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Synthesis of fine tungsten powders with low impurity content

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Abstract. A chemical-metallurgical method was used to synthesize fine tungsten powders with low oxygen content. The tungsten powders were obtained by hydrogen reduction of tungsten trioxide (WO_3) powders. Hydrogen was passed through a column with potassium hydroxide for drying. In the first series of experiments, three fractions of WO_3 powder of grade “P” 64–100 μm, 40–50 μm, and less than 25 μm were reduced at temperatures of 650, 800, and 950 °C. In the second series of experiments, tungsten powders were obtained by hydrogen reduction of three different WO_3 powders of grades “P”, “CP”, and “Tumelom”. The resulting tungsten powders had varying oxygen contents (0.043–2.18 wt. %) and average particle sizes ranging from 35 to 345 nm. *X*-ray diffraction analysis confirmed the presence of pure tungsten. The minimum oxygen content (0.043 wt. %) in the tungsten powder was achieved by reducing tungsten oxide of grade “CP” at 950 °C for 3 h.

Keywords: synthesis, tungsten, powder, reduction, temperature

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Синтез дисперсных порошков вольфрама с низким содержанием примесей

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Аннотация. Для синтеза дисперсных вольфрамовых порошков с низким содержанием кислорода использован химико-металлургический метод. Порошок вольфрама получали водородным восстановлением порошков вольфрамового ангидрида WO_3. Водород пропускали через колонну с гидроксидом калия для осушения. В первой серии экспериментов при температурах 650, 800 и 950 °С восстанавливали три фракции порошка вольфрамового ангидрида WO_3 марки Ч: 64–100, 40–50 и менее 25 мкм. Во второй серии экспериментов порошок вольфрама получали водородным восстановлением трех разных порошков вольфрамового ангидрида WO_3 марок Ч, ХЧ, «Тумелом». Получили порошки вольфрама с различным содержанием кислорода (0,043–2,18 мас. %) и средним размером частиц 35–345 нм. Рентгенофазовый анализ показал чистый вольфрам. Минимальное содержание кислорода (0,043 мас. %) в порошке вольфрама получено при восстановлении оксида вольфрама марки ХЧ при температуре 950 °С в течение 3 ч.

Ключевые слова: синтез, вольфрам, порошок, восстановление, температура

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Introduction

Tungsten powders are widely used in various industries and scientific fields (e.g., radiation shielding for certain medical treatments, nuclear energy, mechanical engineering, etc.) [1–4].

Tungsten is characterized by a high melting point, high thermal conductivity, and low sputtering under plasma exposure, which makes it suitable for the fabrication of internal walls in thermonuclear reactors [5]. However, it is well known that oxygen impurities weaken grain boundaries, thus increasing the risk of cold cracking and leading to a higher ductile-to-brittle transition temperature [6; 7].

Fine tungsten powders are synthesized by various methods. The plasma chemical method is used to produce nanopowders of refractory metals such as W, Mo, Nb, and Ta with average particle sizes ranging from 10 to 100 nm or more [8; 9]. The particles of these powders have a regular shape [10; 11].

Experimental studies on the synthesis of fine tungsten powder from scheelite ($CaWO_4$) by the self-propagating high-temperature synthesis (SHS) method were presented in [12; 13]. After leaching the SHS products with a 20 % aqueous hydrochloric acid solution, tungsten powder with a purity of over 99.9 wt. % and particle size less than 0.5 μm was obtained.

In [14], experimental studies on the hydrogen reduction of tungsten acid vapors $WO_2(OH)_2$ at around 1000 °C were conducted, resulting in powders containing about 70 wt. % tungsten with a particle size of less than 5 nm.

The work [15] presented experimental studies on the hydrothermal synthesis of porous spherical tungsten oxide particles followed by hydrogen reduction at 600–650 °C. The spherical tungsten particles, measuring tens of microns, consisted of crystallites with sizes ranging from 28 to 37 nm.

In industrial practice, tungsten is typically produced using a chemical-metallurgical method [16; 17], which involves the hydrogen reduction of WO_3. This technology does not require expensive specialized equipment. Tungsten ores are enriched to obtain standard concentrates containing 55–65 wt. % tungsten trioxide (WO_3). Various technological schemes are used in industrial practice to process concentrates to produce tungsten trioxide, which serves as a precursor for the production of tungsten, tungsten carbide, and other products. The final compounds in the concentrate processing are usually tungsten acid (H_2WO_4) or ammonium paratungstate (APT) $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$, which, upon calcination, yield WO_3. Tungsten acid completely loses water at $t = 500$ °C, while APT decomposes above 250 °C. The calcination temperature of APT depends on the intended use of WO_3.

The reduction process is conducted in tubular furnaces [18] with an excess of dry hydrogen passed over the powder bed (2–4 cm thick) at a rate ensuring the removal of water vapor at temperatures above 630 °C. The primary impurity in tungsten powders is oxygen, the content of which (depending on the reduction mode) ranges from 0.05 to 0.30 wt. % [19; 20].

Advancements in technology demand higher performance characteristics of tungsten powders, including finer particle size and lower oxygen content [21]. Therefore, the practical task of developing a technology for synthesizing fine tungsten powders with low oxygen content is highly relevant. This study aimed to investigate the influence of precursor particle size and reduction temperature on the particle size and oxygen content in tungsten powders.

Materials and methods

Tungsten powder was obtained by hydrogen reduction of three grades of tungsten trioxide (WO_3) powder: “P” (Pure), “CP” (Chemically Pure) and from LLC “Tumelom”. The hydrogen used conformed to the standard OST 11050.003-83. Hydrogen was passed through a column with potassium hydroxide for drying, ensuring a dew point of approximately –60 °C. The hydrogen flow rate was 1 L/min.

The oxygen content in all powders was analyzed using the infrared absorption method on a “Leco TC-600” (USA) apparatus. The method involves placing a powder sample in a graphite crucible within the analyzer’s furnace, where it melts to form a carbon-saturated melt in a helium atmosphere. The carbon in the molten bath reacts with the sample’s oxygen to form carbon monoxide, which is then flushed out of the furnace by the helium stream. The oxygen content is determined by molecular absorption spectroscopy in the infrared region.

X-ray diffraction analysis was conducted using a “DRON-3M” diffractometer (Burevestnik, Russia) in CuK_α radiation ($\lambda = 1.54158$ Å). Diffraction patterns were recorded in continuous scanning mode over the 2θ angle range of 20 to 80° with a step size of 0.02°. Phase identification was performed using the “Crystallographica Search Match” software based on the Powder Diffraction File (PDF-2) database.

Specific surface area determination by the BET method was performed according to GOST 2405 on a “TriStar 3000” surface area analyzer (Micromeritics, USA). Scanning electron microscopy (SEM) was carried out on an ultra-high resolution field emission scanning electron microscope "Zeiss Ultra plus" based on "Ultra 55" (Carl Zeiss LLC, Germany).

Results and discussions

First series of experiments. WO_3 powder of grade "P" was sieved into three fractions, µm: 64–100, 40–50, and less than 25. These three powders were reduced in a tubular furnace IMETRON for 2 h in a hydrogen stream at temperatures of 650, 800 and 950 °C. A nickel boat containing 5 g of each powder, with a layer thickness of about 3 mm, was placed in a vacuum-tight quartz retort with a diameter of 6 cm and a length of 80 cm. The temperature gradient along the boat was not more than 5 °C. The retort scheme, placed in the furnace, is shown in Fig. 1. Nine reduced tungsten powders were obtained. Table 1 presents the reduction modes for WO_3 powder grade "P" and the characteristics of the obtained tungsten powders.

Experimental data (Table 1) show that, regardless of the particle size of WO_3, increasing the reduction temperature decreases the oxygen content and increases the average particle size of the tungsten powder.

Second series of experiments. This series was performed on unsieved powders. The reduction of three grades of WO_3 powder was conducted for 3 h in a hydrogen stream at 950 °C. Three reduced tungsten powders were obtained (Table 2).

When reduced from WO_3 grade "CP" at 950 °C for 3 h, the tungsten powder with the lowest oxygen content – 0.043 wt. % – was obtained.

The average particle size (d) of the powders was calculated using the formula $d = 6/(\rho S)$, where ρ is the density of tungsten (19.3 g/cm^3), and S is the specific surface area of the powder, m^2/g.

The X-ray diffraction (XRD) results for all powders indicate pure tungsten (Fig. 2). Fig. 3 shows an SEM image of tungsten powder reduced from grade "CP" tungsten oxide at 950 °C for 3 h. The particle shapes of all the powders are similar, regardless of the reduction conditions, with the main difference being particle size.

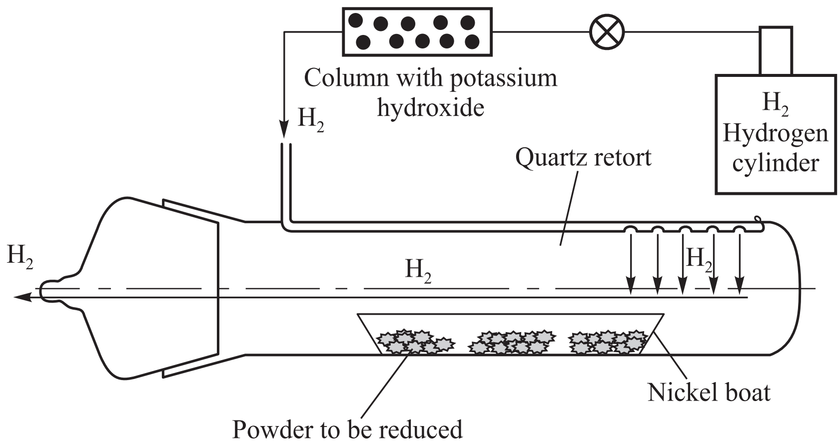

Fig. 1. Scheme of a retort for the reduction of powders

Рис. 1. Схема реторты для восстановления порошков

Table 1. **Reduction modes for WO_3 powder grade "P" and characteristics of tungsten powders**

Таблица 1. **Режимы восстановления порошка WO_3 марки Ч и характеристики порошков вольфрама**

Precursor particle size, µm	Reduction temperature, °C	Oxygen content, wt. %	Specific surface area, m^2/g	Average particle size, nm
<25	650	2.180	8.9	35
	800	0.390	4.5	69
	950	0.150	1.5	207
40–50	650	1.930	7.8	40
	800	0.270	3.6	86
	950	0.100	1.3	239
64–100	650	2.010	7.0	44
	800	0.230	3.3	94
	950	0.073	1.7	183

Table 2. **Characteristics of tungsten powders obtained at a reduction temperature of 950 °C, 3 h**

Таблица 2. **Характеристики порошков вольфрама, полученных при температуре восстановления 950 °C в течение 3 ч**

Tungsten oxide	Oxygen content, wt. %	Specific surface area, m^2/g	Average particle size, nm
P	0.091	1.5	207
CP	0.043	0.9	345
Tumelom	0.122	1.1	283

The results of all experiments are shown in Fig. 4. It can be seen that with an increase in the reduction temperature, there is a significant growth in the average particle size of the reduced tungsten powder, regardless of the precursor's dispersity. Simultaneously, the oxygen content decreases.

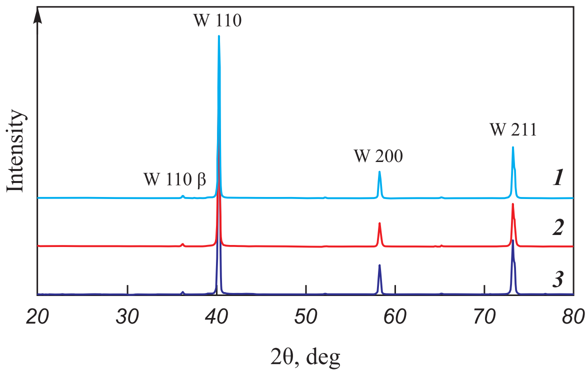

Fig. 2. X-ray patterns of tungsten powders
1 – Tumelom; *2* – P; *3* – CP

Рис. 2. Рентгенограммы порошков вольфрама
1 – Тумелом; *2* – Ч; *3* – ХЧ

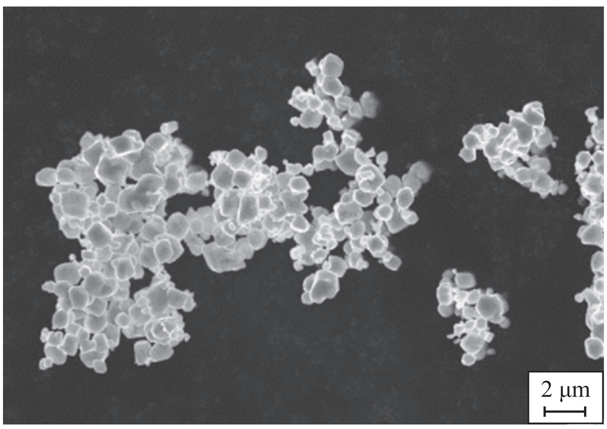

Fig. 3. SEM image of tungsten powder reduced from tungsten oxide of chemical grade "CP" at 950 °C for 3 h

Рис. 3. СЭМ-изображение порошка вольфрама, восстановленного из оксида вольфрама марки ХЧ при температуре 950 °C в течение 3 ч

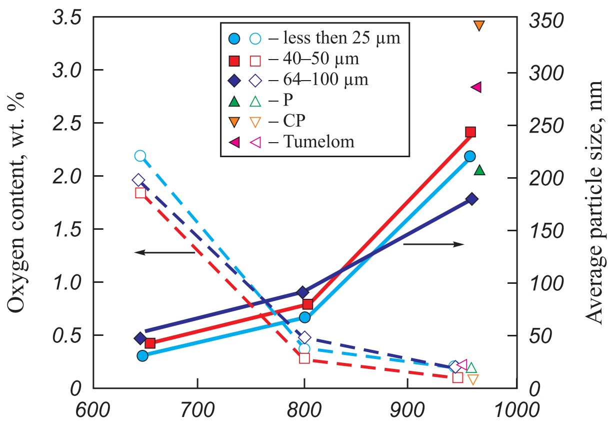

Fig. 4. Dependence of oxygen content and average particle size of tungsten powder on reduction temperature for different tungsten oxide powders

Рис. 4. Зависимость содержания кислорода и среднего размера частиц порошка вольфрама от температуры восстановления для разных порошков оксида вольфрама

Conclusion

Fine tungsten powders with low oxygen content were synthesized from tungsten trioxide using a chemical-metallurgical method. The minimum oxygen content in the powder was obtained by reducing tungsten oxide of grade "CP" at 950 °C for 3 h. The resulting tungsten powder had the lowest oxygen content of 0.043 wt.% and an average particle size of 345 nm.

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A. B. Ankudinov – prepared mixtures and initial samples, conducted experiments, and participated in the discussion of results.

E. V. Evstratov – prepared initial samples, participated in the discussion of results, and wrote the article.
M. I. Alymov – defined the objectives of the work, participated in the discussion of results, and co-authored the article.

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Е. В. Евстратов – исходные образцы, участие в обсуждении результатов, написание статьи.
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