High-Temperature Electrochemical Synthesis of Tungsten and Molybdenum Boride Phases in Chloride—Cryolite—Oxide Melts*

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The high-temperature electrochemical synthesis of tungsten and molybdenum borides has been carried out in the halogenide—oxide melts. It proceeds under the conditions of reaction diffusion. The conditions necessary to obtain the high borides MoB_4 and WB_4 having the most valuable physicochemical properties have been established.

The chemical compounds of metals with boron (borides) belong to the family of inorganic compounds with a variety of valuable properties (high melting points, significant chemical activity, high electric and heat conductivity). Among them, molybdenum and tungsten borides should especially be marked [1].

The electrolytes for electrodeposition of tungsten and molybdenum borides were reported in [2—4]. *Andrieux* and *Weiss* [2, 3] deposited the well-crystallized molybdenum and tungsten borides of the total formula MB by the electrolysis of the $Na_2B_2O_4$—B_2O_3—MO_3—NaF mixtures fused at a temperature of $1000\,°C$. *Aleonard* [4] obtained molybdenum and tungsten borides M_2B_5 and MB_4 from the melts of analogous compositions with the addition of alkali metal fluorides and alkaline-earth metal fluorides.

A thermodynamic analysis of the reactions of electrochemical synthesis has shown that in the systems with a relatively high difference in the deposition potentials of the components and a low energy of formation of a chemical compound, the synthesis can be carried out in the kinetic conditions [5]. In such case, the synthesis proceeds in such a way that a more negative component is deposited onto a more positive one with their subsequent chemical interaction. Such a synthesis proceeds in the reaction diffusion conditions where, in addition to electrochemical factors, the temperature and duration of the process are decisive.

A thermodynamic analysis of the decomposition voltages of boron, tungsten and molybdenum compounds of the same type has shown tungsten to be more electropositive than boron by 0.5—0.7 V [6]. The depolarization value of the boron deposition on tungsten and molybdenum does not exceed 200 mV, and therefore the synthesis of tungsten and molybdenum borides is possible only in the kinetic conditions.

In order to control a synthesis of this kind, it is necessary to know the peculiarities of electrodeposition of the components forming a boride. The peculiarities of the electrodeposition of tungsten and molybdenum in the melts of various systems have been described elsewhere [7—11]. Regarding boron, it was necessary to clarify its electrochemical behaviour in the systems under analysis using the available data [12—15].

A choice of the systems for a synthesis, apart from the thermodynamic analysis, is governed by following considerations. Purely halogenide systems are not suitable in terms of technology because of their high volatility (at a temperature over 850 °C) and the thermal instability of their components (fluoroborates). Therefore, boron oxides, especially B_2O_3, are the most suitable compounds.

The use of the melts of alkali metal fluorides as solvents for B_2O_3 is impossible since they transform boron oxides into high fluorides. In our opinion, the molten $NaCl$—Na_3AlF_6 mixture serves as the most suitable solvent for B_2O_3 since in this mixture, in contrast to the alkali metal fluorides, the fluoride ion is fixed into the $[AlF_6^{3-}]$ ion [10, 11].

The boron oxide is stable and sufficiently soluble in the $NaCl$—Na_3AlF_6 melt. As was shown earlier [10, 11], this system is suitable for electrodeposition of molybdenum and tungsten. According to our equilibrium, stationary and nonstationary measurements, the multielectron reversible equilibria with the participation of the oxide forms of molybdenum(VI) and tungsten(VI) can be carried out in this system.

An analysis of the available data on boron electrodeposition from ionic melts has shown that the melts of alkali metal halogenides and their mixtures containing potassium fluoroborate and boron oxide had mainly been used to electrochemically produce

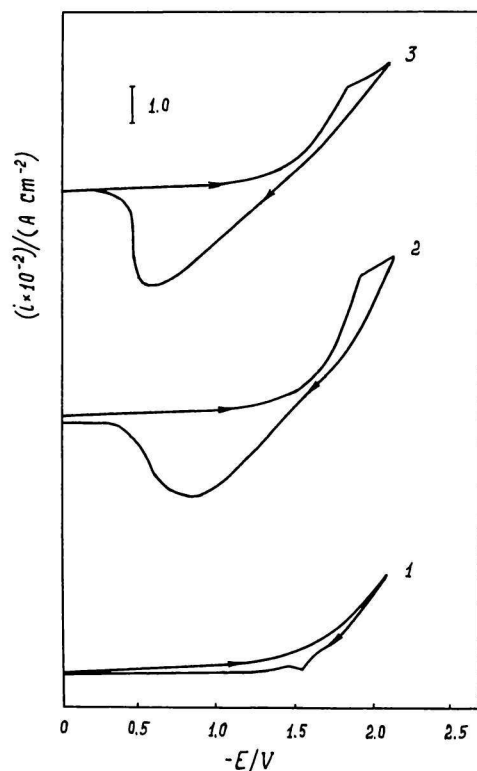*Presented at the *EUCHEM Conference on Molten Salts '96*, Smolenice Castle, Slovakia, 15—20 September, 1996.

Fig. 1. Voltammograms of the NaCl—Na$_3$AlF$_6$ (1 1) melt (1) with the consecutive additions of B$_2$O$_3$ ($\times$ 10^{-5} mol cm^{-3}): 4.8 (2) and 15.0 (3). Here and in Fig. 2, $T =$ 900 °C, glass carbon cathode, depolarization rate 0.1 V s^{-1}

Fig. 2. Voltammograms of the NaCl—Na$_3$AlF$_6$ (1 1) melt with an addition of 1.2 $\times$ 10^{-3} mol cm^{-3} B$_2$O$_3$ (1) and the consecutive additions of Na$_2$WO$_4$ ($\times$ 10^{-5} mol cm^{-3}): 2.0 (2), 3.0 (3).

an elemental boron [12—15]. The electrochemical behaviour of boron against NaCl—Na$_3$AlF$_6$ melt background has not yet been studied. Therefore, in order to carry out an electrosynthesis of tungsten and molybdenum borides, it was necessary to clarify the peculiarities of electrochemical behaviour of boron oxide against the cryolite—chloride melt background.

RESULTS AND DISCUSSION

The voltammetric study of the system chosen was carried out in quartz beakers with three electrodes. The cathode were semidipped glassy carbon electrodes; the anode and container for the melt was a platinum crucible; the reference electrode was a platinum wire dipped in the melt under investigation. A detailed description is given in Refs. [10, 11].

Small additions of boron oxide into the melt NaCl—Na$_3$AlF$_6$ (1 1) results in the appearance of a reduction wave at potentials ranging from −1.5 to −1.9 V relative to platinum-oxygen electrode (Fig. 1). The wave heights increase with increasing the B$_2$O$_3$ concentration in the melt but we failed to find any definite quantitative relationship. The waves are stretched along the potential axis. The cyclic VA diagram indicates an irreversible character of the charge-transfer
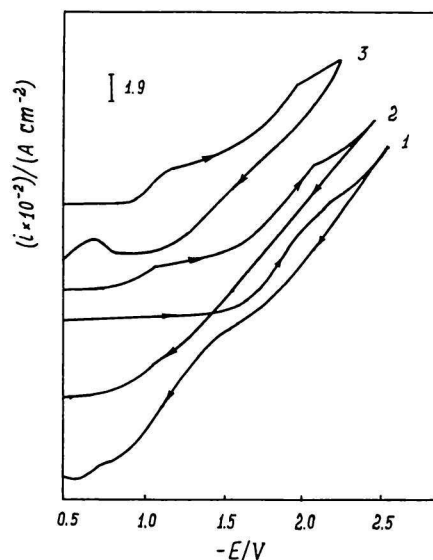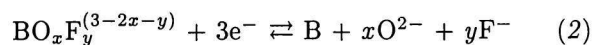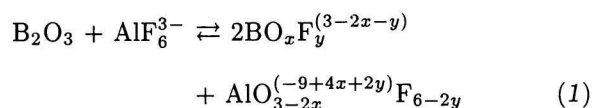
stage. The irreversibility of the process increases with increasing the concentration of boron oxide. The product of a potentiostatic electrolysis at the potential ranging from −1.7 to −1.9 V is the high dispersive powder of amorphous boron.

We have not aimed at clarifying in detail the mechanism of the B$_2$O$_3$ electroreduction but, on the basis of voltammetric measurements, the electroreduction process can schematically be represented as follows

$$B_2O_3 + AlF_6^{3-} \rightleftarrows 2BO_xF_y^{(3-2x-y)}$$
$$+ AlO_{3-2x}^{(-9+4x+2y)}F_{6-2y} \qquad (1)$$

$$BO_xF_y^{(3-2x-y)} + 3e^- \rightleftarrows B + xO^{2-} + yF^- \qquad (2)$$

The voltammetric dependences of the NaCl—Na$_3$AlF$_6$—Na$_2$WO$_4$—B$_2$O$_3$ melt are shown in Fig. 2. The reduction waves of the tungsten and boron fluoride complexes correspond to potentials of −1.0 to −1.2 and −1.5 to −1.9 V, respectively, *i.e.* tungsten is more positive than boron by 0.5 to 0.7 V. The analogous situation is observed in the case of molybdenum and boron oxyfluoride complexes. At such great difference in the electroreduction potentials of the components, a synthesis of tungsten and molybdenum borides can be carried out only at the kinetic conditions.

The electrochemical synthesis of tungsten and molybdenum borides was carried out from the molten NaCl—Na$_3$AlF$_6$—Na$_2$MO$_4$(MO$_3$)—B$_2$O$_3$ mixture where M stands for Mo or W. The molten NaCl—Na$_3$AlF$_6$ (1 1) mixture was used as a solvent for ox-

Table 1. Phase Composition of the Products of Electrolysis of the NaCl—$\mathrm{Na_3AlF_6}$—$\mathrm{Na_2MO_4}$—$\mathrm{B_2O_3}$ System ($T = 1173$ K, $U =$ 4.0 V, NaCl—$\mathrm{Na_3AlF_6}$ (1 1), $\mathrm{B_2O_3}$, 20 mass %

$c(\mathrm{Na_2Mo_4})/(\mathrm{mol\,cm^{-3}})$	Electrolysis time/min					
	5	10	15	30	45	60
1.50 $\mathrm{Na_2MoO_4}$	Mo	Mo	Mo, $\mathrm{Mo_2B}$	$\mathrm{Mo_2B}$, MoB	MoB, $\mathrm{Mo_2B_5}$	$\mathrm{Mo_2B_5}$
			MoB	$\mathrm{Mo_2B_5}$	$\mathrm{MoB_4}$	$\mathrm{MoB_4}$
0.75 $\mathrm{Na_2MoO_4}$	Mo	$\mathrm{Mo_2B}$, MoB	MoB	$\mathrm{Mo_2B_5}$		
	$\mathrm{Mo_2B}$	$\mathrm{Mo_2B_5}$	$\mathrm{Mo_2B_5}$, $\mathrm{MoB_4}$	$\mathrm{MoB_4}$	$\mathrm{MoB_4}$	
1.00 $\mathrm{Na_2WO_4}$	W	W, WB	W, WB	$\mathrm{W_2B_5}$		
			$\mathrm{W_2B_5}$	$\mathrm{WB_4}$	$\mathrm{WB_4}$	

ides and oxide salts of a refractory metal and boron. In these systems, depending on their composition and parameters of electrolysis, we have obtained either the separate phases or a refractory metal and a high boride $\mathrm{MB_4}$ or the mixture of these phases containing also the phases of low borides $\mathrm{M_2B}$, MB, $\mathrm{MB_2}$, $\mathrm{M_2B_5}$ (Table 1). On the whole, the electrosynthesis of molybdenum and tungsten borides is governed by the following interrelated parameters: the composition of electrolytic bath and its voltage, the duration of synthesis, and the temperature.

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