Electrochemical Synthesis of Molybdenum and Tungsten Borides from Cryolite based Melt

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Electrolytic deposition of molybdenum and tungsten boride particles from ionic melts is studied. Conditions are found for preparing different boride phases. If the anode material is graphite and the voltage in the bath does not exceed 2.5 V the cathode deposit consists mainly of molybdenum and tungsten metals. A mixture of phases (M, M_2B, MB, MB_2, M_2B_5), is produced on the cathode with U = 2.5 ÷ 3.5 V while with U = 3.5 ÷ 4.5 V the deposit consists of the B higher content boride MB_4. On the whole, the process of electrochemical synthesis for molybdenum and tungsten borides is governed by the following interconnected parameters: electrolytic bath composition, voltage applied to the bath, temperature, and duration of electrolysis.

Keywords: molybdenum boride, tungsten boride, molten salts, cryolite melts, electrochemical synthesis

Compounds of metals with boron, i.e., borides, are an important class of inorganic compounds with a set of valuable properties. A special place among them is occupied by molybdenum and tungsten borides [1], whose powders may be used in order to prepare new structural materials with high electrical and thermal conductivity and magnetic properties, intended for operation at elevated temperatures and in corrosive media. The high hardness and fineness of powders prepared by electrolysis make possible to use them as abrasives in free grinding of ductile metals and alloys. Molybdenum and tungsten borides in the composition of cermets or in the form of composites with nickel, iron, and cobalt are of interest as new materials for cutting tools. In molten systems, with high refractory component deposition potentials and low energy of chemical compound formation, the electrochemical synthesis is accomplished in a kinetic regime [2]: the more electronegative component is deposited on the more electropositive component followed by their chemical interaction.

It is well known that tungsten and molybdenum are more electropositive than boron by 0.5 0.7V [3]. The depolarization in molten salts of boron deposition on molybdenum and tungsten does not exceed 200 mV, and therefore, electrochemical synthesis of molybdenum and tungsten borides is only possible in a kinetic regime. The molten electrolytes for depositing molybdenum borides are constituted in WO_3-B_2O_3 and MoO_3-B_2O_3 with addition of alkaline metal fluoride and alkaline-earth metal fluorides at 950-1000°C [4,5]. A molten mixture of NaCl-Na_3AlF_6 may serve as a solvent for B_2O_3 since in contrast to alkaline-earth metal fluorides the fluoride ion in this mixture is bonded in a stable complex (AlF_6) [3-6, 7].

An electrolysis product using the system NaCl-Na_3AlF_6-B_2O_3 is a highly dispersed amorphous boron powder. In molten NaCl—Na_3AlF_6 boron oxide dissolves in a sufficient amount.

Since halide systems are distinguished by high volatility, and fluoroborates are generally thermally unstable, the use of the systems is not efficient.

Considering all these boron oxide B_2O_3 was chosen for the study. Electrochemical synthesis of molybdenum and tungsten borides was accomplished from a molten mixture of NaCl-Na_3AlF_6-Na_2MO_4 (MO_3)-B_2O_3 (where M is Mo or W). Depending on melt composition and electrolysis parameters in these systems either an individual borides phase of the refractory metal (higher boride MB_4) or a mixture of it with phases including lower borides (M_2B, MB, MB_2, M_2B_5) were deposited. Optimization of electrochemical synthesis for borides consisted in determining the regimes for preparing the higher boride MB_4 which exhibits the most valuable physico-chemical properties [1].

Experimental part

The electrolysis of melts was performed in graphite containers MPG-7 which simultaneously served as the anodes. Melts were prepared from analytical grade chemicals which were preliminary dried: NaCl, Na_3AlF_6, Na_2MO_4 (MO_3), B_2O_3, where M=Mo, W. The electrolyte was purified by its electrolysis at a cathodic current density of 10 20 A/dm^2 until it provided stable deposition. The cathode represented a glassy carbon plate. Steady-state and transient current modes were controlled by a PI-50.1 potentiostat. The electrolysis products were identified by X-ray diffraction using a DRON-2 unit and CuK_α-radiation with a vanadium filter. The optical images of MoB and WB were obtained using an microscope Hund with camera connected. The miscrostruture of M_2B_5 phases were done by SEM measurements.

Results and discussion

Previously an electrolyte NaCl-Na_3AlF_6-Na_2MO_4(MO_3) was developed for depositing tungsten or molybdenum [6, 8].

For electrochemical synthesis of borides, the molten mixture of NaCl-Na_3AlF_6 (1:1 by weight) served as a solvent for oxides and hydroxy salts of the refractory metal and boron.

Reduction waves for fluoroxide complexes of molybdenum and boron (fig. 1) correspond to the electrode

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potentials -1.0 ÷ -1.2V and -1.5 ÷ -1.9V, meaning that molybdenum is more electropositive than boron by 0.5-0.7 V. A similar picture is also observed with reduction of fluoroxide complexes of tungsten and boron.

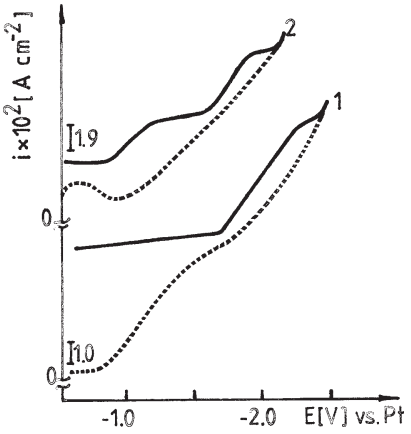


Fig.1. Voltamperograms of molten NaCl-Na_3AlF_6 (1:1) with 1.2 . 10^{-3} mole/cm³ B_2O_3 (1), to which is added 3.0 . 10^5 mole/cm³ Na_2MoO_4 (2); t = 900°C; glassy - carbon cathode; Pt quasi reference electrode; scan rate 0.1 V/s

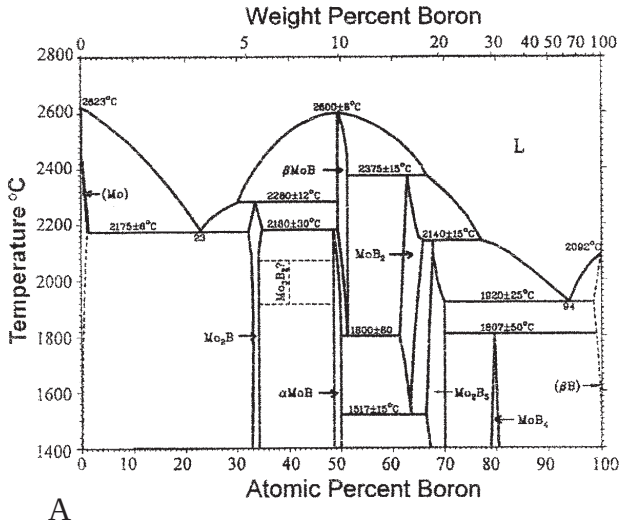
In selecting the concentration of refractory metal oxide and hydroxy salt it is necessary to draw attention to the fact that in the first stage of electrochemical synthesis molybdenum separates as a metal salt bulb like formation.

Deposition of boron commences as the refractory metal oxide of hydroxy salt is depleted. The optimum concentration of both refractory metal oxide and hydroxy salt is 0.75-1.5% (wt.). With higher concentration values the total boronizing of the deposited refractory metal is not achieved, due to instability of the metal-salt deposit.

The effect of boron oxide concentration on the composition of cathode deposits was studied and correlated with phase diagrams of B-Mo and B-W [fig. 2(A,B)].

For phase diagram of the system molybden-boron the existence of six phases has been established: Mo, B_2Mo, B_2Mo_2, BMo, B_2Mo_5 and BMo_4 [9]. For the phase diagram of the system tungsten-boro [10] and boron –tungsten [11] it was established that both systems contain four phases: W_2B, WB, W_2B_5 and WB_4

Boride appears in the cathode deposit with a concentration of boron oxide in the melt of 5% (wt.). With a further increase in this limit, an increase in the content of boride phases in the cathode deposit was observed. In 10-20% (wt) B_2O_3 concentration range the refractory metal is



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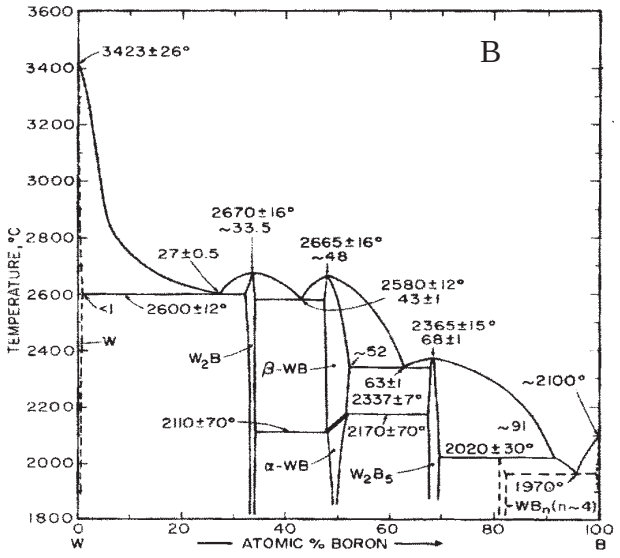

Fig.2. Phase diagrams of binary systems: A. B-Mo ; B. B-W.[9,10]

entirely boronized with formation of higher borides MoB_4 and WB_4.

Electrochemical synthesis of molybdenum and tungsten borides was carried out in a potentiostatic regime since in fact the voltage (potential) determines the course of the reaction and controls the chemical nature of deposits. If the anode material is graphite and the voltage in the bath does not exceed 2.5 V, the cathode deposit consists mainly of molybdenum or tungsten metal.

With U = 2.5-3.5 V a mixture of phases (M, M_2B, MB, MB_2, M_2B_5) is obtained at the cathode, and with U = 3.5-4.5V the cathode deposit consists in higher boride MB_4.

Temperature is a considerably important parameter in electrochemical synthesis. Below 800°C complete interaction of Mo (or W) and B is not performed above 950°C, the stability of the metal-salt deposit falls and borides do not form.

The time duration of the process also affects the composition of the cathode deposit, as figure 3 presents. These data and also those presented in figure 4 for the phase nature of the electrolysis products of the molten system NaCl-Na_3AlF_6-WO_3-B_2O_3 were obtained under optimum conditions (composition, temperature, voltage). In synthesizing borides of the composition MB_4 electrolysis lasts 45-60 min.

One can see that the obtained phase nature of the electrolysis products of the molten systeme NaCl - Na_3AlF_6–B_2O_3 –A (A= Na_2MoB_4 or WO_3) is in very good agreement with the phase diagrams presented in figure 2 (A,B).

On the whole the process of electrochemical synthesis of molybdenum and tungsten borides is governed by the following interconnected parameters: electrolytic bath composition, voltage in the bath , temperature, and duration of electrolysis.

Their optimum values that have been established from our experimental data are the following:melt composition: 39.25÷44.5% (wt.) NaCl, 39.25 ÷ 44.5% (wt) Na_3AlF_6, 1.0÷1.5% (wt) Na_2MO_4 (MO_3), 10 20% (wt.) B_2O_3; voltage 3.5÷4.5 V; temperature 900 950°C; duration of electrolysis 45÷60 min.

Chemical analysis of the electrolyte after electrolysis showed that molybdenum and tungsten species are extracted from the melt almost entirely. In order to carry on the process further it is necessary to adjust the electrolyte by adding oxides or hydroxy salts of the corresponding metal.

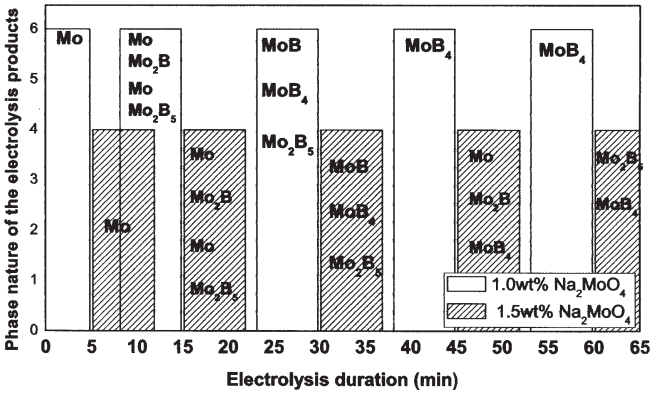

Fig.3. Phase nature of the electrolysis products of the molten system NaCl-Na_3AlF_5-Na_2MoB_4 -B_2O_3 [NaCl-Na_3AlF_6 (1:1) with addition of 20wt% B_2O_3 ; t = 900^{0}C;U = 4V.

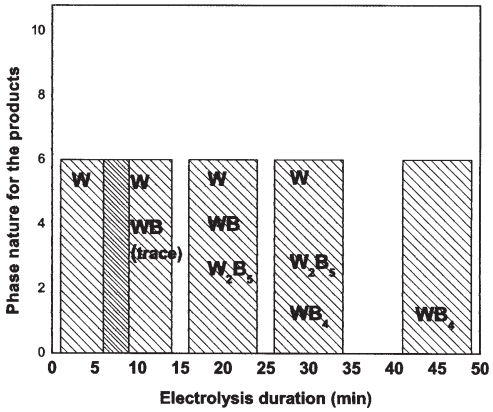

Fig.4. Phase nature of the electrolysis products of the molten system NaCl-Na_3AlF_5-WO_3-B_2O_3 (39.5:39.5:1.0:0.20 % wt); T = 900^0 C , U = 4.0 V.

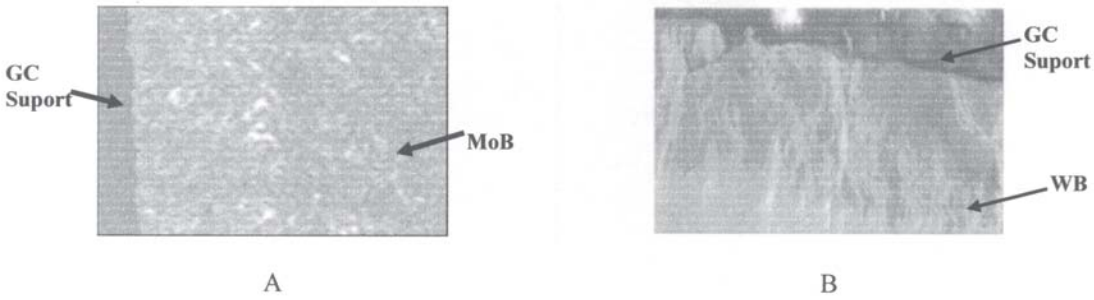

Fig.5. Optical image of the electrolysis product cross-section: A.MoB; B.WB.

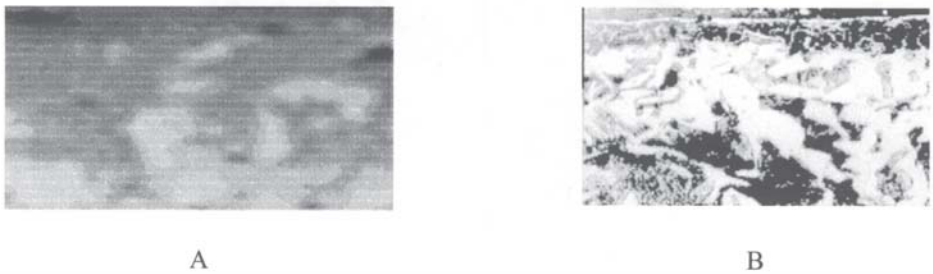

Fig.6. SEM image of the electrolysis high boride products: A.Mo_2B_5 ; B.W_2B_5

The yield of single-phase products MoB_4 and WB_4 is 0.2-0.3 and 0.3-0.45 g/A . h, and the final dispersed MoB_4 and WB_4 powders have a specific surface of 5-15 m^2/g.

We also performed some micrograpy tests on the cross section of the boronized deposits.

As an example of this part of the study we present in figure 5 (A and B) that fine borides (MoB/WB) particles are dispersed uniformly on the glassy carbon catodic support. Figure 6 represents the SEM images of Mo_2B_5 and W_2B_5 phases.

Conclusions

Working conditions were found for preparing different phases by electrodeposition of molybdenum and tungsten boride particles from ionic melts in a cryolite melt. Depending on melt composition and electrolysis parameters in these systems both individual phases of the refractory metal (higher boride MB_4) and a mixture of phases including lower borides M_2B, MB, MB_2, M_2B_5 are deposited.

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