Magnesium vapor reduction of complex double compounds of molybdenum with tungsten

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Abstract. The process of obtaining powder of the Mo-W alloy by magnesium vapor reduction of \( \text{MgW}_x\text{Mo}_{1-x}\text{O}_4 \) and \( \text{CaW}_x\text{Mo}_{1-x}\text{O}_4 \) oxide compounds (\( x = 0.3 \)) with a residual inert gas pressure of 2-20 kPa in the temperature range 700-800°C was investigated. Argon or helium was used as an inert gas. Powders of Mo-W alloy with a specific surface area of up to 20 m²g⁻¹ were obtained. When both types of compounds were reduced at a residual pressure in the reactor of more than 5 kPa, spatial separation of the reaction products was observed with removal of magnesium oxide from the reaction zone.

1. Introduction
Alloys of molybdenum with tungsten are widely used in engineering. Properties that make them popular include high-temperature strength and corrosion resistance at elevated temperatures, high resistance to abrasion and wear [1]. Due to the high melting point, powder metallurgy is often used to obtain them. The alloy is produced by metallothermic reduction [2], by mechanical grinding of the components [3] and other methods [4-6]. However, the existing methods are energy-intensive and give powders with an insufficiently high specific surface area.

Previously, it was shown that a promising method for producing powders of refractory metals with a high specific surface area is the reduction by magnesium vapor of double oxide compounds containing refractory oxides [7,8]. For powders obtained by the magnesium vapor reduction of oxides, the mesoporous structure is characteristic. Its formation is due to the presence in the structure of the reduced metal particles of MgO interlayers and their subsequent leaching with mineral acid solutions.

The purpose of this work is to study the characteristics of the powders of the Mo-W alloy, obtained by magnesium vapor reduction complex oxide compounds containing molybdenum with tungsten, depending on the conditions of their reduction.

2. Thermodynamic analysis
As precursors, powders of double complex oxide compounds \( \text{MgW}_x\text{Mo}_{1-x}\text{O}_4 \) and \( \text{CaW}_x\text{Mo}_{1-x}\text{O}_4 \) were chosen. Their choice is due to the fact that when reduction a mixture of oxides, we should expect the formation of a mechanical mixture of powders. The formation of the alloy is difficult for the following reasons. First, mutual diffusion and atomic mobility in the W-Mo system is low even at high temperatures [9]. In addition, MgO oxide interlayers resulting from the reduction of oxides serve as a diffusion barrier preventing the formation of an alloy. The decrease of the alloying temperature during the reduction of double complex oxides is due to the more dense packing of the metals that make up the alloy. Such a package reduces the length of the diffusion path of the atoms.
To assess the possibility of reduction of double complex oxide compounds, a thermodynamic analysis of the reactions of their reduction with magnesium vapor was performed:

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\begin{align*}
\text{MgW}_x\text{Mo}_{1-x}O_4(s) + 3\text{Mg}(v) &= \text{W}_x\text{Mo}_{1-x}(s) + 4\text{MgO}(s) \quad (1) \\
\text{CaW}_x\text{Mo}_{1-x}O_4(s) + 3\text{Mg}(v) &= \text{W}_x\text{Mo}_{1-x}(s) + 3\text{MgO}(s) + \text{CaO}(s) \quad (2)
\end{align*}
\]

The thermodynamic characteristics of compounds of variable composition, containing molybdenum and tungsten that were absent in literature, were calculated by the method proposed earlier by Amosov [10]. The calculated enthalpy, entropy, and Gibbs energies of reactions (1) and (2) are presented in figure 1. According to the results of calculations, both types of compounds of variable composition with values of \(x\) in the range \(0 < x < 1\) have a high thermodynamic probability of reduction by magnesium vapor. Moreover, the probability of reduction of both types of compounds is much higher at low \(x\) values and decreases with increasing tungsten content. For experimental studies both types of compounds with a value of \(x = 0.3\) were selected. In this case, the features of reduction for reactions with \(\Delta G\) values close to the highest value for both types of compounds are investigated (figure 1b).

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Dependences of enthalpy, entropy (a) and Gibbs energy (b) of magnesium reduction reactions of complex tungsten and molybdenum oxide compounds on the composition: a — CaW\(_x\)Mo\(_{1-x}\)O\(_4\) (1, 4), MgW\(_x\)Mo\(_{1-x}\)O\(_4\) (2, 3); b — CaW\(_x\)Mo\(_{1-x}\)O\(_4\) (1, 2), MgW\(_x\)Mo\(_{1-x}\)O\(_4\) (3, 4).

**3. Experimental**

The Mg\(_{0.3}\)Mo\(_{0.7}\)O\(_4\) and CaW\(_{0.3}\)Mo\(_{0.7}\)O\(_4\) powders were synthesized by sintering the components MoO\(_3\) (pure), WO\(_3\) (pure) and CaO (pure) or Mg\(_5\)(CO\(_3\))\(_4\)(OH)\(_2\)(H\(_2\)O)\(_2\) (analytical pure). The equipment and methods for producing powders are similar to those used previously [8]. The process was carried out under an atmosphere of magnesium vapor and an inert gas (argon (reagent grade) or helium (A)).

Container with magnesium (M95) was installed on the bottom of the reaction vessel. A portion of precursor weighing 3 g was loaded into metal crucibles, which were installed above the container with magnesium. A shield was placed above the crucibles, the distance from which to the precursor surface was 30 mm. The reaction vessel was closed with a lid, in the center of which there was a hole for the thermocouple cover. The vessel was placed in a stainless steel retort, which was sealed, evacuated to a pressure of 5-10 Pa, filled with an inert gas, heated to the required temperature, and again evacuated to a residual pressure of 2-20 kPa. The reduction was carried out in the temperature range of 700-800°C for 4-6 h. The reduction products were treated with a 10% hydrochloric acid solution (reagent grade) to remove magnesium and calcium oxides. The powder of the reduced metal was washed with distilled water until neutral. X-ray phase analysis was performed on a Shimadzu XRD-6000 X-ray diffractometer (Cu K\(_\alpha\)-radiation). The specific surface area and porosity of the powders were measured, respectively, by the BET and BJH methods on a TriStar II 3020 V1.03 instrument.
4. Results and discussion
From the data in figure 1a, it can be seen that reactions (1) and (2) are exothermic and proceed with the release of a large amount of heat (1351 and 1252 kJ/mol). According to the calculations, the adiabatic reaction temperatures exceed 2850°C. The use of an inert gas atmosphere and magnesium vapors as a reducing agent makes it possible to control the rate at which the reducing agent enters the reaction zone, and thereby to control the process temperature (figure 2). At the same temperature and residual pressure, maintained in the reactor volume during the reduction process, the maximum temperature of the reaction mixture is higher when helium is used as inert gas. This is due to the higher diffusion coefficient of magnesium vapor in helium compared with argon, due to the significant difference in the molar masses of these inert gases.

![Figure 2. Reaction mixture temperature as a function of reduction time. Precursors: MgW_{0.3}Mo_{0.7}O_{4} (1), CaW_{0.3}Mo_{0.7}O_{4} (2, 3); atmosphere: argon (1, 3), helium (2); residual pressure 5 kPa. Dotted line — temperature in the reactor bulk.](image)

Source materials, except magnesium, and the products of the reactions (1) and (2) in the working temperature range are characterized by low vapor pressure. Hence it can be expected that after reduction the entire reaction mixture will be in the reaction zone. The crucibles with the reaction mixture and the corresponding shields after the reduction are shown in figure 3. It is seen that after the reduction of both types of precursors with a residual pressure of 2 kPa, the entire reaction mixture is in the crucible, and there are no deposits on the side of the shield facing the precursor (figure 3a1, b1). After the reduction of CaW_{0.3}Mo_{0.7}O_{4} with a residual pressure of 5 kPa there are dense deposits of white substance on the part of the shield facing this precursor, on the inner side surface of the crucible and on the surface of the reaction mixture (figure 3, right crucibles a2, b2). According to X-ray powder diffraction data, the white matter was pure magnesium oxide. After the reduction of MgW_{0.3}Mo_{0.7}O_{4} under the same conditions, the entire reaction mixture is in the crucible, and part of the shield above this precursor still remains clean (figure 3, left crucible a2, b2). However, after reduction at a residual pressure of 10 kPa and above, spatial separation of the reaction products with removal of magnesium oxide from the reaction zone took place for both types of compounds (figure 3a3-a4, b3-b4). A magnesium oxide crust with a thickness of about 1 mm was usually formed on the surface of the reaction mixture (figure 3a5). Under the same conditions supported in the reduction process, the replacement of the argon atmosphere with the helium atmosphere resulted in a decrease in the bulk of MgO deposits on the side of the shield facing the precursor (compare figure 3b3, b4).

Separation of reaction products (figure 3), apparently, is due to the occurrence of electronically mediated reactions [11]. Such reactions can proceed without direct physical contact of the reactants — through the transfer of electrons. At high temperatures, the double oxides MgW_{x}Mo_{1-x}O_{4} and CaW_{x}Mo_{1-x}O_{4} are electrically conductive and capable of transporting electrons. Therefore, during reduction, the formation of a closed circuit including precursors and metal hardware components is possible. Magnesium atoms in the vapor state, colliding with the walls of the container, its lid and the surface of the precursor, can give off electrons, which enter the reaction zone and reduce tungsten and molybdenum ions. To maintain electroneutrality, the oxygen ion must move to the metal ion of the reducing agent. The carrier of the oxygen ion under certain conditions, which are provided by the high thermal effect of the reduction reactions of the oxide compounds, becomes an inert gas atmosphere (Ar or He). It is known that helium has greater thermal conductivity than argon. Therefore, if all other conditions are equal, when compounds are reduced in a helium atmosphere heat loss from the reaction zone to the environment increases. As a result, the amount of magnesium oxide deposits on the side of
the shield facing the precursor decreases (figure 3b3, b4) and a larger amount of MgO remains close to the alloy powder particles.

Figure 3. Crucibles with reaction mixture (a) and corresponding shields (b) after reduction. Precursors: MgW0.3Mo0.7O4 (left crucibles a1-a4), CaW0.3Mo0.7O4 (right crucibles a1-a4, crucible a5); inert gas: Ar (1-3); He (4, 5); residual pressure in the reactor 2 kPa (1), 5 kPa (2), 15 kPa (3-5).

Influence of residual pressure in the reactor on the specific surface area of powders obtained from different precursors is shown on figure 4. As appears from the data provided there in both cases with increase in residual pressure in the reactor the specific surface area of powders decreases. It is connected with removal of magnesium oxide from structure of the reduced alloy particles. During removal of magnesium oxide the quantity of its layers in reaction mixture decreases that promotes coagulation of primary metal particles and it is the reason of decrease of the specific surface area. Greater decrease in a specific surface at increase in pressure during CaW0.3Mo0.7O4 reduction in comparison with MgW0.3Mo0.7O4 reduction is connected with removal from structure a larger amount of MgO.

Figure 4. Dependence of the specific surface area of alloy powders on residual pressure in the reactor. Temperature 740°C; atmosphere — argon; precursors MgW0.3Mo0.7O4 (1), CaW0.3Mo0.7O4 (2)

The study of the porous structure of the powders showed that the specific surface is almost completely determined by the pores surface. At the same time, the growth of specific surface occurs mainly due to an increase in the number of nanopores of smaller diameter (figure 5). The shape of the adsorption curves for all the obtained powders can be attributed to type IV according to IUPAC, which is characterized by a hysteresis loop, and is characteristic of mesoporous materials (figure 6).

Figure 5. Cumulative pore distribution curves for alloy powders obtained by reduction of MgW0.3Mo0.7O4 (1) and CaW0.3Mo0.7O4 (2). The specific surface area of the powders 20 m²g⁻¹ (1) and 12 m²g⁻¹ (2).
5. Conclusion

The thermodynamic analysis of magnesium reduction reactions of the complex oxide compounds MgW_{0.3}Mo_{0.7}O_4 and CaW_{0.3}Mo_{0.7}O_4 by magnesium vapor was performed. The regularities of the reduction of magnesium oxide double-oxide compounds MgW_{0.3}Mo_{0.7}O_4 and CaW_{0.3}Mo_{0.7}O_4 with a residual pressure of argon or helium of 2-20 kPa in the temperature range 700-800°C and the properties of the obtained powders of the Mo-W alloy were investigated. Powders of Mo-W alloy with a specific surface area of up to 20 m² g⁻¹ were obtained.

It was shown that during the reduction of oxide compounds, a spatial separation of the oxide and metal phases occurs with the release of dense MgO condensates on the surface of the reaction mixture and outside the reaction zone. The bulk of MgO deposits outside the reaction zone increases with an increase in the residual inert gas pressure in the reactor.

It was determined that the shape of the adsorption curves for the obtained powders can be attributed to type IV according to IUPAC, which is characterized by the presence of a hysteresis loop, and is characteristic of materials with a mesoporous structure.

Acknowledgments

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