Preparation of W-Cr powder via the magnesiothermic reduction of trirutile Cr₂WO₆

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Abstract. The process of producing W-Cr powders by the reduction of trirutile Cr₂WO₆ with magnesium vapor in the temperature range 700–850 °C at residual pressure of 5-20 kPa was studied. W-Cr powders with a specific surface area at the level of 43-47 m²·g⁻¹ were obtained. The resulting W-Cr powders are characterized by a mesoporous structure.

1. Introduction
The use of tungsten as a pure metal is limited by its oxidation at elevated temperatures [1]. A possible way to suppress oxidation is its fusion with chromium, which is predominantly oxidized in the alloy and forms continuous protective layers of Cr₂O₃ oxide [2]. This is due to the fact that the W-Cr alloy is an isomorphic system, and the Gibbs free energy of the formation of Cr₂O₃ is more negative than the formation energy of WO₃ [3]. Since the interdiffusion in the W-Cr system is low even at high temperatures [4], it is difficult to prepare dense W-Cr alloys by powder sintering. During sintering, the addition of auxiliary activator elements to the charge is usually required. Palladium is one of the effective activators [5]. It activates diffusion in the W-Cr system by forming a liquid Cr-Pd phase during sintering. However, the presence of palladium limits the high-temperature capabilities of the alloy due to a decrease in the solidus temperature. In addition, palladium is a rare and expensive metal. Along with palladium, other elements have been investigated as activators. In particular, silicon [6], titanium [7] and yttrium [8] were used to create self-passivating alloys based on W-Cr, suitable for operation as a material for thermonuclear reactors. The disadvantage of silicon is its ability to form brittle intermetallics, which negatively affect the machinability of alloys. The presence of titanium in the alloy promotes the accumulation and retention of deuterium in the alloy, which is also unacceptable. Another approach to improving the sintering ability of powders of the W-Cr system is high-energy mechanical grinding, which can reduce the particle size to nanodispersed [9]. Sintering of nanosized powders occurs at significantly lower temperatures compared to microcrystalline powders. The disadvantages of the mechanical grinding method are the high energy consumption and the contamination of the powder by the grinding medium. It is of interest to study the possibility of obtaining nanosized powders of a W-Cr mixture with a larger specific surface by other methods.

As was previously reported the possibility of obtaining powders of metals of the chromium subgroup (W, Mo or Cr) with a high specific surface by metallothermic reduction of their double oxides with magnesium or calcium vapors was shown [10-12]. In particular, tungsten powders with a surface of 41 m²·g⁻¹ were obtained by reduction of tungstate MgWO₄ with magnesium vapor [12]. This compound
has a monoclinic structure with unit cell parameters $a=4.6723\ \text{Å}$, $b=5.7731\ \text{Å}$, $c=4.8519\ \text{Å}$, $\alpha=\gamma=90^\circ$, $\beta=89.0652^\circ$, and $V=130.8556\ \text{Å}^3$ [13]. It was assumed that if we choose a precursor with a similar structure in which magnesium is replaced by chromium, then, upon its reduction, we can expect to obtain a mixture of W-Cr powders also with a large specific surface area. As such a precursor, we chose the Cr$_2$WO$_6$ compound with a trirutile structure. This compound has unit cell parameters $a=4.666\ \text{Å}$, $b=4.666\ \text{Å}$, $c=9.087\ \text{Å}$, $\alpha=\beta=\gamma=90^\circ$, and $V=197.875\ \text{Å}^3$ [14]. For this structure, the angles $\alpha$ and $\gamma$ are the same as for MgWO$_4$, and the parameters $a$, $b$ and the angle $\beta$ differ insignificantly. The unit cell volume of Cr$_2$WO$_6$ is 1.5 times larger due to the $c$ cell parameter.

The aim of this work is to study the reduction of the Cr$_2$WO$_6$ compound by magnesium vapor to obtain a mixture of W-Cr powders with a developed specific surface area.

2. Experimental
The starting components for the synthesis of Cr$_2$WO$_6$ were Cr$_2$O$_3$ obtained by calcining in air (NH$_4$)$_2$Cr$_2$O$_7$ (analytical grade), and WO$_3$ (pure). It should be noted that the preparation of complex oxides with two or more metal ions includes cycles of fine grinding of the initial powders of simple oxides and sintering at high temperatures for a long time. The long sintering time is a consequence of the low diffusion rate in the solid state for most ions in oxide media. This also manifested itself during the synthesis of Cr$_2$WO$_6$. The charge was prepared by mixing the amount of simple oxides corresponding to the stoichiometry in a ceramic ball mill for 6 hours. The resulting mixture was sintered in a slightly compacted state at 800 °C for 6 hours. After this sintering, a mixture of compounds containing 85% WO$_3$ and 15% Cr$_2$O$_3$ was obtained. For the synthesis of Cr$_2$WO$_6$, re-sintering was carried out at a temperature of 1000 °C. For comparison, a mixture of Cr$_2$O$_3$ and WO$_3$ powders was also subjected to reduction. The mass ratio of chromium to tungsten in the mixture was the same as in this compound. The equipment is similar to those used earlier [12]. The process was carried out at a temperature of 700–850 °C and a residual argon pressure of 5–20 kPa. The reduction products were treated with a 30% solution of nitric acid (reagent grade) to remove magnesium oxide. The process was carried out in an atmosphere of magnesium and argon (analytical grade) vapors. A container with magnesium (pure) was placed on the bottom of the reaction beaker. Weighed portions of the precursor were loaded into metal crucibles, which were installed over a container with magnesium. A screen was placed above the crucibles, the distance from which to the precursor surface was about 30 mm. The reaction vessel was closed with a lid, in the center of which there was a hole for a thermocouple sheath. The assembly was placed in a stainless steel retort, which was sealed, evacuated, filled with argon, and heated to the required temperature with the lid of the reaction beaker closed to avoid loss of magnesium. The resulting powder was washed with distilled water until neutral and dried in air at 80 °C. X-ray phase analysis was performed on a Shimadzu XRD-6000 X-ray diffractometer (Cu K$_\alpha$-radiation). The size of the coherent scattering region was determined by Sherrer method in reflections at small scattering angles (factor of the form $K = 0.9$). 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. The SEM analyses were carried out in scanning electron microscope (Model no: LEO 420).

3. Results and discussion
The reduction of compounds proceeds according to reactions (1) - (3) and in the selected temperature range is accompanied by a significant decrease in the Gibbs energy (table 1). The reactions of magnesium reduction of the selected chromium and tungsten compounds are exothermic and proceed with the release of a large amount of heat. For example, the adiabatic temperature by reactions (1) and (2) reached 2708°C [15], and 3420 °C [16], respectively which exceeds the boiling point of chromium is 2672 °C. Reduction with magnesium vapor allows us to regulate the rate of supply of the reducing agent in the reaction zone and thereby limit the reaction temperature, as well as control its course throughout the reduction process.

The view of crucibles with a reaction mass after reduction of a mixture of Cr$_2$O$_3$-WO$_3$ powders and Cr$_2$WO$_6$ is shown in Figure 1. After the reduction of a mixture of Cr$_2$O$_3$-WO$_3$ powders under all
investigated modes, on the inner side surface of the crucible above the loading level, on the surface of the reaction mixture and on the side of the screen facing the precursor, white deposits with a thickness of about 1 mm are clearly manifested (Figure 1 (a, b)).

Table 1. Thermodynamic characteristics of the reduction reactions of chromium and tungsten oxide compounds by magnesium vapor.

| Reaction                                      | \(-\Delta H_r\), kJ mol\(^{-1}\) | \(-\Delta S_r\), J (mol K\(^{-1}\)) | \(\Delta Q_{298}\), kJ kg\(^{-1}\) | \(-\Delta G_{973}\), kJ mol\(^{-1}\) | \(-\Delta G_{1123}\), kJ mol\(^{-1}\) |
|-----------------------------------------------|-----------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------|
| Cr\(_2\)O\(_3\) + 3Mg = 2Cr + 3MgO            | 1049                              | 445                                  | 4683                                 | 615                                   | 571                                   |
| WO\(_3\) + 3Mg = W + 3MgO                     | 1346                              | 440                                  | 4428                                 | 918                                   | 874                                   |
| Cr\(_2\)WO\(_6\) + 6Mg = 2Cr + W + 6MgO      | 2395                              | 885                                  | 4536                                 | 1533                                  | 1445                                  |

Figure 1. (a, c) Crucibles with reaction products and (b, d) corresponding screens after reduction; precursors: (a) Cr\(_2\)O\(_3\)-WO\(_3\) mixture, (c) trirutil Cr\(_2\)WO\(_6\); temperature in the reactor 750 °C, residual pressure 10 kPa.

The amount of deposits of white matter on the surface of the reaction mass and the screen increased with an increase in the residual pressure in the reactor. After the reduction of Cr\(_2\)WO\(_6\) for all studied modes, a very thin (fractions of microns) coating of white matter was also observed on the surface of the reaction mixture and on the side of the screen facing the precursor (Figure 1 (c, d)). The dense deposits of white matter in the first case (Figure 2 (a)), and a thin white coating in the second case were pure magnesium oxide (Figure 2 (b)).

Since, after the reduction of the Cr\(_2\)O\(_3\)-WO\(_3\) mixture (Figure 2 (c), X-ray diffraction pattern 1), most of the magnesium oxide was in the form of deposits outside the reaction zone, and its content in the bulk of the product in the crucible was insignificant, in this case it can be assumed that the reduction process proceeds to a large extent as an electronically mediated reactions (EMR) – by means of electron transfer [17]. From the point of view of charge transfer, in this case, the starting reagents at high temperatures are an electrically conductive medium capable of providing electron transfer. WO\(_3\) oxide is an n-type semiconductor [18]. Thus, there is a closed circuit that includes reactants and metal parts of the equipment, which ensures the transfer of electrons. The atoms of the reducing agent in a vapor state, colliding with the walls of the crucibles, its lid and the surface of the material being reduced, give up electrons, which enter the reaction zone along the chain and reduce the metal ion. To maintain electroneutrality, the oxygen ion must move to the metal ion of the reducing agent. Under certain conditions, which are provided by the high thermal effect of the reduction reactions (1) and (2), the medium of an inert argon gas becomes the carrier of the oxygen ion. This is how the experimentally observed deposits of reductant oxide layers are formed outside the reaction zone. After reduction of Cr\(_2\)WO\(_6\), (Figure 2 (c), X-ray diffraction pattern 2) the product in crucibles was a homogeneous mixture that practically corresponded to the stoichiometric ratio of reaction (3). Thus, the reduction of Cr\(_2\)WO\(_6\) proceeds mainly with direct physical contact between it and magnesium, as evidenced by a very thin
layer of magnesium oxide on the surface of the reaction mixture and on the screen (Figure 1 (c, d)). The Cr₂WO₆ compound is also a semiconductor, but, unlike WO₃, it is a p-type semiconductor [19].

According to the XRD data, the washed powder in both cases contained a mechanical mixture of chromium and tungsten (Figure 2 (d)). Formation of Cr-W alloy is difficult because mutual diffusion and mobility of atoms in the system are low even at higher temperatures [4]. The specific surface area of powders of a mixture of chromium with tungsten obtained by reduction of Cr₂WO₆ was 43-47 m² g⁻¹ which is 8-10 times higher than the surface area of powders obtained by reduction of a mixture of Cr₂O₃-WO₃ under similar conditions (Figure 3). With the reduction of Cr₂WO₆ with an increase in the residual pressure in the reactor, the specific surface area of metal powders increases (Figure 3 (a), curve 2). This dependence is due to the fact that an increase in the residual pressure reduces the evaporation rate of magnesium and, thereby, reduces the amount of its vapors. Therefore, an increase in pressure leads to a decrease in the temperature of the reaction mixture. The magnesium oxide formed by the reduction remains in the reaction zone. In addition, during the reduction of Cr₂WO₆, a smaller dependence of the powder surface area on the process temperature is observed (Figure 3 (b), curve 2). This is due to the fact that the interlayers of MgO formed between the particles during reduction impede the coagulation of metal particles. When reducing the Cr₂O₃-WO₃ mixture with an increase in the residual pressure in the reactor, the specific surface area of metal powders decreases (Figure 3 (a), curve 1). This dependence is due to a decrease in the number of interlayers of magnesium oxide in the structure of reduced metal particles due to the occurrence of reduction by the type of EMR. This promotes coagulation of the primary metal particles and is the reason for the decrease in the specific surface area of the powders. SEM image of W-Cr powder obtained by reduction of Cr₂WO₆ oxides is shown in Figure 4 (a).

The average crystallite size determined by Sherrer method for the specific surface area of powders 43-47 m² g⁻¹ corresponds to the size 15-20 nm. However, as can be estimated from the SEM images of the W-Cr powder shown in Figure 4 (a), the powder is represented by rather large aggregated particles with an average size of more than 200 nm. According to the model of the formation of powder particles during the reduction of oxide compounds of refractory metals by magnesium vapor, the high specific surface area of the powder is a consequence of its nanoporous structure [10]. In this case, the growth of
the specific surface area occurs mainly due to the increase in the number of nanopores of a smaller diameter. For the obtained powders of the W-Cr mixture, this is confirmed by the results of porosity measurements (Figure 4 (b)).

![Figure 3](image1.png)

Figure 3. Specific surface area of W-Cr powders as a function of (a) pressure in the reactor at \( t = 740^\circ C \) and as a function of (b) temperature at \( p = 5 \) kPa; precursors: (1) \( \text{Cr}_2\text{O}_3-\text{WO}_3 \) mixture, (2) \( \text{Cr}_2\text{WO}_6 \).

![Figure 4](image2.png)

Figure 4. (a) SEM image of W-Cr powder, (b) dependence of the total pore area of powder on its average diameter; precursors: (b, curve 1) \( \text{Cr}_2\text{O}_3-\text{WO}_3 \) mixture, (b, curve 2) \( \text{Cr}_2\text{WO}_6 \); specific surface area of W-Cr powders: (b, curve 1) 5 m\(^2\)g\(^{-1}\), (a and b, curve 2) 47 m\(^2\)g\(^{-1}\).

The total surface area of the powder is practically equal to the total surface area of the pores. The form of adsorption-desorption isotherms of W-Cr mixture powders obtained from a mixture of \( \text{Cr}_2\text{O}_3-\text{WO}_3 \) powders and \( \text{Cr}_2\text{WO}_6 \) corresponds to type IV according to the IUPAC classification, which is characteristic of mesoporous substances. The amount of adsorbate adsorbed at the same relative pressures by W-Cr powder obtained by reduction of \( \text{Cr}_2\text{WO}_6 \) is 5-10 times greater than the powder obtained using \( \text{Cr}_2\text{O}_3-\text{WO}_3 \) mixture as a precursor (Figure 5).

Thus, the possibility of using \( \text{Cr}_2\text{WO}_6 \) with a trirutile structure to obtain W-Cr powders with a developed surface by magnesium thermal reduction has shown.
4. Conclusion
The reduction of Cr$_2$O$_3$-WO$_3$ mixture and Cr$_2$WO$_6$ compound by magnesium vapor at residual pressure of 5-20 kPa in the temperature range of 700–800 °C was studied.

It was found that when reducing Cr$_2$O$_3$-WO$_3$ mixture there is a spatial separation of the metal and oxide phases with the deposition of magnesium oxide outside the reaction zone, due to the flow of electronically mediated reaction.

Powders of W-Cr mixture with a surface of 43-47 m$^2$·g$^{-1}$ were obtained by reduction of Cr$_2$WO$_6$. 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.

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Figure 5. Curves of nitrogen adsorption-desorption by W-Cr powders with a specific surface area: (a) 5 m$^2$·g$^{-1}$, (b) 47 m$^2$·g$^{-1}$; precursors: (a) Cr$_2$O$_3$-WO$_3$ mixture, (b) Cr$_2$WO$_6$. 
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