Production of tungsten carbide powder by the reaction of tungsten with ethanol

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Abstract. The possibility of synthesizing tungsten carbide powders by carburizing mesoporous tungsten powders using ethanol as a carbon source is shown. WC carbide was synthesized at the temperature of 730-900 °C, using argon or helium as a carrier gas in the interaction of tungsten with the products of thermal decomposition of ethanol. Carbide has a hexagonal crystal structure. The specific surface area of carbide powders reaches 13 m²·g⁻¹. Their average crystallite size determined by the X-ray method is 17-25 nm.

1. Introduction

Tungsten carbide WC is not the hardest and most refractory of the transition metal carbides [1]. Its melting point at 2690 °C is significantly lower than the melting point of carbides such as HfC (3928 °C), NbC (3613 °C) and TaC (3985 °C). The hardness at room temperature is also lower than the hardness of nonstoichiometric carbides HfCₓ, NbCₓ, and TaCₓ [2, 3]. However, the hardness of WC carbide is quite stable. An increase in temperature from 25 °C to 1100 °C is accompanied by a threefold decrease in the WC hardness, while the hardness of other transition metal carbides in the same temperature range decreases more – by a factor of about five [4]. High physical characteristics of WC carbide and their stability under high-temperature heating led to the use of WC carbide as a basis for the production of wear-resistant hard alloys. Tungsten carbide is also used as a catalyst for processes such as electrooxidation of methanol [5] and ethanol [6], synthesis and decomposition of ammonia [7] and in other catalytic reactions [8-10].

The traditional industrial method for producing tungsten carbides involves carburization for a long time a metal powder of tungsten mixed with soot in the temperature range 1050-2100 °C in a vacuum or in a hydrogen atmosphere [11]. If the carburization is carried out in a vacuum, the carbon transfer is limited to very short distances, with the result that the formation of WC occurs only in direct contact with a solid carbon source. The hydrogen atmosphere promotes uniform distribution of carbon during carburization. In the presence of hydrogen, carbon can be transported in the form of hydrocarbons over a distance from several millimeters to centimeters [12]. However, the method is energy intensive and results in products with particle sizes in the tens of micrometers range. Such carbide is difficult to
transform into a dense material that has high performance under heavy loads and high temperatures. They also have lower efficiency as catalysts due to their large particle size and low surface area. Currently, many efforts have been made to synthesize nanocrystalline carbide powders. The developed methods can be classified into the following categories: sol-gel method [13], self-propagating high-temperature synthesis [14], plasma methods [15], mechanosynthesis [16], etc. [17]. However, these methods are not effective enough. To obtain highly dispersed powders of tungsten carbides with a high specific surface at low reaction temperatures, temperature-programmed reduction of oxide precursors with mixtures of hydrogen and combustible gases is most often used [18-20]. However, in order to obtain reproducible powder characteristics, many process parameters must be monitored and work with flammable and explosive gases. In addition, with this synthesis method, the resulting carbide may contain free carbon [18]. In [21], a safer method was proposed for producing tungsten carbide powders using the initial reagents in the form of WO₃ powder and methyl alcohol vapor as a reducing agent and a carbon source. It was found that at low and moderate temperatures, the final product WC is formed via intermediates W₁₈O₄₉, WO₂, partial metallic W and W₂C; while at high temperatures, WO₃ was first reduced to WO₂ with the intermediate phase W₁₈O₄₉, and then reduced to metallic tungsten. The morphology of the final products almost retains the same shape as that of the WO₃ starting materials. Thus, the smaller the particle size of the precursor, the finer the tungsten carbide powder can be obtained. In this regard, it was of interest to obtain finely dispersed tungsten carbide by carburizing with alcohol vapor, using a powder of metallic tungsten with a large specific surface as a precursor.

The aim of this work is to study the possibility of obtaining tungsten carbide powders with a developed specific surface using alcohol vapor as a carbon source.

2. Materials and Methods
Ethanol (C₂H₅OH) was used as a carbon source. It is a more affordable and less toxic alcohol than methanol. The influence of the conditions of interaction of the tungsten metal powder with the products of thermal decomposition of ethanol was investigated. Mesoporous W powders with specific surface area of 5.6-22.4 m²·g⁻¹, obtained by reduction of MgWO₄ by magnesium vapor, were used as a precursor [22]. Magnesium tungstate was synthesized by sintering WO₃ with Mg₅(CO₃)₄(OH)₂·(H₂O)₂ [23]. A schematic diagram of an experimental setup for carburizing metals is shown in Figure 1. It is a reactor 4, in which an allund or quartz boat 6 with metal powder is installed. Heating is carried out by a tube furnace 5, the temperature is controlled by a thermocouple 7, the hot junction of which is located at the location of the metal powder, and is maintained by means of a temperature regulator – thermodat 8. An inert gas (argon or helium) carrying ethanol vapors into the reaction zone is supplied from gas cylinder through pipeline 2. The carrier gas feed rate is regulated by a rotameter 1. A quartz tube 22 mm in diameter is used as a reactor. The working zone of the furnace is 70 mm. The carburizing process was carried out for 0.5-3 h at a temperature of 600-900 °C. The weight of the powder W loaded into the alundum boat was 0.3–0.5 g. The weights of the precursor and reaction products were measured at room temperature on a VMR-200 laboratory balance (error ± 10⁻⁴ g).
Figure 1. Experimental setup diagram: 1 – rotameter, 2 – ethanol pipeline, 3 – thermostat for ethanol, 4 – quartz tube-reactor, 5 – tubular furnace, 6 – boat for loading the precursor, 7 – thermocouple, 8 – thermodate, 9 – buffer tank, 10 – water seal.

The phase composition of the reaction products was determined on a SHIMADZU XRD-6000 diffractometer (CuKα radiation). The phases were identified using the PDF-2 ICPDS-ICCD 2002 diffractometric data base. The specific surface area was measured by the static adsorption BET method ($S_{\text{BET}}$) and the porosity parameters were measured by the BJH method on Micromeritics TriStar II 3020 device. The average crystallite size ($d$) was estimated by the X-ray method according to the Scherer formula:

$$d = \frac{K\lambda}{\beta \cos \theta}, \quad (1^*)$$

where the form factor is $K = 0.94$, the X-ray wavelength is $\lambda = 0.15406$ nm, $\beta$ is full width at half maximum (FWHM) of the diffraction peak, and $\theta$ is the Bragg angle. The average particle size of the powder ($d_{\text{BET}}$) was estimated from the specific surface area $S_{\text{BET}}$ on the assumption that the particles are spherical:

$$d_{\text{BET}} = \frac{6}{S_{\text{BET}} \rho}, \quad (2^*)$$

where $S_{\text{BET}}$ is the specific surface of the powder, and $\rho$ is the density of the carbide.

The powder was first heated in a flowing atmosphere of an inert gas (30-40 cm$^3$·min$^{-1}$) to the reaction temperature, and then a flow of argon or helium was directed into a flask with liquid ethanol. The flow rate of the inert gas during carburization was 40-80 cm$^3$·min$^{-1}$. The ethanol temperature with an error of ± 0.3 °С was maintained in the temperature range of 17-35 °С. In this case, the partial pressure of ethanol vapor in the gas mixture varied in the range 4.57–13.35 kPa. Gas-phase reactions in the pyrolysis of ethanol at high temperatures have been studied in detail in [24-25]. First, the dehydrogenation reaction occurs with the formation of acetaldehyde and hydrogen:

$$C_2H_5OH \rightarrow CH_3CHO + H_2, \Delta H^o = +285 \text{ kJ·mol}^{-1} \quad (1)$$

Then decarbonization of acetaldehyde takes place with the formation of methane and carbon monoxide:

$$CH_3CHO \rightarrow CH_4 + CO, \Delta H^o = -80 \text{ kJ·mol}^{-1} \quad (2)$$

Carbon for the synthesis of carbides can be obtained from gases formed during the thermal decomposition of ethanol. The reaction of its formation from carbon monoxide:

$$2CO \rightarrow C + CO_2; \Delta H^o = -172 \text{ kJ·mol}^{-1} \quad (3)$$

The reaction for the formation of carbon from methane:
\[
\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2; \Delta H^\circ = +75 \text{ kJ} \cdot \text{mol}^{-1} \quad (4)
\]

Reaction (4) is endothermic and occurs only at high temperatures. Thus, the direct sources of carbon involved in the synthesis of carbides will be carbon monoxide and methane (Figure 2).

![Figure 2. Scheme of thermal decomposition of ethanol](image)

3. Results and discussion

The phase composition and crystallite size of the products obtained by carburizing tungsten under various conditions are shown in Table 1. As can be seen from the data in the table, despite the change in the carburization regimes within wide limits, no carbide phase was found in the reaction products of the initial experiments. They were a mixture of tungsten oxide compounds of various compositions (WO₂, W₁₈O₄₉, H₀.₅₃WO₃, etc.). Despite the formation of oxides, the mass of the products decreases in comparison with the precursor mass. After a series experiments, metallic tungsten appears in the reaction products along with oxides. In this case, the mass of the reaction products increases in comparison with the mass of the precursor. Finally, after experiments 10 and 11 (Table 1), the reaction product was only tungsten carbide WC with a hexagonal structure (Figure 3). According to X-ray data, no phases other than WC were detected.

| No | Precursor | Production conditions | Characteristics of reaction products |
|----|-----------|----------------------|--------------------------------------|
|    |           | Carrier gas | T<sub>r</sub>, °C | T<sub>e</sub>, °C | V, cm<sup>3</sup>·min<sup>-1</sup> | t, ч | Δm·m<sub>0</sub>%, | Phase composition | d, nm |
| 1  |           | Ar         | 850            | 30          | 80       | 3      | -3.2  | 60% W₁₈O₄₉, 40% WO₂ | 57.8   |
| 2  |           | Ar         | 650            | 30          | 60       | 1.0    | -5.7  | 60% H₀.₅₃WO₃, 40% WO₂ | 21.9   |
| 3  |           | Ar         | 727            | 35          | 40       | 2.5    | -7.6  | 75% WO₂, 25% H₀.₅₃WO₃ | 56.5   |
| 4  |           | Ar         | 727            | 35          | 40       | 2.5    | -7.6  | 55% WO₃, 45% H₀.₃₃WO₃, 10% W₁₀O₂₉ | 54.9   |
| 5  |           | He         | 800            | 30          | 60       | 1.5    | -7.2  | 35% H₀.₅₃WO₃, 10% W₁₀O₂₉ | 55.4   |
| 6  |           | He         | 900            | 30          | 60       | 1.0    | -11.2 | 100% WO₂   | 60.4   |
| 7  |           | Ar         | 770            | 17          | 40       | 2.5    | +0.6  | 30% W, 70% WO₂ | 26.7   |
| 8  |           | Ar         | 730            | 17          | 40       | 2.5    | +1.5  | 85% W, 15% WO₂ | 39.6   |
| 9  |           | Ar         | 900            | 21          | 50       | 2.5    | +2.0  | 95% W, 5% WO₂ | 59.6   |

Table 1. Influence of tungsten carburization conditions on the characteristics of reaction products.
In our opinion, the change in the composition of the reaction products in the course of experiments on the carburization of tungsten, which ultimately led to the formation of carbide, is due to the following. The experiments were carried out sequentially without cleaning the reaction chamber. Apparently, during the decomposition of ethanol in the initial experiments, in parallel with the dehydrogenation reaction (1), the dehydration reaction actively proceeded with the formation of ethylene and water [26]:

$$\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}, \Delta H^o = + 8.4 \text{ kJ} \cdot \text{mol}^{-1}$$

(5)

Water vapors formed as a result of reaction (5) interact with tungsten. It is known that tungsten powder actively reacts with water vapor in the temperature range 600–1200 °C with the formation of WO$_2$ and other oxide compounds [11]. In addition to the compounds listed in Table 1, apparently, as a result of this interaction, a volatile compound WO$_2$(OH)$_2$ is formed during the reaction:

$$\text{W} + 4\text{H}_2\text{O} = \text{WO}_2(\text{OH})_2 + 3\text{H}_2, \Delta H^o = -117.3 \text{ kJ} \cdot \text{mol}^{-1}$$

(6)

It provides all vapor-phase transport processes at temperatures when the volatility of oxides can be neglected [11]. An indirect confirmation of the formation of WO$_2$(OH)$_2$ is a significant reduction in the weight of the obtained products, consisting of non-volatile oxide compounds of tungsten (Table 1). The experiments were carried out sequentially without cleaning the reaction chamber. In the course of experiments on metal carburization due to ethanol decomposition, carbon accumulated in the form of a film on the walls of the quartz tube-reactor 4 (figure 1). At the same time, it is known that during the catalytic pyrolysis of ethanol in the presence of amorphized carbon, its decomposition proceeds mainly according to the reactions (1)-(4) [25]. According to XRD data, the film formed on the walls of the reactor is partially amorphous graphite (Figure 4, halo in the angle range 20=10-40°). The calculated value of the crystallite size $d$ of the graphite film based on X-ray is 17.7±0.7 nm.

| Sample | $S_{BET}$ | $d$ (nm) | $T_r$ (°C) | $T_e$ (°C) | $V$ (l/min) | $t$ (h) | $\Delta m/m_0$ | WC (%) | W (%) | WO$_2$ (%) |
|--------|-----------|---------|-----------|-----------|-------------|--------|----------------|---------|-------|------------|
| 10     | 16.7      | 16.9    | 900       | 21        | 40          | 2.0    | +5.3           | 100% WC | 19.3  | 80.7       |
| 11     | 20.0      | 15.5    | 900       | 21        | 50          | 2.5    | +5.9           | 100% WC | 21.0  | 79.0       |
| 12     | 16.7      | 16.9    | 900       | 21        | 50          | 2.5    | -4.7           | 56% W, 44% WO$_2$ | 29.1  | 27.9       |

Note: $S_{BET}$ is the specific surface area, $d$ is the crystallite size, $T_r$ is the reaction temperature, $T_e$ is the ethanol temperature, $V$ is the gas flow rate, $t$ is the reaction time, $\Delta m/m_0$ is the mass change as a result of the reaction.
It was assumed that the resulting film of amorphized graphite provides the catalytic decomposition of ethyl alcohol mainly by reactions (1)-(4). To test this assumption, the quartz tube was largely refined from the graphite film. The refinement was carried out by burning graphite while supplying air with a compressor inside a quartz tube-reactor heated to a high temperature. The experiments carried out after partial refining of the reactor from amorphized graphite showed that no carbide is formed under the same conditions (Table 1, experiment 12).

Depending on obtaining conditions, samples of WC carbide powder were obtained, the specific surface area of which was in the range of 4-13 m² g⁻¹. According to the ratio (2*), such a specific surface area corresponds to the average particle size of 35-109 nm. The average crystallite size of WC powders calculated by the Scherer formula is much smaller and is in the range of 17-25 nm. The study of the porous structure showed that the adsorption curves of tungsten carbide powders correspond to type IV according to IUPAC. They are distinguished by the presence of a hysteresis loop and are characteristic of materials with a mesoporous structure (Figure 5).

Thus, the possibility of using ethanol to obtain WC carbide powder with a hexagonal crystal structure and developed surface has shown.

4. Conclusion
When tungsten interacts with the products of thermal decomposition of ethanol at a temperature of 730-900 °C using argon or helium as a carrier gas, WC carbides with a hexagonal crystal structure are synthesized. Their specific surface area reaches 13 m² g⁻¹. The average crystallite size determined by the X-ray method is 17-25 nm.
Compared with the traditional method of carbide synthesis by solid-phase reactions of tungsten powders with carbon, the process temperature is 500-700 °C lower. In relation to the methods used for obtaining these materials by temperature-programmed reduction of oxide precursors with mixtures of combustible gases (methane, propane, etc.) with hydrogen, the method is simpler and safer.

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