Magnesium thermal nano-sized powders of the chromium subgroup metals

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Abstract. A method for magnesium vapor reduction of the double oxides of chromium subgroup metals at low static pressure and dynamical vacuum was used. The study results of the production and investigation of tungsten, molybdenum, chromium, W-Cr mix and Mo-W alloy powders are presented. The specific surface area of the resulting powders was in the range from 14 to 41 m²·g⁻¹. The average crystalline grain size estimated from the value of the range of coherent X-ray scattering was 8-40 nm.

1. Introduction
One of the methods for producing refractory metals is metallothermal reduction of oxide compounds. Due to the high melting point, the product of the reduction of oxide compounds is usually a metal powder. A significant increase in the specific surface area of the powder can be achieved by the reduction of double metal oxides with magnesium vapor [1, 2]. This is due to the fact that the reduction occurs in the particle volume and the reduction product is an alternation of MgO interlayers and metal particles [3]. The presence of MgO or CaO oxide in the precursor increases the number of interlayers. The number of pores increases and, accordingly, the specific surface of the powders increases. At the same time, when oxide compounds of metals of the chromium subgroup were reduced by magnesium vapor, the separation of reaction products with the formation of dense layers of the MgO reaction product outside the reaction zone was found [4, 5]. Moreover, the mass of MgO, located outside the reaction zone increases with increasing residual pressure in the reactor. Removal of MgO from the particle structure leads to decreasing in the porosity of the metal powder and, accordingly, decreasing in its specific surface area [4]. A high temperature of the process also leads to decreasing in the surface of the powders due to coagulation of particles of the reduced metal.

The aim of this work is to study the possibility of obtaining nanosized powders of metals of the chromium subgroup by reduction of their double oxide compounds with magnesium vapors at reduced temperature and pressure.

2. Experimental
Powders of MgMoO₄, CaMoO₄, MgWO₄, MgCr₂O₄, CaW₀.₃Cr₀.₆₅O₄, MgW₀.₃Mo₀.₇O₄ and CaW₀.₃Mo₀.₇O₄, which were synthesized according to the procedures described in [2, 5, 6], were used as precursors. The process was carried out under an atmosphere of magnesium vapor and an inert gas.
("high pure" argon) using an experimental setup schematized in figure 1. A vessel (1) containing magnesium (M95) was mounted on the bottom of a reaction beaker (4). Weighed amounts (5 g) of precursors were loaded into metallic containers (3), which were placed over the magnesium-containing vessel. A shield (5) was placed over the containers. The separation between the surface of the reactants and the shield was 27–30 mm. The reaction beaker was covered with a lid (7), which had an orifice in its center for the thermocouple sheath (10). The beaker was mounted in a stainless steel retort, which was hermetically sealed, pumped down to a pressure of 7–10 Pa, filled with argon, heated to a required temperature, and then again pumped down to a residual pressure not exceeding 5 kPa, or the process was carried out under continuous evacuation of the reactor (residual pressure 150-250 Pa). The reduction process was run in the temperature range 600–750°C for 3–5 h.

The reduction products were treated with a hydrochloric or nitric acid (reagent grade) solution to remove the MgO and CaO. The powder was washed with distilled water until neutral pH was reached and then dried in air at a temperature of 80°C. The phase composition of the powders was determined by X-ray diffraction on a Shimadzu XRD-6000 X-ray diffractometer (CuKα radiation). The specific surface area and porosity of the powders were determined by BET and BJH measurements on a TriStar II 3020 V1.03 analyzer.

3. Results and discussion
For the precursors listed above, the Gibbs energy ΔG of magnesium reduction reactions was calculated. In the selected temperature range, the calculated ΔG values are in the range -(530–900) kJ·mol⁻¹, which confirms the high probability of reduction of the studied binary oxide compounds.

Figure 2 shows crucibles with a reaction product after passing through the corresponding reactions. It is seen that during the process under the dynamic vacuum, the separation of products does not occur. With increasing pressure, the deposition of a white MgO layer begins on the surface of the reaction product and the crucible walls above the loading level. Depending on the composition of the precursor, the separation of the oxide and metal phases begins in the pressure range of 1-5 kPa. Such separation can occur even at temperatures below the melting point of magnesium (figure 1c). The spatial separation of the metal and oxide phases is apparently due to the occurrence of the reduction reaction by the mechanism of the electronically mediated reaction without direct physical contact between the reacting substances [7].
Figure 2. Crucibles with a reaction product after reduction. Precursors: MgWO$_4$ (crucibles 1a, 1b, 1c), MgW$_{0.3}$Mo$_{0.7}$O$_4$ (left crucibles 1d, 1e), CaW$_{0.3}$Mo$_{0.7}$O$_4$ (right crucibles 1d, 1e), MgMoO$_4$ (left crucibles 2a, 2b, 2c), CaMoO$_4$ (right crucibles 2a, 2b, 2c), MgCr$_2$O$_4$ (left crucibles 2d, 2e), CaW$_{0.35}$Cr$_{0.65}$O$_4$ (right crucibles 2d, 2e); temperature, °C: 1a – 600, 1c, 2a – 630, 1b, 1d, 2b, 2d – 700, 1e, 2c, 2e – 750; residual pressure, kPa: 1a – 0.15, 2a – 0.2, 1b – 0.5, 2b, 2d – 1, 1c, 2c, 2e – 5.

The influence of the reduction conditions and the composition of the precursor on the characteristics of the powders are presented in the table. From the data of the table it can be seen that carrying out the process under these conditions allows completely reducing the selected compounds.

Table 1. The dependence of the characteristics of metal powders on the conditions for the reduction of oxide compounds.

| Precursor          | Reduction conditions | Product characteristics (PC) and powder properties after leaching (PP) |
|--------------------|----------------------|---------------------------------------------------------------------|
|                    | T, °C | P, kPa | t, ч | matter | XRD | FWHM (110), deg. | S$_{BET}$, m$^2$·g$^{-1}$ | d$_{CSR}$, nm |
| MgMoO$_4$          | 640   | 0.5    | 5    | PC     | Mo, MgO | 0.856 | - | - |
|                    | 720   | 3      | 4    | PP     | Mo     | 0.812 | 24.8 | 24 |
| CaMoO$_4$          | 630   | 0.15   | 4    | PC     | Mo, MgO, CaO | 0.421 | - | - |
|                    | 700   | 1      | 4    | PP     | Mo     | 0.315 | 14.7 | 40 |
| MgWO$_4$           | 640   | 0.2    | 5    | PC     | W, MgO, | 0.892 | - | - |
|                    | 730   | 5      | 3    | PP     | W     | 0.591 | 25.2 | 23 |
| MgW$_{0.3}$Mo$_{0.7}$O$_4$ | 750   | 5      | 5    | PC     | Mo-W alloy, MgO, | 0.491 | - | - |
|                    | PP     |     |     | PP     | Mo-W alloy, | 0.421 | - | - |
| CaW$_{0.3}$Mo$_{0.7}$O$_4$ | 750   | 5      | 5    | PC     | Mgo, CaO | 0.436 | - | - |
|                    | PP     |     |     | PP     | Mo-W alloy, | 0.331 | - | - |
| MgCr$_2$O$_4$      | 700   | 1      | 4    | PC     | Cr, MgO | 0.472 | - | - |
|                    | PP     |     |     | PP     | Cr | 0.391 | 16.3 | 27 |
| CaW$_{0.35}$Cr$_{0.65}$O$_4$ | 750   | 5      | 5    | PC     | Cr, W, MgO | - | - | - |
|                    | PP     |     |     | PP     | Cr, W | - | 33.0 | - |

Note: XRD is an X-ray phase analysis, FWHM (110) is the full line width at half maximum, S$_{BET}$ is the specific surface of the powder, d$_{CSR}$ is the average crystallite size calculated from the values of coherent
scattering regions.

As a result, powders of tungsten, molybdenum, chromium, a mixture of tungsten with chromium and Mo-W alloy with a specific surface area of 14-41 m²·g⁻¹ were obtained, which significantly exceeds that one for powders obtained from the same precursors at higher pressures and temperatures [2, 4]. The values of the total width of diffraction lines at half height (FWHM (110)) after washing the powders decrease. Apparently, this is due to the removal of fine metal particles as a result of washing. The adsorption curves of the obtained powders of all metals correspond to type IV according to the IUPAC classification (figure 3).

![Figure 3. Nitrogen adsorption-desorption isotherms for (a) Mo, (b) Cr (c) W and (d) W-Mo alloy powders. Precursors: (a) MgMoO₄, (b) MgCr₂O₄, (c) MgWO₄, (d) MgW₀.₃M₀.₇O₄; T = 730 °C, t = 4 h.]()

The specific surface area of the obtained powders is almost completely determined by the pore area, and the specific surface area increases primarily on account of an increase in the amount of small nanopores (figure 4). The larger specific surface area of the powders prepared by reducing MgW₀.₃M₀.₇O₄ in comparison with CaW₀.₃M₀.₇O₄ seems to be due to the removal of a smaller amount of MgO from the reaction zone (figure 2). The removal of a larger amount of MgO from the structure of the reduced particles of the oxide compound leads to a decrease in the porosity of the powder and, accordingly, to a decrease in its specific surface area. This effect is responsible as well for the observed decrease in the specific surface area of the powders with increasing residual pressure in the reactor.

![Figure 4. Total pore area as a function of average pore diameter for the Mo-W alloy powders. Precursors: (1) CaW₀.₃M₀.₇O₄, (2) MgW₀.₃M₀.₇O₄; temperature, 750°C; pressure, 5 kPa; time, 5 h; specific surface area of the Mo-W alloy powders: (1) 16.3, (2) 20.3 m²·g⁻¹.]()}
Thus, the present results demonstrate the feasibility of obtaining nanosized powders of metals of the chromium subgroup with a large specific surface area by reduction of their double oxide compounds with magnesium vapors at reduced temperature and pressure. Note that the specific surface area and nanopore structure of the powders can be controlled by properly selecting the starting oxide compound and reduction conditions.

4. Conclusion
The reduction by magnesium vapor of the oxide compounds of metals of the chromium subgroup under dynamic vacuum and low static rarefaction (0.15-5 kPa) in the temperature range of 600–750 °C was studied.

The lower range of residual argon pressures of 1-5 kPa was established, at which the separation of the metal and oxide phases in the reaction products begins with the formation of dense MgO layers outside the reaction zone. It is apparently due to the reaction proceeding by the electron-mediated reaction mechanism without direct physical contact between reactants.

Powders of W, Mo, Cr, a mixture of W, Cr and a Mo-W alloy with a surface of 15-41 m²·g⁻¹ were obtained. The crystallite size estimated by the X-ray method is 8-40 nm.

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
This study was partially supported by the RFBR grant, the project 18-03-00248.

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