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# Investigation of the preparation of W-Cr system powders from oxide compounds by magnesium vapors reduction

V N Kolosov, M N Miroshnichenko and T Yu Prokhorova

Tananaev Institute of Chemistry - Subdivision of the Federal Research Centre Kola Science Centre of the Russian Academy of Sciences, 184209, Apatity, Murmansk region. Russia

E-mail: v.kolosov@ksc.ru

Abstract. The process of producing W-Cr powders by the reduction of the oxide compounds mixture Cr<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub> and CaCrO<sub>4</sub>-CaWO<sub>4</sub> with magnesium vapor in the temperature range 700-800 °C at rarefaction of 5-15 kPa was studied. W-Cr powders with a specific surface area at the level of 34 m<sup>2</sup>·g<sup>-1</sup> were obtained during the reduction of mixture of CaCrO<sub>4</sub>-CaWO<sub>4</sub> compounds. The resulting W-Cr powders are characterized by a mesoporous structure.

# 1. Introduction

The use of tungsten as a pure metal in air at moderate temperatures is largely limited by its oxidation [1]. Two oxide layers are formed in this case. The outer layer is a porous, powdery yellow tungsten oxide, and the inner layer, which is thinner, is a dark blue, tight-fitting oxide. The inner oxide continuously transforms into the outer oxide. One of the effective ways to suppress the oxidation of tungsten is doping it with chromium, which is predominantly oxidized and forms layer of oxide  $Cr_2O_3$ to protect W from further oxidation [2]. The use of chromium as an anticorrosive element is due to the fact that the W-Cr alloy is an isomorphic system, and the Gibbs free energy of the formation of  $Cr_2O_3$ is more negative than the energy of formation of WO3 [3]. Due to the high melting point, the consolidation of W-Cr alloys requires a high temperature and a long time, leading to significant grain growth and deterioration in mechanical properties. In order to reduce the sintering temperature, activator elements such as palladium [4, 5] or silicon [6, 7] are used. However, the presence of palladium in the alloy limits its high-temperature capabilities due to a decrease in the solidus temperature of the alloy, and silicon leads to the formation of brittle intermetallic compounds and, thus, negatively affects the further processing of the material. An alternative to adding activators during sintering is the use of nanosized powders with a high specific surface area. Such powders provide a large driving force during sintering due to the presence of excess surface energy and lead to dense compacts at lower temperatures [8]. Earlier it was shown that a promising method for obtaining powders with a high specific surface area of the W-Mo system in the form of a solid solution of these metals is the reduction of double oxide compounds with magnesium vapor [9, 10]. For this, presynthesized double oxides  $MgMo_xW_{1-x}O_4$  and  $CaMo_xW_{1-x}O_4$  were used. When they are restored, the temperature of alloy formation decreases due to the denser packing of the system components and, thereby, the diffusion path of W and Mo atoms decreases during the formation of a solid solution during the reduction.



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The aim of this work is to study the possibility of obtaining powders of the W-Cr system with a highly developed surface by reduction of complex oxides of these metals with magnesium vapor.

### 2. Experimental

As a possible precursor the double oxide compound  $CaW_xCr_{1-x}O_4$  was chosen by analogy with  $CaMo_xW_{1-x}O_4$  [9]. For its synthesis,  $Cr_2O_3$  ("pure"), obtained by calcining  $(NH_4)_2Cr_2O_7$  ("pure"), and  $WO_3$  ("pure") were used as starting components. Water was added to the mixture (solid: water ratio = 1: 6) and stirred with a stirrer for 3 hours. The mixture was dried at 100 °C and sintered at 620 °C for 6 hours, then ground and re-sintered at 1000 °C. However, synthesis under these conditions did not lead to the formation of  $CaW_xCr_{1-x}O_4$  compound. The resulting product usually consisted of a mixture of  $CaCrO_4$  and  $CaWO_4$  compounds. For the experiments, a mixture of these compounds was chosen in the ratio of 65% wt.  $CaCrO_4$  and 35% wt.  $CaWO_4$ . Figure 1 shows XRD pattern of the mixture of these compounds.



**Figure 1.** XRD patterns of the synthesized CaCrO<sub>4</sub>-CaWO<sub>4</sub> mixture.

In order to estimate the effect of refractory oxide CaO, which is a part of binary compounds, on the characteristics of powders of the W-Cr system, a mixture of Cr<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub> oxides was used as a reference precursor. The weight ratio of chromium to tungsten was the same as in the mixture of double oxides. The equipment for producing and studying powders are similar to those used earlier [9]. Container with magnesium (M95) was installed on the bottom of the reaction vessel. A portion of precursor weighing 5 g was loaded into steel crucibles, which were installed above the container with magnesium. The vessel was placed in a stainless steel retort, which was sealed, evacuated to a pressure of 5-10 Pa, filled with argon (reagent grade), heated to the required temperature, and again evacuated to a rarefaction of 5-15 kPa. The reduction was carried out in the temperature range of 700-850 °C for 4-6 h. The reduction products were treated with a 30% nitric acid solution (reagent grade) to remove magnesium and calcium oxides. The powder of the reduced metal was washed with distilled water until neutral. 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 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 of the magnesium reduction reaction of WO<sub>3</sub> is 3400 °C which exceeds the boiling point of chromium [11]. 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 initial substances, with the exception of magnesium, and the products of reactions in the investigated temperature range 700-850 °C are characterized by low vapor pressure, not exceeding

 $10^{-17}$ - $10^{-14}$  Pa [12-14]. Hence, it should follow that the resulting reaction mass will be homogeneous and located at the place of loading the precursor. However, in practice, in a number of experiments this was not the case. The view of the crucibles after the reduction of Cr<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub> and CaCrO<sub>4</sub>-CaWO<sub>4</sub> mixtures is shown in Figure 2. It can be seen that after the reduction of  $Cr_2O_3$ -WO<sub>3</sub> on the inner side surface of containers above their loading level and on the surface of the reaction mass there are white deposits of substance (Figure 2, left crucibles). According to XRD data, the white substance on the surface of the reaction mixture and on the side surfaces of the crucibles is identical and is pure magnesium oxide (Figure 3, pattern 1). A homogeneous mixture of chromium and tungsten powder with an admixture of magnesium oxide was found under the white crust. The amount of magnesium oxide in the mixture under the crust decreases, and the thickness of the crust on the surface increases with an increase in the residual argon pressure in the reactor. Previously it was shown that the spatial separation of the metal and oxide phases upon reduction with Mg or Ca vapors of a number of oxide compounds of tungsten or molybdenum is due to the occurrence of electronically mediated reaction (EMR) without direct physical contact of the reactants [15, 16]. Cr<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub> oxides at high temperatures are an electrically conductive medium capable of transferring electrons. Under certain conditions, which are provided by the high thermal effect of the reduction reaction, the medium of an inert argon gas becomes the carrier of oxygen ions. With an increase of the residual argon pressure in the reactor, the fraction of metal reduced in the EMR mode increases (Figure 2, left crucibles). For the CaCrO<sub>4</sub>-CaWO<sub>4</sub> mixture under the studied conditions, the separation of the reaction products did not observed. They were a homogeneous mixture of dark color with the composition corresponding to the stoichiometric ratio of the reaction (Figure 2, right crucibles).



**Figure 2.** Crucibles with a reaction mass after reduction of mixtures  $Cr_2O_3$ -WO<sub>3</sub> (a-c, left crucibles) and CaCrO<sub>4</sub>-CaWO<sub>4</sub> (a-c, right crucibles). Residual argon pressure in the reactor, kPa: a - 5, b - 10, c -15; temperature in the reactor 750 °C.



Figure 3. XRD patterns of white substance on the crucible surface after reduction of a mixture of  $Cr_2O_3$ -WO<sub>3</sub> (1) and after reduction of of CaCrO<sub>4</sub>-CaWO<sub>4</sub> mixture (2).

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According to XRD data, the washed powder in both cases contained a mechanical mixture of Cr and W (Figure 3, pattern 2). Formation of W-Cr alloy is difficult because mutual diffusion and mobility of atoms in the system are low even at higher temperatures [17]. The specific surface area of powders of W-Cr mixture obtained by reduction of CaCrO<sub>4</sub>-CaWO<sub>4</sub> was 28-34 m<sup>2</sup>·g<sup>-1</sup>, which is 3-6 times higher than the surface of powders obtained by reduction of a mixture of  $Cr_2O_3$ -WO<sub>3</sub> under similar conditions. In addition, when using double oxide compounds, a smaller dependence of the powder surface on the process temperature is observed. This is due to the fact that the refractory oxide CaO presents in them, creating additional interlayers between the particles of the formed metals, impedes the coagulation of the particles. With the reduction of the  $Cr_2O_3$ -WO<sub>3</sub> mixture with an increase in the residual pressure in the reactor, the specific surface area of metal powders decreases. 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 without direct physical contact of the reacting substances by means of electron transfer. This promotes the coagulation of primary metal particles and is the reason for a decrease in the specific surface area of the powders. With the reduction of double oxides with an increase in the residual pressure in the reactor, the specific surface area of metal powders increases. This dependence is due to the fact that an increase in the residual pressure reduces the rate of evaporation of magnesium and thereby reduces the amount of its vapor. 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. The refractory oxide CaO, which is part of the binary oxide compounds, creates additional interlayers between the particles of the reduced metals and, thereby, increases the number of pores remaining after leaching, resulting in an increase in the specific surface area of the powder. SEM image of W-Cr powder obtained by reduction of CaCrO<sub>4</sub>-CaWO<sub>4</sub> oxides is shown in Figure 4.



Figure 4. SEM image of W-Cr powder obtained by reduction of CaCrO<sub>4</sub>-CaWO<sub>4</sub> oxides with a specific surface area of  $34 \text{ m}^2 \cdot \text{g}^{-1}$ .

The average crystallite size determined by Sherrer method for the specific surface area of powders  $28-34 \text{ m}^2 \cdot \text{g}^{-1}$  corresponds to the size of metal particles 25-30 nm. However, as can be estimated from the SEM images of the W-Cr powder shown in Figure 4, the powder is represented by rather large aggregated particles with an average size of more than 200 nm. The high specific surface area of the powder is a consequence of its nanoporous structure. Moreover, the growth of the specific surface occurs mainly due to an increase in the number of nanopores of a smaller diameter (Figure 5). The curves of adsorption of powders obtained by reduction of both CaCrO<sub>4</sub>-CaWO<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub> 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. The amount of adsorbate

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adsorbed at the same relative pressures by the W-Cr powder obtained by reduction of  $CaCrO_4$ -CaWO<sub>4</sub> is 4-8 times higher than the powder obtained using  $Cr_2O_3$ -WO<sub>3</sub> as a precursor (Figure 6).



**Figure 6.** Curves of nitrogen adsorption-desorption by chromium powders with a specific surface area:  $a - 5 \text{ m}^2 \cdot \text{g}^{-1}$  (precursor Cr<sub>2</sub>O<sub>3</sub>-WO<sub>3</sub>),  $b - 34 \text{ m}^2 \cdot \text{g}^{-1}$  (precursor CaCrO<sub>4</sub>-CaWO<sub>4</sub>).

Thus, the results of the performed studies have shown the possibility of using  $CaCrO_4$ -CaWO<sub>4</sub> mixture to obtain nanostructured W-Cr powders with a developed surface by magnesium thermal reduction.

# 4. Conclusion

The reduction by vapor of magnesium of  $Cr_2O_3$ -WO<sub>3</sub> and  $CaCrO_4$ -CaWO<sub>4</sub> mixture compounds of at rarefaction of 5-15 kPa in the temperature range of 800–850 °C was studied.

It was found that when reducing  $Cr_2O_3$ -WO<sub>3</sub> 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 28-34  $m^2 \cdot g^{-1}$  were obtained. The crystallite size estimated by the X-ray method is 25-30 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.

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