



HIGH TEMPERATURE ELECTROCHEMICAL SYNTHESIS OF MOLYBDENUM, TUNGSTEN AND CHROMIUM BORIDES FROM HALIDE-OXIDE MELTS

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The conditions of high-temperature electrochemical synthesis of borides of molybdenum, tungsten and chromium, respectively, as highly dispersed powders are established using cyclic voltammetry and potentiostatic electrolysis.

INTRODUCTION

Compounds of the VI-A Group metals with boron form an important class of inorganic compounds with many valuable benefits.¹ Their powders can be used for production of new constructive materials with high electrical and thermal conductivities as well as with magnetic properties intended for operation at elevated temperatures and in corrosive media. The extreme hardness and high degree of dispersal of the powders produced by electrolysis makes it possible to use them as abrasives in free polishing, components of metal-ceramics and composites with nickel, iron, and cobalt.

Synthesis from elements in an inert atmosphere at a temperature of 1273-1473 K is a widespread technique of producing VI-A group metal borides. Among the new production techniques, high-temperature electrochemical synthesis (HES) shows considerable promise.² Andrieux³ was the first that synthesized borides by electrolysis of fluoride-oxide melts containing oxides of boron and of a highly melting metal. Borides like CrB₂, Mo₂B₅, and WB were synthesized in this manner (Table 1). Regarding

the mechanism, it is believed that oxides of a highly melting metal and of boron are reduced by an alkali or alkaline-earth metal first separated at the cathode. Andrieux and Weiss⁴ and also Aleonard⁵ have reported the production of MoB, WB, Mo₂B₅, and W₂B₅ by electrolysis of mixtures of fluorides, oxides, and borates (fluoroborates) of alkali and alkaline-earth metals (Table 1). Electrolytes for electrodeposition of a whole series of chromium borates from silicate (borate) - fluoride melts with additions of alkali and alkaline-earth metals are known.^{6,7}

The thermodynamic analysis of the HES reactions demonstrated that, in systems in which the deposition potentials of components differ strongly and energy of formation of a chemical compound is small, the electrosynthesis can be performed under kinetic control.⁸ Under these conditions, a more electronegative component is deposited onto the surface of a more electropositive one with their subsequent chemical interaction. Thermodynamic analysis of the decomposition potential of similar compounds of boron, chromium, molybdenum, and tungsten demonstrated that the metals are more electropositive than boron by 0.5-0.8 V.⁹

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Table 1

Electrochemical systems and conditions for high-temperature electrochemical synthesis (HES) of VI-A group metal borides.

Electrolyte	VIA Group metal component	Boron containing component	U [V]	T [K]	Cathodic product	References
${}^a\text{M}_x\text{F}_y - {}^a\text{M}_x\text{O}_y$	${}^b\text{M}_z\text{O}_y$	B_2O_3	3-10	1273	Mo_2B_5 , Cr_xB_y , WB	3
${}^a\text{M}_x\text{F}_y - {}^a\text{M}_x\text{O}_y$	M_zO_y	MBO ₂	5-8	1323	MoB, WB	4
KF	WO_3 (MO_3)	KBF ₄	2-6	1273	W_2B_5 , WB (Mo_2B_5 , MoB)	5
KCl-KF	Cr_2O_3	KBF ₄	5-6	750-800	Cr_xB_y	6
CaB_4O_7 - CaF_2	Cr_2O_3	B_2O_3	-	1372	Cr_3B_4 , CrB, Cr_5B_3 , Cr_2B	7
$\text{NaCl-Na}_3\text{AlF}_6$	$\text{Na}_2\text{M}^c\text{O}_4$ (MO_3)	B_2O_3	2-4	1173	M_2B , MB, M_2B_5 , MB_4	This work
$\text{NaCl-Na}_3\text{AlF}_6$	K_2CrO_4	B_2O_3	3-5	1173	Cr_2B , CrB, CrB_4	This work

^aM=alkali or alkaline-earth metal^bM=Cr, Mo, W^cM=Mo, W

However, the depolarization value of the boron separation on chromium (molybdenum, tungsten) is not more than 200 mV and therefore, the synthesis of borides of these metals is possible only under kinetic conditions.

Our choice of molten systems for the synthesis, in addition to the thermodynamic analysis, stems from the following considerations. Purely halide systems are not technologically efficient at 1123 K because volatile oxohalide compounds are formed upon the addition of boron oxide. Therefore, oxide compounds of boron, namely B_2O_3 , are most suitable. The use of fluoride melts as solvents for B_2O_3 seems impossible because they convert oxide compounds of boron into higher fluorides. Therefore, $\text{NaCl-Na}_3\text{AlF}_6$ molten mixture is the most suitable solvent for B_2O_3 because the fluoride ion in this mixture is bounded to a strong complex unlike fluorides of alkali metals.¹⁰

In the present work we considered that it is necessary to know specific features of electrodeposition of the components that form a boride to carry out the synthesis under the kinetic control. Previously, we found out that a system based on $\text{NaCl-Na}_3\text{AlF}_6$ is suitable for electroseparation of chromium, molybdenum, and tungsten.^{10,11} We mention that the electrochemical behavior of boron was not studied in the case of $\text{NaCl-Na}_3\text{AlF}_6$ melt.

RESULTS AND DISCUSSION

The Electrochemical Behavior of B_2O_3 Containing NaCl-NaAlF_6 Electrolyte

In Figure 1 a series of cyclic voltammograms recorded on glassy carbon electrode in NaCl-

$\text{Na}_3\text{AlF}_6\text{-B}_2\text{O}_3$ without and with addition of Na_2MoO_4 is presented. Figure 1 shows that small additions of boron oxide to the $\text{NaCl-Na}_3\text{AlF}_6$ melt (1:1) lead to the appearance of a reduction wave at the potentials from -1.1 to -2.2 V vs. the platinum-oxygen electrode as quasi reference electrode (Figure 1, curve 1). The wave height rises with increasing B_2O_3 concentration in the melt. However, we could not find a strict quantitative correlation. Waves are spread along the axis of potentials. The shape of the cyclic voltammogram indicates the irreversible nature of the charge transfer stage. Also the results suggested that irreversibility is more significant with an increasing concentration of boron oxide. We noticed that the product of the potentiostatic electrolysis at the potentials from -1.7 to -1.9 V is highly dispersing amorphous boron.

The Electrochemical Synthesis of Molybdenum or Tungsten Borides

The reduction wave of oxo-fluoride complexes of molybdenum and boron (shown also in Figure 1, curve 2) corresponds to the potentials within interval -1.0 ÷ -1.2V. This indicates that molybdenum is more electropositive than boron by 0.5-0.7 V. A similar picture is also observed in the reduction of oxofluoride complexes of tungsten and boron. Therefore, in deciding on concentrations of an oxide or oxo salt of a highly melting metal, it is necessary to consider that, at the first stage of the electrochemical synthesis, tungsten and molybdenum are deposited with the formation of a metal-salt bulb. Boron starts to separate if the oxide or oxo salt of a highly melting metal is spent.

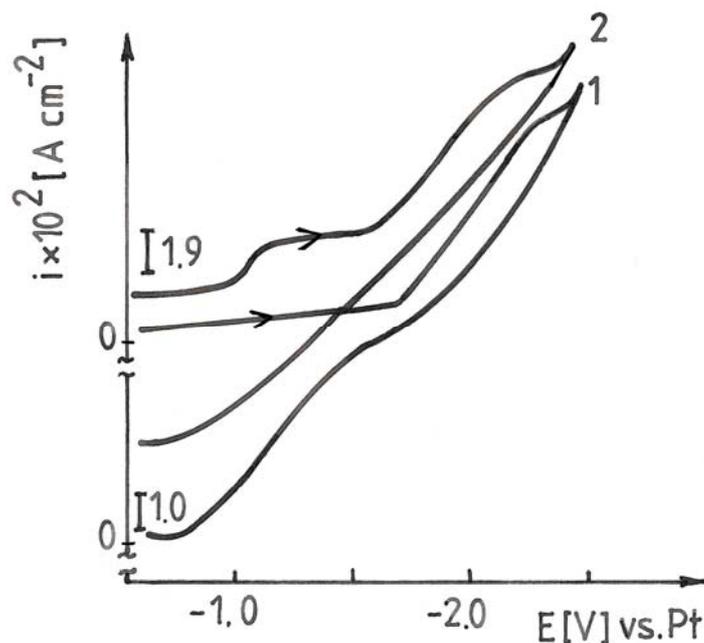


Fig. 1 – Voltammograms for NaCl–Na₃AlF₆ melt (1:1 by weight) with $1.2 \times 10^{-5} \text{ mol/cm}^3 \text{ B}_2\text{O}_3$ (1) and on addition of $3 \times 10^{-5} \text{ mol/cm}^3 \text{ Na}_2\text{MoO}_4$ (2). $T = 1173 \text{ K}$; cathode = glassy carbon; quasi reference electrode = Pt; scan rate = 0.1 V/s.

The electrochemical syntheses of molybdenum and tungsten borides on Ni or W cathodes were performed from molten NaCl–Na₃AlF₆–Na₂Mo₄ (MO₃)–B₂O₃ mixtures (where M = Mo, W). In these systems, all individual components as boride of a metal with high boron content (MB₄) and mixtures including lower boron content borides (M₂B, MB, MB₂, and M₂B₃) are separately produced depending on the melt composition and electrolysis parameters.

The optimization of the electrochemical synthesis of borides consists in the determination of conditions for the production of higher boride MB₄ having most valuable physico-mechanical properties.¹

A concentration of 0.75–1.5 wt % for an oxide or oxo salt of a highly melting metal is optimal. At higher concentrations, complete borating of the deposited highly melting metal is not achieved because of the instability of the metal-salt bulb.

Regarding the effect of boron oxide concentrations on the cathodic deposits composition we found that boron appears in the cathodic deposit if 5wt% boron oxide is present in the melt; the content of boride phases in the cathodic deposit grows with a further increase in its amount in the melt. In the concentration range of 10–20 wt % B₂O₃ the highly melting metal is completely borated to the higher borides, MoB₄ and WB₄. We performed the electrochemical synthesis of either molybdenum or tungsten borides under potentiostatic

conditions and Ni or W bars as cathodes because the electrode potential determines precisely the reaction path and controls the nature of deposit. If graphite is the anode material and the cell voltage U does not exceed 2.5 V, the cathodic deposit consists mainly of metallic molybdenum or tungsten. At $U = 2.5\text{--}3.5 \text{ V}$, a mixture of phases (M, M₂B, MB, MB₂, and M₂B₃) is produced at the cathode, while at $U = 3.5\text{--}4.5 \text{ V}$, the cathodic deposit consists of high boride. The phase composition of the electrolysis products obtained in the NaCl–Na₃AlF₆–Na₂Mo₄ (or WO₃)–B₂O₃ molten electrolytes are presented in Tables 2 and 3.

The temperature is of great importance for the electrochemical synthesis of borides.

The completeness of the Mo(W) + B reaction is not ensured below 1073K; beyond 1223K the stability of a metal salt bulb drops, and borides do not form. The time duration of the process also affects the composition of the cathodic deposit.

On the whole, the electrochemical synthesis of molybdenum and tungsten borides is controlled by the following related parameters: composition of the bath, cell voltage, temperature, and duration of electrolysis.

The data listed in Table 2 and 3 were obtained under various conditions of melt composition and electrolysis duration. When borides having MB₄ composition are synthesized, the electrolysis lasts 45–60 min.

Table 2

Phase composition of products resulted from the electrolysis of NaCl-Na₃AlF₆-B₂O₃ (40 : 40 : 20 wt %) system, depending on the Na₂MoO₄ concentration for various electrolysis durations at 1173 K and cell voltage of 4 V

Na ₂ MoO ₄ concentration [wt %]	Electrolysis duration [min]					
	5	10	15	30	45	60
0.50	Mo, Mo ₂ B, MoB	Mo ₂ B, MoB, Mo ₂ B ₅	MoB, Mo ₂ B ₅ , MoB ₄	MoB ₄	MoB ₄	It was not worked It was not worked MoB ₄
0.75	Mo, Mo ₂ B	MoB, Mo ₂ B ₅	MoB, Mo ₂ B ₅ , MoB ₄	MoB ₄ , Mo ₂ B ₅	MoB ₄	
1.0	Mo	Mo, Mo ₂ B ₅	Mo, Mo ₂ B, Mo, Mo ₂ B ₅	MoB, MoB ₄ , Mo ₂ B ₅	MoB ₄	
1.50	Mo	Mo	Mo, Mo ₂ B, MoB, Mo ₂ B ₅	Mo, Mo ₂ B, Mo, Mo ₂ B ₅	Mo, Mo ₂ B, Mo, MoB ₅	

Table 3

Phase composition of products resulted from the electrolysis of NaCl-Na₃AlF₆-B₂O₃-WO₃ (39.5 : 39.5 : 20.0 : 1.0 wt %) system; (T = 1173K, U = 4.0 V)

Duration of electrolysis [min]	Phase
5	W
10	W, WB(tr.)
20	W, WB, W ₂ B ₅
30	W, W ₂ B ₅ , WB ₄
45	WB ₄

For instance, we establish the following optimal conditions for MoB₄: melt composition (wt%): 39.25-44.5 NaCl, 39.25-44.5 Na₃AlF₆, 1.0-1.5 Na₂MoO₄ and 10-20 B₂O₃, cell voltage 3.5-4.5 V, working temperature 1173-1223K and electrolysis duration 45-60 min.

Chemical analysis of the spent electrolyte has shown that molybdenum and tungsten were almost completely extracted from the melt. Therefore it is necessary to correct the electrolyte composition by adding oxides or oxo salts of a corresponding metal for the further progress of the process.

Regarding the yield of the single-phase MoB₄ or WB₄ the values are 0.2-0.3 and 0.3-0.45 g/Ah respectively; the final MoB₄ and WB₄ dispersed deposits have specific surface of 5-15 m²/g.

The Electrochemical Synthesis of Chromium Borides

In Figure 2 a series of cyclic voltammograms recorded on glassy carbon electrode in NaCl-Na₃AlF₆ without and with addition of B₂O₃ and B₂O₃ + K₂CrO₄ is presented. Figure 2, curve 1 presents the voltammogram for the background electrolyte consisting in NaCl-Na₃AlF₆. Small additions of boron oxide to the NaCl-Na₃AlF₆ melt (1:1) lead to the appearance of a reduction wave within -2.1 ÷ -2.5 V potentials vs. platinum-oxygen

electrode as quasi reference electrode (Figure 2, curve 2). By increasing B₂O₃ concentration in the melt the wave height rises and a second anodic wave will appear (Figure 2, curve 3).

However, we could not find a strict quantitative correlation and cannot say anything about the nature of the second anodic peak. Working with NaCl-Na₃AlF₆-B₂O₃-K₂CrO₄ the Cr(VI) oxo-fluoride complex is electroreduced to Cr₂O₃ (first wave in curve 4 and 5) by the reversible three-electron mechanism, this cathodic process being diffusion-controlled.

In these voltammograms for melts with B₂O₃+K₂CrO₄ two reduction waves are observed at electrode potentials which differ with cca 1V (Figure 2, curve 4 and 5). We suppose that chromium species deposited as oxide, Cr₂O₃, in the first stage of the electrochemical synthesis reacts with boron formed at the second stage to form chromium borides.

Also, we synthesized chromium borides electrochemically from a molten mixture NaCl-Na₃AlF₆-B₂O₃-K₂CrO₄ using Ni or W cathodes. Depending on the melt composition and electrolysis parameters phases of Cr₂O₃, Cr₂B, CrB, and CrB₄ as individual species or their mixtures were obtained (Table 4).

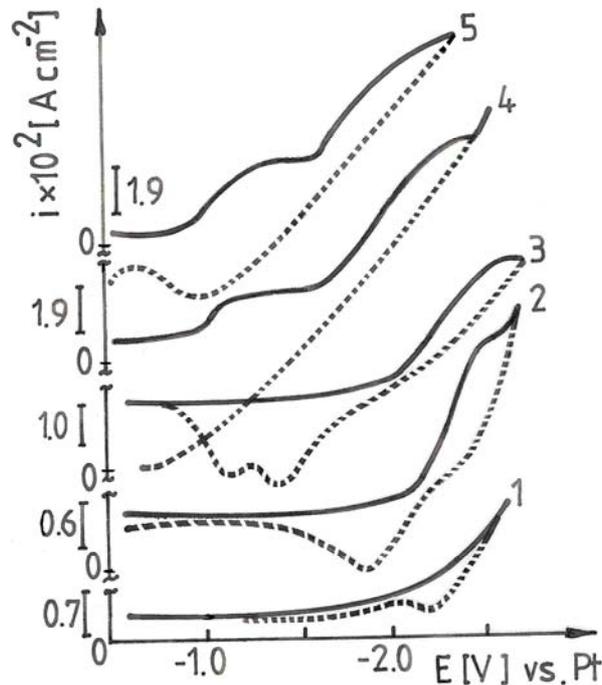


Fig. 2 – Voltammograms for the NaCl-Na₃AlF₆ (1:1 by weight) with successive additions of B₂O₃ and K₂CrO₄: (1) NaCl-Na₃AlF₆ melt; B₂O₃ concentration: (2) 1.2 × 10⁻⁵ and (3,4 and 5) 7.2 × 10⁻⁵ mol/cm³; K₂CrO₄ concentration: (4) 2 × 10⁻⁵ and (5) 3 × 10⁻⁵ mol/cm³; T = 1173 K; cathode = glassy carbon; quasi reference electrode = Pt; scan rate = 0.1 V/s.

Table 4

Phase composition of products resulted from the electrolysis of NaCl-Na₃AlF₆-B₂O₃ (45:45:10 wt %) system, depending on the K₂CrO₄ concentration, from various electrolysis durations at 1173 K and cell voltage 3.5 V

K ₂ CrO ₄ concentration [wt %]	Electrolysis duration [min]				
	5	15	30	45	60
0.5	Cr ₂ B	Cr ₂ B, CrB	Cr ₂ B, CrB	CrB, CrB ₄	CrB ₄
1.0	Cr ₂ O ₃ , Cr ₂ B	Cr ₂ B, CrB	CrB	CrB ₄	CrB ₄ , B

It is worth to mention that we did not make the thermodynamic calculation of the boron-induced thermal reduction of Cr₂O₃ because there are no reference data for chromium borides.

It is obvious that the high-temperature synthesis of chromium borides is controlled by the following interrelated parameters: composition of the bath, voltage at the bath, temperature, and electrolysis duration.

From the experiments performed we determined the optimal electrolysis parameters: composition of the melt (wt %): 39.25-44.5 NaCl, 39.25-44.5 Na₃AlF₆, 1.0-1.5 K₂CrO₄, and 10.0-20.0 B₂O₃; cell voltage 3.5-4.5 V; temperature 1173-1223 K; electrolysis duration 45-60 minute and current density 1.0-1.8 A/cm².

The chemical analysis of the spent electrolyte demonstrated that chromium species are almost

completely extracted from the melt. It is necessary to correct the electrolyte by addition of potassium chromate for the continuation of the process.

The yield of the single-phase product CrB₄ was 0.14-0.21 g/Ah. The final disperse material had a specific surface of 10-20 m²/g.

EXPERIMENTAL

The cyclic voltammetry technique and glassy carbon electrode were employed to study B₂O₃ electroreduction and its electroreduction together with VI-A Group metal species as molybdenum, tungsten or chromium as borides. The voltammetric procedure and electrochemical cell design were described in previous papers.¹⁰⁻¹² A platinum wire immersed in the melt was a quasi-reference electrode. Graphite MPG-7 crucibles served as both anode and container for the melt. Electrolyses with nickel or tungsten bars as cathode were also performed. The bath preparation and analyses during electrolysis

were described previously.¹⁰⁻¹² The powdered product from the working cathode was separated mechanically and crushed. Borides were separated from the solidified electrolyte by consecutive leaching with hot water and 10% H₂SO₄ aqueous solution heated at 50-70°C. The phase composition of the powders was determined using a DRON-2 diffractometer with CuK_α radiation and a vanadium filter. The specific surface of boride powders was determined using "Gasmeter GH-1" equipment and the B.E.T. method⁷ (based on adsorption of gas on a surface) by low-temperature argon sorption.

CONCLUSIONS

We can conclude that we have succeeded to establish the optimal parameters for the electrosynthesis of the VI-A group metal (Mo, W, Cr) borides using halide-oxide melts of the type NaCl-Na₃AlF₆.

REFERENCES

1. G.V. Samsonov, T.I. Serebryakova and V.A. Neronov, "Boridy (Borides)", Ed. Metallurgiya, Moscow, 1975, p. 376.
2. V.I. Shapoval, V.V. Malyshev, I.A. Novoselova and Kh.B. Kushkhov, *Usp. Khim.*, **1995**, *64*, 133.
3. L. Andrieux, *Ann. Chim.*, **1929**, *1*, 422.
4. L. Andrieux and G. Weiss, *Ann. Chim.*, **1946**, *18*, 446.
5. S. Aleonard, *Bull. Soc. Chim. Fr.*, **1960**, *4*, 653.
6. G.I. Miller, *J. Electrochem. Soc.*, **1959**, *106*, 815.
7. P. Hagenmuller, "Preparative Methods in Solid State Chemistry", Academic Press, New York, 1972.
8. Kh.B. Kushkhov, S.V. Devyatkin and V.I. Shapoval, *Ukr. Khim. Zh.* (Russ. Ed.), **1991**, *57*, 827.
9. Kh.B. Kushkhov, V.I. Shapoval and I.A. Novoselova, "VINITP", 1956, no. 7147B, Kiev, p. 18.
10. Kh.B. Kushkhov, V.V. Malyshev, V.I. Shapoval and S.G. Gasviani, *Ukr. Khim. Zh.* (Russ. Ed.), **1991**, *57*, 375.
11. V.V. Malyshev, Kh.B. Kushkhov, V.I. Shapoval and S.G. Gasviani, *Poroshk Metall.* (Kiev), **1994**, *1/2*, 11.
12. V.V. Malyshev, N.N. Uskova and V.I. Shapoval, *Russ. J. Inorg. Chem.*, **1996**, *41*, 1682.