MECHANOCHEMICAL SYNTHESIS OF $MgWO_4$, $MgMoO_4$ AND ITS REDUCTION

T.A. Udalova[1, 2*], S.V. Vosmerikov[1], E.T. Devyatkina[1],
T.F. Grigoreva[1], N.Z. Lyakhov[1]

[1]Institute of Solid State Chemistry and Mechanochemistry of SB RAS,
Novosibirsk 630128, Russia
[2]Novosibirsk State Technical University, K. Marx av. 20, Novosibirsk
630073, Russia

**e-mail: udalova@solid.nsc.ru*

The influence of mechanochemical treatment conditions on the formation of magnesium tungstate $MgWO_4$ and magnesium molybdate $MgMoO_4$ with its subsequent mechanochemical reduction with magnesium was studied by X-ray diffraction analysis and scanning electron microscopy. The mechanochemical treatment of a mixture of tungsten (molybdenum) (VI) oxide with magnesium oxide (WO_3 (MoO_3):MgO = 1:1) for 8 minutes leads to the formation of magnesium tungstate (molybdate). The mechanochemical reduction of magnesium tungstate (molybdate) with magnesium is completed after 8 min of mechanical treatment with the formation of the mechanochemical composites W(Mo)/MgO. The separation of tungsten (molybdenum) and magnesium oxide from W(Mo)/MgO mechanochemical composite was carried out using 1M H_2SO_4. The SEM method showed that the tungsten (molybdenum) powder is highly dispersed with particle sizes of 100 nm, which are aggregated into larger particles with sizes up to 4 μm.

Introduction

Tungsten and molybdenum, possessing properties such as high T_{melt} and T_{boil}, density, hardness, low coefficient of linear thermal expansion and steam pressure, good electrical and thermal conductivity [1, 2], find application from metallurgy to electronics [3].

Highly dispersed tungsten and molybdenum powders are used in the preparation of various materials with the necessary physicochemical characteristics: increased porosity (manufacture of battery electrodes, fuel cells, in filters and adsorbents); catalysts, additives for sintering micro powders of various compositions; modification of the properties of polymer matrices (increase in strength, wear resistance, micro hardness); highly dispersed systems with a liquid medium [4].

Currently, heat exchangers, honeycomb panels of spacecraft, shells of rockets and capsules returning to the Earth, heat shields, wing-sheathing, and stabilizers in supersonic planes are made from molybdenum. Moreover, the material requires not only high resistance to oxidation and gas erosion, but also high long-term strength and resistance to impact. At temperatures below 1643 K, molybdenum and its alloys are used to manufacture these parts. Many tungsten and molybdenum compounds are excellent catalysts [2]: sulfides, oxides, pigment dyes, and components of glazes [5].

There are various methods for producing highly dispersed metal powders, such as self-propagating high-temperature synthesis (SHS) [6, 7], chemical vapour deposition [8], electrochemical [9] and metal thermal [10 – 12] reduction of tungsten and molybdenum compounds, sol−gel method, hydrothermal synthesis, reactions in non-aqueous solutions, shock wave synthesis, plasma−chemical and mechanochemical synthesis [13]. The specific surface of the powders, generally, is at the level of hydrogen reduction powders and does not exceed 10 m^2/g.

Magnesium tungstate ($MgWO_4$) is used as a scintillation detector of X-rays and other ionizing radiations in nuclear physics and nuclear medicine, optoelectronic devices [14]. This compound is a luminophore (blue glow radiation in the spectral range of 0.5−0.7 μm, excited by gamma-cathode, X-ray and ultraviolet rays), which has its own emission, intensifying with decreasing temperature [15, 16]. Therefore, it may be of interest for tungstate scintillators in cryogenic studies. The main emission band assigned to the structural phase of $MgWO_4$ (tungstate) is 480 nm [17].

The traditional method of $MgWO_4$ ($MgMoO_4$) synthesis is sintering [17 – 20], but its drawbacks are the high synthesis temperature (~1173K) and the duration (from 10 to 24 hours). From literature data, it is known to use sintered magnesium tungstate (molybdate) in the synthesis of finely dispersed tungsten (molybdenum) (self-propagating high-temperature synthesis).

Of interest is the study of the possibility of obtaining $MgWO_4$ and $MgMoO_4$ by mechanical activation of a mixture of tungsten (molybdenum) and magnesium oxides, as well as the use of magnesium tungstate (molybdate) for its mechanochemical reduction by magnesium in the synthesis of finely dispersed tungsten and molybdenum.

The mechanochemical reduction of metal oxides by an active metal, which leads to the simultaneous grinding of the substance, acceleration of mass transfer, increase in the contact surface area, strain mixing of the components of the mixtures and, respectively, activation of their mechanochemical interaction, leads to the formation of composites ($Me/(Me_{act})_xO_y$) – powder mixtures of highly dispersed particles metal and active metal oxide.

Among the active metals, magnesium has several advantages: in the process of a mechanochemical redox highly exothermic reaction, the MgO phase is formed (T_{melt} ~ 3100 K), which prevents the sintering of activation products. On the other hand, the MgO is well soluble in solutions of sulfuric and hydrochloric acids [21].

The goal of the work was to study the possibility of mechanochemical synthesis of magnesium tungstate (molybdate) from tungsten (molybdenum) and magnesium oxides, the formation of a W(Mo)/MgO composite during the mechanochemical reduction of $MgWO_4$ ($MgMoO_4$) by magnesium, and the subsequent separation of highly dispersed tungsten (molybdenum) and MgO from the composites W(Mo)/MgO.

Experimental

Reagents used: MoO_3 (p, GOST TU6-09-4471-77), WO_3 (p, TU 6-09-17-250-88), MgO (p.a., GOST 4526-75) and Mg (magnesium shavings MGS-99). The mechanical activation of a mixture of tungsten (molybdenum) and magnesium oxide powders in strict stoichiometry (1:1) and the mechanochemical reduction of the synthesized $MgWO_4$ ($MgMoO_4$) with an active metal, magnesium, were carried out in an AGO-2 high-energy planetary ball mill. Stainless steel vials and balls were used. The vial volume was 250 cm^3, the ball diameter was 5mm, the ball loading was 200 g, the sample weight was 10 g, the speed of vial rotation around a common axis was 1000 rpm, the atmosphere was Ar. For X-ray diffraction analysis of the samples, a D8 Advance diffractometer ($CuK_{\alpha1}$ radiation, λ = 1.5406 Å) was used. The morphology of the obtained samples was studied by scanning electron microscopy (Hitachi TM 1000, Hitachi S3400N (Japan)).

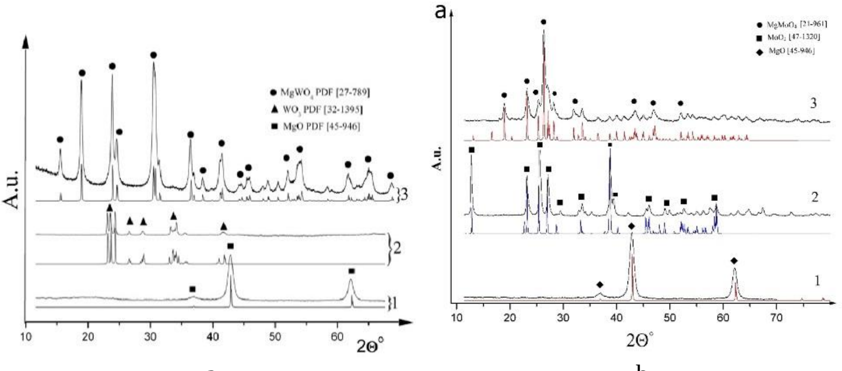
Results and discussion

The reactions of the formation of magnesium tungstate ($MgWO_4$) and molybdate ($MgMoO_4$) from tungsten and molybdenum oxides with magnesium oxide are exothermic:

$$MgO + WO_3 = MgWO_4;\ \Delta_rH^o_{298} = -71.1\ \text{kJ/mol} \qquad (1)$$

$$MgO + MoO_3 \rightarrow MgMoO_4;\ \Delta_rH^o_{298} = -54.05\text{kJ/mol} \qquad (2).$$

X-ray phase studies of the mechanochemical interaction of magnesium oxide (Fig. 1a (b), curves 1) and tungsten (molybdenum) oxides (Fig .1a (b), curves 2) showed that, when the activation time reaches 8 minutes, magnesium tungstate (molybdate) are formed (Fig. 1a (b), curves 3): only $MgWO_4$ ($MgMoO_4$) reflections are recorded on the diffractogram (PDF2 [27-789] ([21-961])). Only broadened reflections of $MgWO_4$ (PDF2 [27–789]), $MgMoO_4$ (PDF2 [21–961]) are observed in X-ray diffraction patterns without reflections of WO_3 (PDF2 [47–1320]), MoO_3 (PDF2 [47–1320]) and MgO (PDF2 [45–946]).



a b

Fig. 1. (a) The X-ray patterns of the oxides: (a) MgO (1), WO_3 (2) and the MA product – $MgWO_4$ (3); (b) MgO (1), MoO_3 (2) and the MA product – $MgMoO_4$ (3).

It can be seen from the results of scanning electron microscopy that the sizes of the initial tungsten oxide and $MgWO_4$ synthesized by mechanical activation are comparable (Fig. 2, a and b). The particle sizes of the initial molybdenum oxide and mechanochemically synthesized magnesium molybdate differ by several orders of magnitude (Fig.2, c and d).

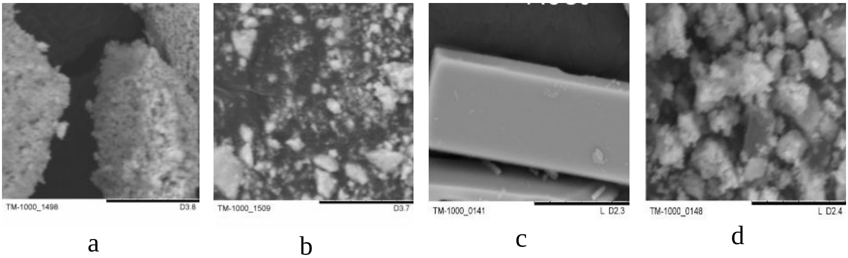


Fig. 2. SEM: – (a) tungsten oxide and (b) mechanochemically synthesized $MgWO_4$; (c) molybdenum oxide and (d) mechanochemically synthesized $MgMoO_4$, magnification ×10000.

Further, this mechanochemically synthesized magnesium tungstate (molybdate) was used as a precursors for the mechanochemical synthesis of highly dispersed tungsten (molybdenum).

Mechanochemical reduction of $MgWO_4$ and $MgMoO_4$ with magnesium, proceeding with a high exothermic effect:

$$MgWO_4 + 3Mg = 4MgO + W;\ \Delta_r H^o_{298} = -874 \text{ kJ/mol} \qquad (3),$$

$$MgMoO_4 + 3Mg \rightarrow 4MgO + Mo;\ \Delta_r H^o_{298} = -1006.0 \text{ kJ/mol} \qquad (4),$$

can be carried out only in the process of mechanical activation with the formation of a mechanochemical composites W/MgO and Mo/MgO.

X-ray diffraction of $MgWO_4$ ($MgMoO_4$) mechanochemical reduction samples obtained with various stoichiometric compositions and mechanical activation modes showed that, with a ratio of $MgWO_4$ ($MgMoO_4$):Mg = 1:3.1, the rotation speed of the vials around the common axis 1000 rpm, the reduction is complete by 8 min (Fig. 3, curve 2) with the formation W(Mo)/MgO composite. In the diffractograms of the samples of the mechanochemical reduction of magnesium tungstate (molybdate), only broadened reflections of MgO (PDF2 [45–946]) and W (PDF2 [4–806]) or Mo (PDF2 [42–1120]) are recorded.

Further, the W/MgO composite obtained by mechanochemical reduction of magnesium tungsten (molybdenum) oxide was subjected to acid treatment to separate tungsten (molybdenum) from magnesium oxide.

It was shown that sequential treatment of W(Mo)/MgO composites with solutions of 1M H_2SO_4, H_2O dist., 4% HF, H_2O dist., acetone leads to a product containing predominantly metallic tungsten (molybdenum), which is confirmed by XRD analysis (Fig. 3, a and b , curves 3). Only reflections corresponding to tungsten (molybdenum) are visible in the X-ray diffraction patterns, reflections corresponding to magnesium oxide are absent.

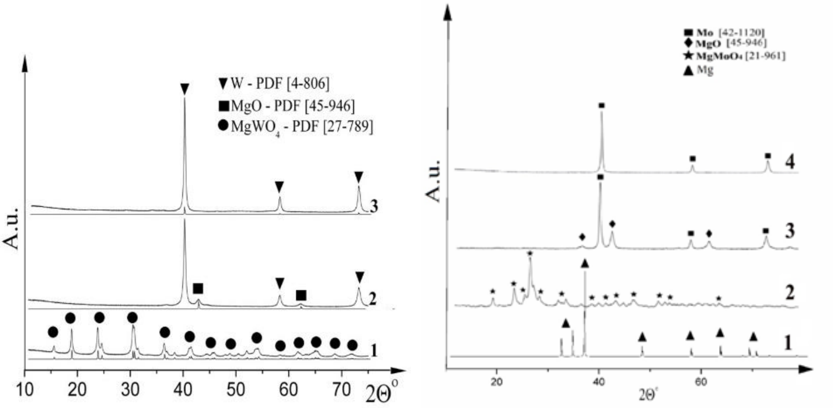


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Fig. 3. The X-ray patterns of the: (a) $MgWO_4$ (1), W/MgO composite formed in a result of mechanochemical reduction of $MgWO_4$ with magnesium (2), highly dispersed W after acid separation of MgO from W/MgO composite (3); (b) Mg (1), $MgMoO_4$ (2), Mo/MgO composite formed in a result of mechanochemical reduction of $MgMoO_4$ with magnesium (3), highly dispersed Mo after acid separation of MgO from Mo/MgO composite (4).

The particle size of highly dispersed tungsten (molybdenum) was determined by scanning electron microscopy. Particles of finely dispersed tungsten (molybdenum) have sizes of ~ 0.1 μm, aggregated into larger ones, with sizes of 2 – 4 μm (Fig. 4, b and d).

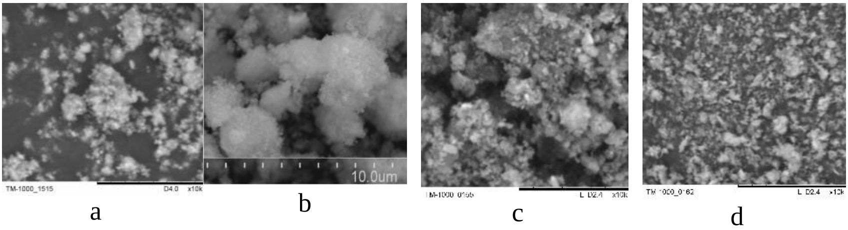

Fig. 4. SEM: (a) W/MgO mechanocomposite; (b) highly dispersed W after acid treatment of mechanochemical composite W/MgO; (c) Mo/MgO mechanocomposite; (d) highly dispersed Mo after acid treatment of mechanochemical composite W/MgO.

By the method of energy dispersive analysis, it was shown that the magnesium content in highly dispersed tungsten is less than 2%.

Conclusion

This paper shows the possibility of obtaining highly dispersed composites W (Mo)/MgO by the two-stage mechanochemical synthesis without the use of high pressure and temperature techniques: 1 stage – the mechanochemical synthesis of magnesium tungstate (molybdate) from solid mixtures of tungsten (molybdenum) (VI) oxide and magnesium oxide; 2 stage – mechanochemical reduction of synthesized magnesium tungstate (molybdate) by an active metal - magnesium. It was shown that subsequent treatment of W (Mo)/MgO composite with acid solutions leads to a product containing predominantly metallic tungsten (molybdenum). Particles of finely dispersed tungsten (molybdenum) have sizes of ~ 0.1 µm, aggregated into larger ones, with sizes of 2 – 4 µm.

Acknowledgements

The work was carried out as part of the state task of ISSC SC RAS (project №. AAAA-A17-117030310277-6) and as thematic plan TP - Chemistry and chemical technology -1_20.

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