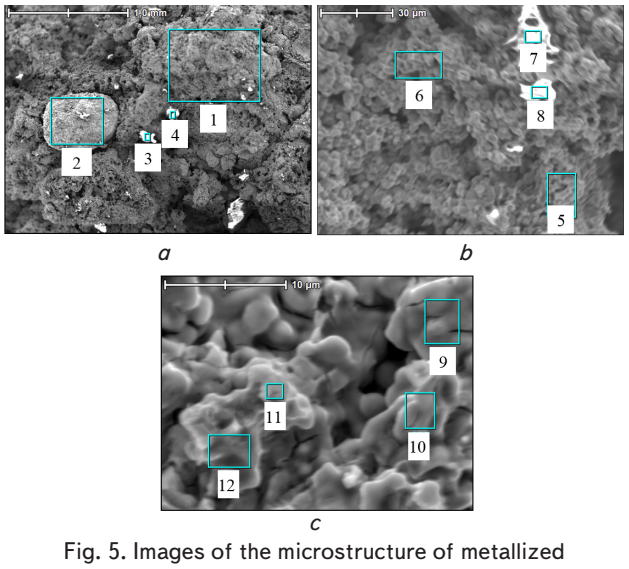

Fig. 5. Images of the microstructure of metallized molybdenum concentrate at magnification: *a* – ×50, *b* – ×1000, *c* – ×5000

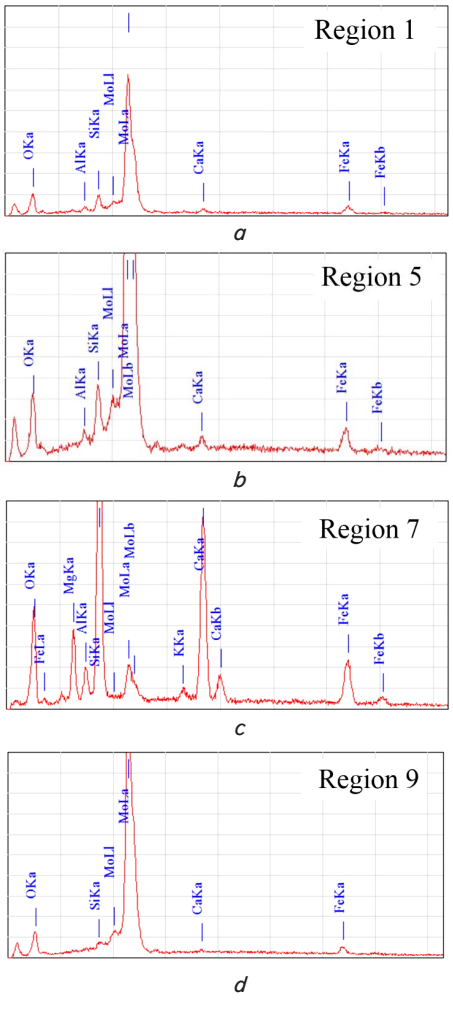

Fig. 6. Spectrograms of some specified areas related to Fig. 5: *a* – 1, *b* – 5, *c* – 7, *d* – 9

Table 2

Results of x-ray microanalysis of the sample of metallized molybdenum concentrate related to Fig. 5

Area	Content of elements, % by weight									
	O	Na	Mg	Al	Si	K	Ca	Fe	Mo	Total
1	12.12	0	0	0.85	2.96	0	1.82	9.47	72.78	100
2	2.91	0	0.23	0.58	2.11	0	1.04	67.80	25.33	100
3	40.83	0	0	0	55.07	0	0	0	4.10	100
4	55.66	2.66	0.85	6.58	0	5.83	4.77	16.14	7.51	100
5	9.36	0	0	0.49	2.25	0	1.36	7.71	78.83	100
6	8.50	0	0	0.80	2.43	0	1.78	11.43	75.06	100
7	15.97	0	4.82	1.96	23.55	1.24	24.71	21.01	6.74	100
8	5.02	0	0	0	11.74	0	20.08	41.75	21.41	100
9	9.33	0	0	0	0.48	0	0.64	5.84	83.71	100
10	8.84	0	0.30	0.36	0.83	0	1.01	6.59	82.07	100
11	23.77	0.51	0.44	2.11	18.43	1.62	1.42	3.03	48.67	100
12	16.45	0.55	0.37	2.51	16.09	2.04	3.19	6.23	52.57	100

Note: Determining of element C was not conducted

Ore impurities are, obviously, relatively light sections (Fig. 5, areas 3, 4, 7, 8). One can also see an iron-containing section of round shape, introduced to the furnace charge as a cast iron shaving (Fig. 5, area 2).

6. Discussion of results of examining the indicators of properties of oxide and metallized molybdenum concentrates

We established almost complete fixing of Mo in oxide molybdenum concentrate in the MoO_3 oxide with a relatively small amount of tungsten-containing and other ore impurities. Exploring the microstructure testifies to the developed micro porosity, which does not lead to the complication of diffusion processes while lead to high losses of molybdenum in the form of sublimation of MoO_3 during steel smelting.

To reduce the losses of Mo, it is necessary to maintain relatively low-temperature heat treatment, however expedient and sufficient to activate and maintain the processes of restoration. Especially prior to the moment of transition of the larger share of MoO_3 to lower oxide compounds, which possess vapor elasticity several orders of magnitude less [9]. This agrees with the results of research conducted by authors of articles [6, 7, 10], in which Mo_4O_{11} and MoO_2 are the intermediate products of restoration that subsequently may pass into metal Mo metal or carbide compounds.

The carbides of Mo_2C and MoC, discovered in metallized molybdenum concentrate, indicate parallel course of the processes of carbide-formation and restoration. This agrees with the results of research obtained by authors of papers [10, 15], from which it follows that obtaining a carbon-free product after carbon-thermal restoration is not possible. Spongy structure of the resulting metallized product makes it possible to relatively rapid dissolve in a liquid metal in the process of alloying, providing for a reduction in the losses of the target element. In this case, the total time of smelting reduces, resulting in lower consumption of production energy.

Post-restoration of oxide molybdenum-containing component will occur directly during introduction of the received material to molten metal as an alloying additive, due to excessive carbon from carbide and oxy-carbide compounds. In this case, we achieved a transition of the dominant share of MoO_3 from the concentrate to compounds that have significantly lower vapor elasticity, which ensures reduction of molybdenum losses as a result of the sublimation.

A weak point of the present study is probably the lack of research results into dependence of the phase composition and microstructure of metallized raw molybdenum-containing raw material on temperature of the carbon-thermal restoration. Another relevant problem is to control the assigned density of the resulting metallized product. Research in this direction could provide the most favorable conditions for the dissolution and absorption of an alloying additive in a liquid metal, thus the research in the future is expedient.

Efficiency of applying metallized molybdenum concentrate was confirmed during alloying of the steel 38HNM under experimental-industrial conditions at smelting in an open-hearth furnace. The use of the new molybdenum-containing alloying additive did not cause any technological difficulties. Experimental smelting of the steel 38HNM was conducted in 150-tonne open-hearth furnaces that worked by a scrap-ore process. Metallized molybdenum concentrate was added to the furnace and ladle by the following variants of technology:

1) during filling and partially during finishing;
2) during filling;
3) during finishing and partially to a ladle;
4) to a ladle.

During experimental smelting, adding to the ladle 100...150 kg of the new molybdenum-containing material, a degree of assimilation reached 70...90 %. During smelting when adding a larger amount of metallized molybdenum concentrate (300...520 kg), a degree of assimilation increased to 92 %. The introduction of metallized molybdenum concentrate to the liquid bath and ladle enables a relatively high assimilation of Mo (3...5 % larger compared to the introduction of ferromolybdenum to the furnace). Quality of the steel 38HNM smelted with the use of the new alloying material, complied with the requirements of OST 14.21–77 [16].

7. Conclusions

1. Phase composition of oxide molybdenum concentrate is represented mostly by MoO_3, as well as a relatively low amount of MoO_2, WO_3, Mo_2C and associated impurities of Al_2O_3, CaO, SiO_2 and MgO. The microstructure is heterogeneous: in the form of plates, granules of round shape, and thread-like formations.

2. Phase composition of the metallized molybdenum concentrate, obtained under experimental-industrial conditions, mainly consists of metal Mo, as well as carbides MoC and Mo_2C. Unrecovered component is represented by oxy-carbide and molybdenum oxides, such as MoO_2 and Mo_8O_{23}. The microstructure is spongy, with the inclusions of associated oxide ore impurities of Si, Al, Ca, Mg, K, Na. The received metallized product mainly consists of compounds that are not prone to sublimation and possess high restoration ability. Residual carbon in the form of carbides makes it possible to conduct post-restoration of oxide molybdenum-containing component directly in a liquid bath in the process of alloying. It provides additional protection against secondary oxidation and thus reduces Mo losses by the sublimation of oxide compounds.

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