

Preparation of tungsten-molybdenum alloy powder by “hydride” technology

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The paper presents the findings of a study investigating the production and characterisation of tungsten and molybdenum powders through the application of two distinct methodologies: mechanical mixing and sol-gel technology. Moreover, the resulting powders were subjected to reduction in a hydrogen current. The objective of this study was to compare the characteristics of the resulting materials and to identify the most effective method for achieving the desired properties. In the course of the experiments, samples of tungsten and molybdenum powders were prepared using both methods. Subsequently, the physical and chemical properties of the samples, including particle size, surface morphology, crystal structure, and chemical composition, were subjected to detailed examination. The findings revealed that each method possesses distinctive advantages and disadvantages with regard to the resulting powders. The mechanical mixing process yielded powders with relatively fine particles and a non-homogeneous structure, which may be advantageous for certain applications that do not necessitate the formation of alloys. In contrast, the sol-gel method yielded particles of comparable coarseness and chemical homogeneity, which is crucial for enhancing mechanical properties.

Key words: tungsten, molybdenum, powder metallurgy, ammonium paratungstate, ammonium paramolybdate hydrogen reduction, sol-gel process.

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Introduction

The objective of this research is to develop a technology for obtaining tungsten-molybdenum powder materials of a specified composition in a finely dispersed state. This will be achieved by employing chemical reduction methods involving a mixture of paratungstate and ammonium paramolybdate in a hydrogen environment.

Molybdenum is a refractory metal that is often used in metallurgy [1]. It is at number 42 in the D. I. Mendeleev periodic table of chemical elements. According to the source, the mass content of metal in the earth's crust is 3×10^{-4} %, however, molybdenum is not found in free form [2]. High-purity molybdenum oxide is in demand in the production of molybdenum-containing catalysts, which are widely used in oil refining (cracking, hydrotreatment, reforming), conversion of methanol to formaldehyde, vapor-phase oxidation of propylene to acrolein, ammonolysis of toluene, epoxidation of various alkenes, and others [3].

Metallic tungsten is widely used in the electric lamp, radio engineering and vacuum tube industries [4]. Tungsten alloys, possessing high strength, heat resistance and other valuable qualities, are in demand in a number of areas of technology. Tungsten and its alloys are used to manufacture incandescent filaments, radio tube parts, heaters and screens of high-vacuum furnaces. Using the high emission capacity of tungsten, emitters, cathodes of X-ray tubes

and kenotrons, cathodes of electron-beam installations, plasma and ion engines are made from it [5].

Tungsten-Molybdenum (W – Mo) alloy has recently garnered significant attention as a material with the potential to withstand high temperatures [6]. Its applications span a diverse range, including electrical engineering, microelectronics, nuclear reactors, and spacecraft. This is attributed to the alloy's distinctive properties, which include a high melting point, low thermal expansion, high thermal conductivity, and exceptional mechanical strength at elevated temperatures [7].

The extremely high melting points of tungsten and molybdenum render the production of their alloys by traditional melting and casting methods a challenging endeavour. In this regard, the powder metallurgy technique is traditionally employed for the production of alloys comprising metals with significantly disparate melting points [8]. To guarantee the superior quality and dependability of high-temperature products, it is essential to utilize W – Mo alloy powders that adhere to specific parameters. The aforementioned parameters include a narrow particle size distribution, an appropriate particle shape and an effective dispersion.

In the context of microelectronics development, there is a need to increase the current density and specific power dissipation in microelectronic devices, while requiring the reduction of device components to a submicron scale. However, this results in the occurrence of detrimental

processes, including electromigration, interlayer diffusion, and intermetallide formation at interlayer interfaces [9]. The most efficacious method to circumvent these negative effects is to utilize refractory metals, such as Mo and W, for metallization purposes. Refractory metal powders employed for metallization pastes must exhibit high chemical and structural homogeneity [10].

There are numerous methodologies for synthesizing W – Mo alloy powder. One of the most prevalent methodologies is the high-energy mechanical milling of a mixture of Mo and W powders in ball mills. This approach has been documented in numerous studies, including those referenced in [11]. Nevertheless, this approach presents a number of drawbacks, including prolonged energy consumption and the potential for contamination of the final product with the materials used for grinding. In [12], a one-step soft chemistry approach was employed to synthesize W – Mo nanoalloys of variable composition with an average size of approximately 40 nm. Although this method yielded nanoalloys with favourable characteristics, the Mo content was constrained to a range of 20 to 40%. In a further contribution to the field, the authors [13] put forward an alternative methodology for the production of Mo – W alloy nanopowders. The sol-gel synthesis of double oxides of tungsten and molybdenum, followed by hydrogen reduction, was employed. This method permits a considerable reduction in the alloying temperature, due to the dense packing of the alloy components in the precursor and the shorter diffusion path of atoms during the formation of the solid solution. The paper [14] presents a method for the preparation of a porous Mo – 30 wt.% W alloy with a controlled pore structure. The method comprises freeze drying and sintering, which enables the production of sintered bodies comprising a Mo – W alloy phase with macroscopic aligned pores of 200 μm in size. However, the morphology and size of the Mo – W particles were not controlled during the sintering process. In a recent study, the authors [15] investigated the production of molybdenum-tungsten alloy powders via the reduction of mixed oxide compounds, namely $\text{Mo}_{0.3}\text{W}_{0.7}\text{O}_3$, $\text{CaMo}_{0.7}\text{W}_{0.3}\text{O}_4$ and $\text{MgMo}_{0.7}\text{W}_{0.3}\text{O}_4$, with magnesium and calcium vapors at temperatures between 750 and 880 $^{\circ}\text{C}$. The calculated crystallite size of the alloy is observed to be within the range of 12–35 nm on average.

Nevertheless, the techniques for producing powders with a narrow particle distribution are not published in open access sources. It is therefore imperative to develop new methods for synthesizing W – Mo alloy powders with specified properties. The proposed solution is expected to enhance the quality and reliability of high-temperature products and metallization pastes. Additionally, it is anticipated that the material will gain new applications in new areas.

Materials and methods

The starting materials for powder synthesis were crystalline ammonium paratungstate PTA ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot 5\text{H}_2\text{O}$), ammonium paramolybdate PMA ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot$

$4\text{H}_2\text{O}$), polyvinylpyrrolidone PVP ($(\text{C}_6\text{H}_9\text{NO})_n$, molecular weight: 10.000) and hydrochloric acid.

The powder mixture was obtained through two distinct methods: mechanical mixing of powders and the sol-gel method. The mechanical mixing of the powders was conducted in a mass ratio of PTA : PMA – 76 : 24, with the assumption that following the reduction of the powders to metals, the mass ratio of W : Mo would be 80 : 20. To ensure uniform mixing and grinding of the powder materials, the mechanical mixture was subjected to processing in a planetary mill Activator-4M for 15 minutes at a speed of 14 Hz. This was done with the addition of grinding bodies based on tungsten carbide in a ratio of 2 : 1 to the mass of powder.

In order to obtain the chemical mixture, the measured weights of PTA and PMA were initially dissolved in distilled water. The solution was agitated until the components were fully dissolved. Subsequently, polyvinylpyrrolidone (PVP) was introduced to the solution at a rate of 1 g per liter. The precipitation was conducted via reverse precipitation, employing a calculated quantity of hydrochloric acid. The concentration of the hydrochloric acid solution was 15%. Subsequently, the solution was subjected to centrifugation, and the precipitate was dried for a period of 12 hours at a temperature of 110 $^{\circ}\text{C}$.

Subsequently, the resulting product was subjected to reduction in a hydrogen current. Specific reduction modes were selected according to patent and literature sources. The reduction temperature has a significant effect on the coarseness of tungsten powder. In the temperature range 650–900 $^{\circ}\text{C}$ the method provides powders with optimal particle size. Reduction at temperatures above 1000 $^{\circ}\text{C}$ leads to changes in the structure of tungsten powder (enlargement, agglomeration).

The process was conducted in a flow-through quartz reactor with a continuous hydrogen flow. The program heating was conducted in accordance with the following scheme:

1. Heating to 450 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}$ per minute.
2. The temperature was increased to 850 $^{\circ}\text{C}$ at a rate of 5 $^{\circ}\text{C}$ per minute.
3. Subsequently, the sample was soaked for 30 minutes.
4. The temperature was then cooled to 500 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}$ per minute.
5. Further cooling without adjustment.

A QL500 hydrogen generator was employed for the synthesis of hydrogen. The hydrogen supply was conducted at a rate of 400 milliliters per minute. The sample was cooled to 100 $^{\circ}\text{C}$ in a hydrogen current. Subsequently, the sample was returned to room temperature in a nitrogen current. Hydrogen and nitrogen were dehydrated by passing them through a column containing calcium chloride.

An electron microscopic study of the powder microstructure was conducted using scanning electron microscopy on an EVO 50 and TESCAN Mira instrument, both of which were equipped with an attachment for elemental composition analysis by energy dispersive X-ray spectroscopy (EDS). Phase analysis was conducted using X-ray

diffraction on a Shimadzu XRD-6000 instrument. Imaging was performed on copper irradiation (K α) using the Bragg-Bretano scheme with a step of 0.050°, a point exposure time of 2 sec and an angular range of 10°–80°. The X-ray tube voltage was set to 40 kV, and the beam current was 30 mA. The dispersibility of powder materials was investigated by laser diffraction methods on a Malven Mastersizer 2000. Prior to analysis, the material was treated in an ultrasonic bath to facilitate the rapid dispersion of any agglomerates that may have formed.

Results and discussion

In the initial stage, preliminary studies were conducted to examine the properties of the initial PTA and PMA powders. **Figs. 1, 2** illustrate the microstructure of the initial PTA and PMA powders, respectively.

The microstructure images indicate that both powders are composed of large particles of a slice shape, with particles of regular cubic and rhombic shapes also present (**Fig. 1, b** and **Fig. 2, b**). As evidenced by electron iso-images of the powder microstructure, the particle size of PTA is within the range of 100 to 250 micrometers. The PMA powder is represented by larger particles up to 500 μm and more.

The results of the powder dispersity analysis indicated that the average particle size of the PTA powder was approximately 40 micrometers, with a maximum particle size of up to 130 micrometers and a minimum particle size of approximately 0.5 micrometers. The average particle size of PMA powder was determined to be $\sim 424 \mu\text{m}$, with a maximum particle size of up to $\sim 1 \text{ mm}$ and a minimum particle size of at least $\sim 34 \mu\text{m}$.

1.1. Mechanical mixing of powders

The diffraction pattern of the powdered material obtained by hydrogen reduction of the mechanical mixture of PTA and PMA powders is illustrated in **Fig. 3**.

The X-ray phase studies yielded the result that the obtained metal powder is composed of two phases of W and Mo in a mass ratio of approximately 80 : 20, with no impurity phases present. This experimental confirmation substantiates the feasibility of employing the proposed hydrogen reduction methodology to synthesize W – Mo powders from the initial charge comprising PTA and PMA powders. Using the Smelyakov-Sherrer method, the crystallite size of the obtained material equal to 12.6 nm was calculated by the half-width of the most intense diffraction reflection.

Fig. 4 depicts the microstructure of the W – Mo powder obtained through the aforementioned process. As evidenced

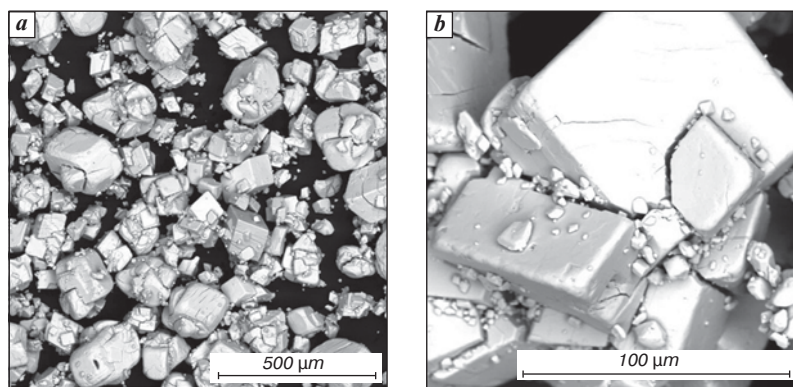


Fig. 1. Electron images of the microstructure of ammonium paratungstate powder (PTA): *a* – general view; *b* – view of an individual powder particle

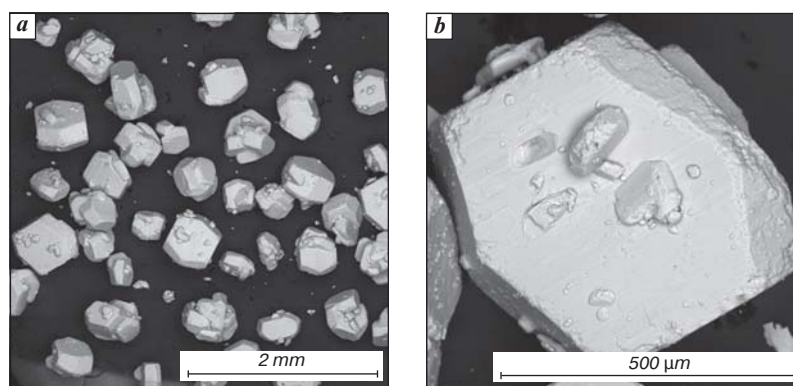


Fig. 2. Electron images of the microstructure of ammonium paramolybdate powder (PMA): *a* – general view; *b* – view of an individual powder particle

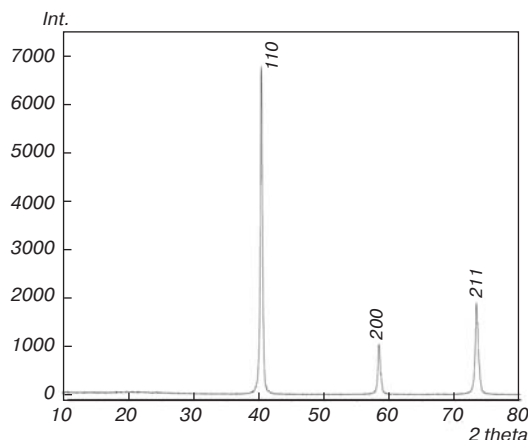


Fig. 3. Diffractogram of reduced W – Mo powder

by the microstructure images, the resulting powder material is constituted by a mixture of irregularly shaped splintered particles that closely resemble the morphology of the original charge material. As the images were obtained using a backscattered electron detector (BSE), their tonality is dependent on the difference in density between the materials under study. A material with a higher density will appear lighter in the resulting image. It can thus be postulated that the lighter particles are composed of a more dense tungsten, while the darker particles are composed of molybdenum. The results of the elemental EDS analysis corroborate these findings.

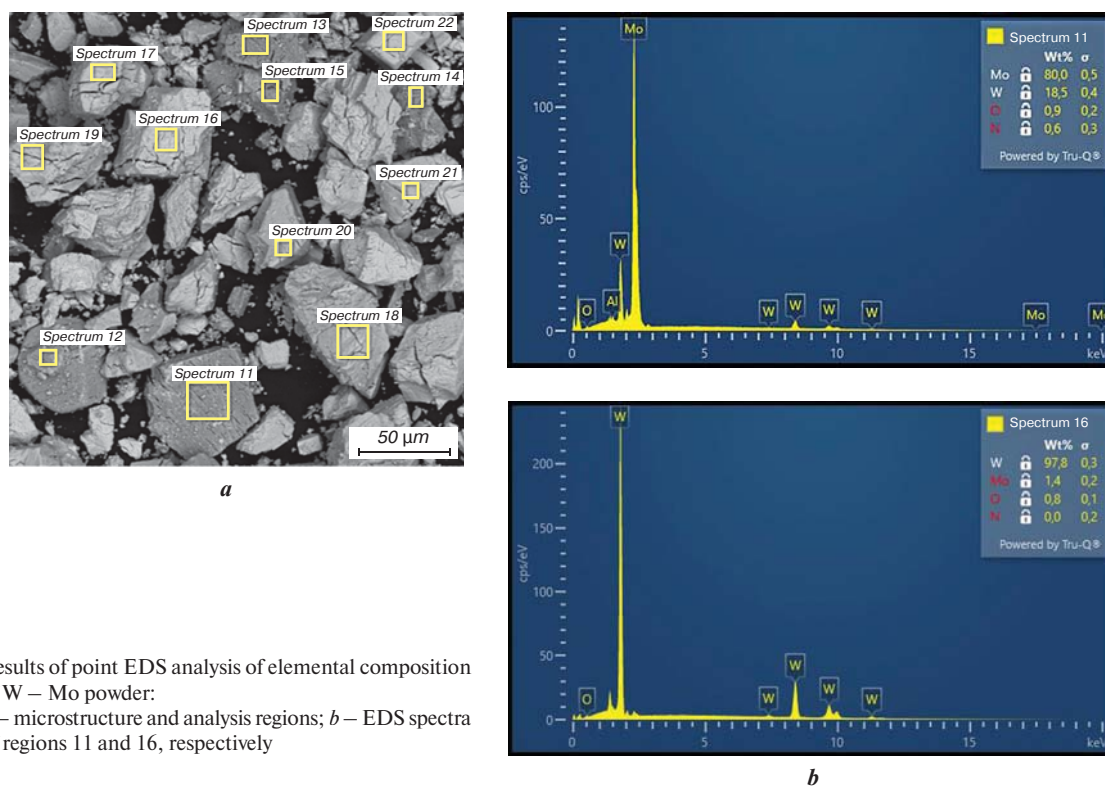


Fig. 4. Results of point EDS analysis of elemental composition of W – Mo powder: *a* – microstructure and analysis regions; *b* – EDS spectra of regions 11 and 16, respectively

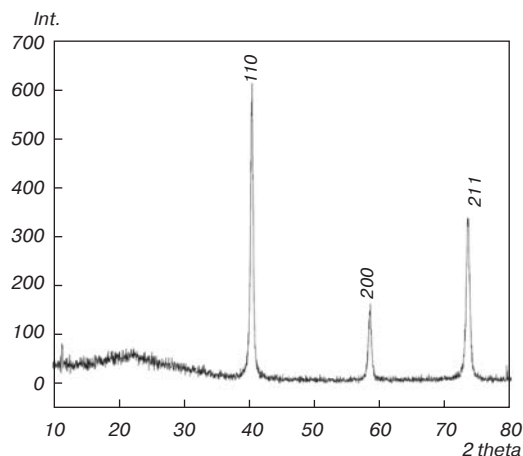


Fig. 5. Diffractogram of reduced W – Mo powder

The results of the dispersity analysis indicate that the powder material exhibits an average particle size of approximately 20 micrometers.

According to the results of dispersity analysis, the obtained powder material is characterised by an average particle size of ~20 μm, with a minimum particle size of ~0.5 μm and a maximum particle size of ~81 μm.

1.2. Sol-gel method

The diffraction pattern of the powdered material obtained by hydrogen reduction of the chemical mixture of PTA and PMA powders is illustrated in Fig. 5.

The X-ray phase studies yielded the following results: the obtained metal powder is represented by a W and Mo alloy phase of 74 wt.%, with the remainder represented

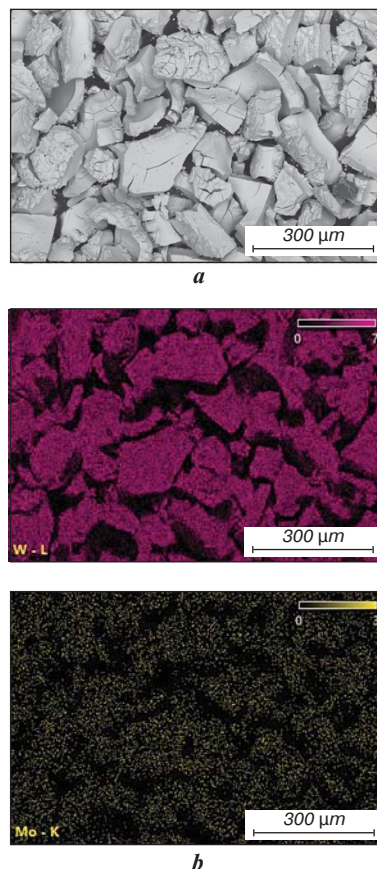


Fig. 6. Results of EDS analysis of elemental composition of W – Mo alloy powder: *a* – microstructure and analysis area; *b* – EDS spectra of the area

by an amorphous phase. Additionally, the mean crystallite size was determined to be 9.2 nm.

Fig. 6 shows electron images of the microstructure of the obtained W – Mo powder alloy.

As evidenced by the microstructure images, the resulting powder material is constituted by a mixture of irregularly shaped particles. It was observed that the surface of the alloy particles exhibited evidence of cracking. It seems reasonable to posit that the observed particle shape is a consequence of the material being subjected to immediate reduction in a hydrogen atmosphere subsequent to drying. In this regard, the observed shape of powder agglomerates probably repeats the shape of the precursor and grinding the powder after drying will significantly reduce the particle size. The results of the elemental EDS analysis corroborate the formation of a solid solution W – Mo alloy. The EDS analysis corroborated the formation of the W – 20Mo alloy.

According to the results of dispersity analysis, the obtained powder material is characterised by an average particle size of ~30 µm, with a minimum particle size of ~0.5 µm and a maximum particle size of ~120 µm.

Conclusion

In conclusion, W – 20 wt.% Mo solid solution nanopowders were synthesized via two distinct methodologies: mechanical stirring and the sol-gel method in conjunction with hydrogen reduction. The phase composition and morphology of the synthesized W – Mo solid solution alloy powder were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive spectroscopy (EDS). These analyses confirmed the uniform distribution of tungsten and molybdenum within the solid solution phase throughout the sol-gel synthesis process. The mechanical mixing of the powder results in a mixture of tungsten and molybdenum powders.

In order to obtain metal alloys, it is necessary to employ the sol-gel method. By modifying the parameters of co-precipitation and milling of co-precipitation products, it is possible to obtain a material with a specified dispersion composition. Subsequent studies will be conducted to ascertain the impact of sol-gel process parameters on the dispersity of the resulting powders. The advancement of technology for obtaining W – Mo alloy powders will enhance the quality parameters of the products derived from them, thereby reducing the reliance on imported powders.

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