

Electrochemical Synthesis of Borides and Silicides of Chromium, Molybdenum and Tungsten in Molten Salts

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On the basis of thermodynamic analysis of chemical and electrochemical reactions possible systems and conditions have been determined for the electrosynthesis of boride and silicides of chromium, molybdenum and tungsten in molten salts. Electrosynthesis of chromium, molybdenum, tungsten and boride and silicide powders was realized under kinetic conditions.

Keywords: molten salts, borides, silicides, chromium, molybdenum, tungsten

Samsonov G.V., et al. [1,2] make a comparative analysis of existing methods for obtaining chromium, molybdenum, tungsten silicide and boride, and has shown that one of the most promising methods is electrochemical synthesis in molten salts (ESMS), which was used also for borides high temperature electrodepositions [3,4]; Novoselova I.A., et al. [5], described theoretical backgrounds for different classes of compounds, including carbides, silicides, borides, sulphides, and intermetallides and Malyshev V.V., et al. [6,7] the possibility of ESMS on the surface of the semiconducting and dielectric materials was shown. Detailed descriptions were published of the theoretical foundations and practical implementation of the synthesis of tungsten carbide [8,9] and Mo [10]. First electrochemical synthesis of silicide was carried out by the French explorer Dodero M. [apud 11,12]. Silicides of titanium, zirconium, and chromium were synthesized by him through electrolysis of molten mixtures of K_2SiF_6 and Na_2SiF_6 with oxides and fluorides of titanium, zirconium, and chromium. Delimarskii Yu.K. et al. [13] have synthesized $TiSi_2$ by electrolysis of molten $NaCl-KCl-K_2SiF_6-K_2TiF_6$ system. An attempt was made [13] to study the cathode processes during the deposition of $TiSi_2$ from chloride-fluoride melts. In the US, patent [14] was issued for the electrodeposition of coatings of IV-A and V-A groups refractory metal silicides. Electrodeposition of silicides as a coatings was carried out [15] from molten eutectic mixture of alkali metal fluorides (LiF, KF; NaF, KF; LiF, NaF, KF), of silicon in the form of K_2SiF_6 , and refractory metal in the form of K_2TaF_7 , K_2TiF_6 , K_2ZrF_6 etc. at the temperature 1023 K with silicon anodes under cell voltage 1.2 V. In 1929, Andrieux [16] has published his outstanding job on obtaining borides by electrolysis of melts. He was successful in synthesis of 17 borides, including TiB_2 , ZrB_2 , Cr_3B_2 , VB_2 , NbB_2 , TaB_2 . Later, Andrieux and Weiss have reported about obtaining of MoB and WB [11,17]. For these purposes, electrolysis was conducted at the temperature of 1223-1323 K in mixtures of fluorides, oxides, and borates of alkali metal and alkaline-earth metals in the presence of transition metal oxide. Andrieux and Marion [11] have synthesized a series of chromium borides, including Cr_3B_4 , CrB , Cr_3B_3 , Cr_2B , Cr_4B . These compounds were prepared by sequential changing

of Cr_2O_3 content in the mix consisting of CaB_4O_7 , B_2O_3 , and CaF_2 .

Later on, the electrosynthesis of borides was developed in three areas [18]:

- electrosynthesis from oxide melts;
- electrosynthesis from halide melts;
- electrosynthesis from mixed halide-oxide melts.

Oxide melts [molten alkali borates (preferably $LiBO_2$ and $NaBO_2$)] and alkaline earth borates, to which titanium compounds are added (TiO_2 , Li_2TiO_3 , or Na_2TiO_3), were used by the authors [19-22] for obtaining of titanium boride coatings on conductive substrates (Ni, Mo, stainless steel etc.). As the anode, Ti or sintered TiB_2 were used; temperature was 1123-1223 K; cathodic current density i was 0.04-0.4 $A \cdot cm^{-2}$; coating growth rate was between 22 and 220 microns per hour. The anode made of TiB_2 ensures the stability of the bath composition.

In the US, patent was issued in 1960 [23] for electrodeposition of titanium and zirconium diborides (this method can also be applied for other borides) from fluoride-chloride melt $NaCl-KCl-K_2TiF_6(K_2ZrF_6)-KBF_4$. In [24], other method for the obtaining of coatings by cathodic deposition of TiB_2 in salt melt, to which BF_4^- ions are introduced through gaseous BF_3 dissolution, with soluble titanium anode and pure boron anode. Melt must necessarily contain an alkali metal fluoride; the BF_4^- ions concentration in it should be 20.0 wt.%, and the concentration of titanium ions: 0.5-4.0 wt.%. Besides the indicated components, additives of fluorides of Mg, Ba, Ca, Sr etc. can be added to the melt. Coatings deposition temperature was 810-1033 K, and cathodic current density (i), was 10-500 $mA \cdot cm^{-2}$.

A method for the preparation of titanium diboride coating on various products surface is known [25] This method requires using the melt of the following composition, wt. %: LiF-KF(1:1 by weight):70.0, KBF_4 :10.0, K_2TiF_6 :15.0, TiF_3 :5.0; at the temperature 943-1073 K with the optimum current density 50-200 $mA \cdot cm^{-2}$.

In [26], a tantalum boride electrosynthesis from chloride-fluoride melt $KCl-K_2TaF_7-KBF_4$ was described. By varying the composition of the electrolyte, the anode voltage, and current applied to the bath, either a mixture of tantalum mono- and diboride or one of these borides were obtained.

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For mixed halide-oxide systems, method of producing TiB_2 and ZrB_2 in molten sodium salts [27] should be noted. To obtain TiB_2 at 1273 K with the current density $150 \text{ A}\cdot\text{dm}^{-2}$, electrolysis should be carried out in the melt of the following composition, wt. %: TiO_2 :3.0, Na_2CO_3 :4.0, Na_3AlF_6 :20.0, $Na_2B_4O_7$:28.0, $NaCl$:45.0. For zirconium diboride obtaining, electrolysis was carried out at 1298 K with current density $120\text{-}240 \text{ A}\cdot\text{dm}^{-2}$ in the melt of the following composition, wt. %: $ZrSiO_4$:12.0, $NaOH$:4.0, Na_3AlF_6 :40.0, $Na_2B_4O_7$:20.0, $NaCl$:20.0, NaF :4.0.

In [28], the electrolytic production of diborides from oxides is described. For TiB_2 , ZrB_2 , and HfB_2 obtaining, corresponding melts were used based on $NaCl$ - Na_3AlF_6 - $Na_2B_4O_7$ ($NaOH$) containing TiO_2 , ZrO_2 , and HfO_2 , respectively. Electrolysis temperature was 1323 K, and the current density was $150 \text{ A}\cdot\text{dm}^{-2}$.

A process is known [29] for preparation of zirconium diboride at 1023 K with the cathode current densities within the $5\text{-}100 \text{ mA}\cdot\text{cm}^{-2}$ range from the fluoride-oxide melt of the following composition, wt. %: FLINAK ((Li, Na, K)/F):80.0, K_2ZrF_6 :10.0, B_2O_3 :10.0. Instead of K_2ZrF_6 , zirconium tetrafluoride ZrF_4 can be used. Zirconium diboride was also obtained from ZrO_2 and B_2O_3 dissolved in equimolar K_2ZrF_6 - KBF_4 at 873 K [30]. The process is controlled by the concentration of B_2O_3 in the melt, and, at high current densities, zirconium is coprecipitated.

Aleopard [31] has used the method of Marion to obtain other compounds. He was also able to synthesize the molybdenum and tungsten borides. For this purpose, molten KF - KBF_4 - WO_3 (MoO_3) system was used. Varying amounts of oxides of molybdenum and tungsten, Aleopard has synthesized borides W_2B_5 , WB , Mo_2B_7 , and MoB .

Among the works carried out recently, high-temperature synthesis of dispersed powders of borides of vanadium [32], niobium [33], and tantalum [34] from halide melts should be noted. Of particular interest are articles [35, 36] concerning the synthesis of dispersed powders of titanium and zirconium borides. According to the authors of these articles, in the latter case, discharge of heteronuclear complexes of titanium (zirconium) and boron occurs at the cathode.

Thus, analysis of the current state of the problem of IMES of silicides and borides shows that the further development of the method is possible only on the basis of clarifying the mechanism of, and of the development of principles for the implementation and management of, multi-electron electrode reactions of electrodeposition of chromium, molybdenum, tungsten, silicon, and boron. As a prerequisite for the electrodeposition of compounds is, according to [5], the proximity of potentials of deposition of components, it is necessary to develop ways to bring them together and to find the conditions for the alignment of the potentials of various components deposition processes.

Experimental part

Cyclic voltammetry studies were carried out with a TACUSSEL potentiostat PRT 20-10X connected to a PC for data acquisition and control. The electrochemical cell design was described in figure 1.

A platinum wire immersed in the melt was a quasi-reference electrode (QRE). Graphite MPG-7 crucibles served as container for the melt; the same sort of graphite was anode.

Electrolyses with nickel or tungsten bars as cathode were also performed.

The powdered product from the working cathode was separated mechanically and crushed.

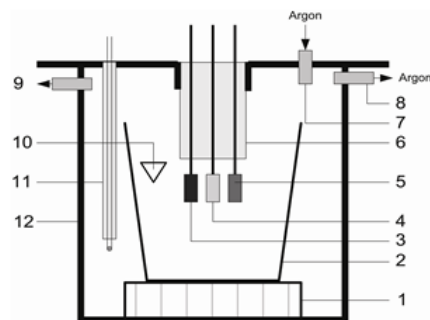


Fig. 1. Experimental set-up 1-ceramic support; 2-graphite crucible; 3-WE (cathode); 4-AE (anode); 5-QRE(Pt); 6-alumina sheath; 7-Ar (in); 8-Ar (out); 9- vacuum; 10-molten salts; 11-thermocouple (type S);12-electrical furnace

Borides and silicides were separated from the solidified electrolyte by consecutive leaching with hot water and 10% H_2SO_4 aqueous solution heated at $50\text{-}70^\circ\text{C}$. The phase composition of the powders was determined using a DRON-2 diffractometer with $CuK\alpha$ radiation and a vanadium filter. The specific surface of boride powders was determined using *Gasmeter GH-1* equipment and the B.E.T. method 7 (based on adsorption of gas on a surface) by low-temperature argon sorption.

The temperature was measured via a calibrated Type S thermocouple (Pt/Rh90%/10%Pt by weight), with reference junction 273 K and hot junction placed directly in the melt, with an accuracy of $\pm 1.5^\circ\text{C}$; this thermocouple was protected with gas tight ceramic tubes and a secondary tube of alumina. For the conversion of the thermoelectric voltage in millivolts, we used the revised ITS-90 thermocouple reference tables. The constant temperature of the furnace within $\pm 1.5^\circ\text{C}$ was ensured during the measurement.

Results and discussions

Thermodynamic backgrounds of ESMS

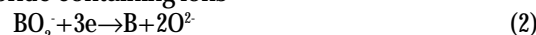
Equilibrium potentials of compounds decomposition were calculated from the standard Gibbs free energy for the decomposition reaction:

$$E_p^\circ = -\Delta G_T^\circ / (nF) \quad (1)$$

where ΔG_T° -standard free energy of the decomposition reaction of the compound to the corresponding components at the temperature T, n-the number of electrons involved in the redox reaction; F-Faraday number. In calculations, thermodynamic values were used from references [37,38].

During electroreduction of silicon and boron compounds at the cathode, as in the case of carbonates [8,10], several cathode processes occurrence are possible:

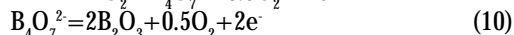
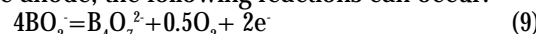
1) formation of elementary silicon and boron from oxide and fluoride containing ions

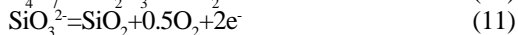
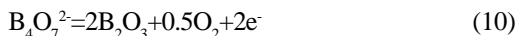


2) alkali metal deposition



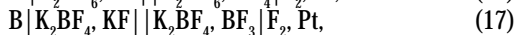
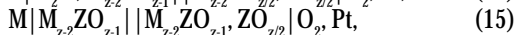
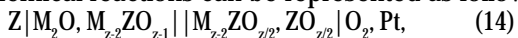
At the anode, the following reactions can occur:





Combinations of the anodic reaction with various realizations of cathodic reduction give chemical reactions shown in tables 1 and 2.

Electrochemical circuits corresponding to these chemical reactions can be represented as follows:



where $Z=B, Si$; $M=Na, K, Li$; z -valence of Z .

From values of decomposition voltage, it follows that process of immediate deposition of boron and silicon should be energetically more favorable. However, which reaction will really occur, will depend on the kinetic characteristics of the processes.

Table 1 and 2 show the values of the equilibrium potentials of deposition of boron and silicon from their oxide and halide compounds calculated from the EMF of cells (14) and (18).

Values of equilibrium potentials of deposition of chromium, molybdenum, and tungsten from their oxides,

Table 1

THE VALUES OF THE EQUILIBRIUM POTENTIAL (V) OF DEPOSITION OF SILICON VERSUS OXYGEN (FLUORINE) ELECTRODE

Decomposition reaction	Temperature/K				
	298	900	1000	1100	1200
$SiO_{2(g)} = Si + O_2$	2.202	1.928	1.882	1.836	1.794
$Li_2SiO_{3(g)} = Si + Li_2O_{(g)} + O_2$	2.533	2.275	2.231	2.189	2.148
$Li_2Si_2O_{5(g)} = 2Si + Li_2O_{(g)} + 2O_2$	2.341	2.093	2.053	2.025	1.986
$MgSiO_{3(g)} = Si + MgO_{(g)} + O_2$	2.364	2.080	2.034	1.988	1.945
$Mg_2SiO_{4(g)} = Si + 2MgO_{(g)} + O_2$	2.585	2.272	2.227	2.169	2.121
$Na_2SiO_{3(g)} = Si + Na_2O_{(g)} + O_2$	2.716	2.486	2.447	2.409	2.373
$Na_2Si_2O_{5(g)} = 2Si + Na_2O_{(g)} + 2O_2$	2.475	2.233	2.193	2.153	2.114
$SiF_{4(g)} = Si + 2F_2$	4.074	3.848	3.810	3.773	3.736
$K_2SiF_{6(g)} = Si + 2KF_{(g)} + 2F_2$	5.855				
$Na_2SiF_{6(g)} = Si + 2NaF_{(g)} + 2F_2$	5.830				

Table 2

VALUES OF THE EQUILIBRIUM POTENTIAL (V) OF DEPOSITION OF BORON VERSUS OXYGEN (CHLORINE, FLUORINE) ELECTRODE

Decomposition reaction	Temperature/K				
	298	900	1000	1100	1200
$4LiBO_{2(g)} = 2Li_2O_{(g)} + 4B + 3O_2$	2.371	2.120	2.081	2.047	2.005
$4NaBO_{2(g)} = 4B + 2Na_2O_{(g)} + 3O_2$	2.547	2.272	2.233	2.190	2.148
$2B_2O_{3(g)} = 4B + 3O_2$	2.038	1.793	1.755	1.717	1.679
$Na_2B_4O_{7(g)} = 4B + Na_2O_{(g)} + 3O_2$	2.353	2.068	2.023	1.980	1.937
$2Na_2B_4O_{7(g)} = 6B + 2Na_2O_{(g)} + 5O_2$	2.235	1.941	1.895	1.852	1.805
$2Na_2B_4O_{7(g)} = 8B + 4Na_2O_{(g)} + 7O_2$	2.268	1.976	1.930	1.886	1.841
$Na_2B_4O_{7(g)} = 2B_2O_{3(g)} + 2Na_2O_{(g)} + 0.5O_2$	3.045	3.073	2.986	2.908	2.806
$2Na_2B_4O_{7(g)} = 4B + 4NaBO_{2(g)} + 3O_2$	2.159	1.857	1.815	1.771	1.726
$Li_2B_4O_{7(g)} = 4B + Li_2O_{(g)} + 3O_2$	2.252	1.976	1.938	1.899	1.856
$2Li_2B_4O_{7(g)} = 4B + 4LiBO_{2(g)} + 3O_2$	2.135	1.843	1.795	1.751	1.707
$K_2B_4O_{7(g)} = 4B + K_2O_{(g)} + 3O_2$	2.399	2.113	2.090	2.049	2.009
$2KBF_{4(g)} = 2B + 2KF_{(g)} + 3F_2$	4.323	3.851	3.782	3.714	3.689
$2NaBF_{4(g)} = 2B + 2NaF_{(g)} + 3F_2$	4.131				
$2BCl_{3(g)} = 2B + 3Cl_2$	1.340	1.235	1.218	1.200	1.182
$2BF_{3(g)} = 2B + 3F_2$	3.865	3.739	3.718	3.695	3.673

Table 3
COMPONENTS FOR THE ELECTROCHEMICAL SYNTHESIS OF CHROMIUM, MOLYBDENUM AND TUNGSTEN, METAL BORIDES AND SILICIDES

Compounds	T/K	$\Delta E^\circ/V$
$\text{SiO}_2\text{-K}_2\text{CrO}_4$	298	0.53
$\text{SiO}_2\text{-Na}_2\text{MoO}_4$	298	0.58
$\text{Na}_2\text{SiO}_3\text{-Na}_2\text{MoO}_4$	298	1.03
$\text{SiO}_2\text{-Na}_2\text{WO}_4$	900	0.37
$\text{Na}_2\text{SiO}_3\text{-Na}_2\text{WO}_4$	900	0.93
$\text{B}_2\text{O}_3\text{-Na}_2\text{CrO}_4$	298	0.56
$\text{B}_2\text{O}_3\text{-Na}_2\text{MoO}_4$	298	0.35
$\text{B}_2\text{O}_3\text{-Na}_2\text{WO}_4$	900	0.23

oxyhalides, halides, and oxo-salts of alkali and alkaline earth metals have been calculated by us previously [5,8,10].

From the results of calculations (Table 3), it can be seen that the deposition potentials for Cr, Mo and W metals and silicon (boron) are significantly different. Therefore, unlike electro-synthesis of Cr, Mo and W metal carbides, electrochemical synthesis at high temperature of their silicides and borides is possible only in a kinetic mode.

Synthesis in this case occurs in such a manner that more electronegative component is deposited onto more electropositive component with subsequent chemical reaction. This variant of the synthesis takes place in the reaction diffusion mode; therefore, in addition to the electrochemical factors, temperature and time are also determinants. Electro-synthesis will be carried out at higher temperatures compared with the synthesis occurring in thermodynamic mode, and phase composition will depend on process duration.

Thermodynamic analysis of the decomposition voltage of similar compounds of boron, silicon, chromium, tungsten, and molybdenum has shown that these metals are more electropositive than boron and silicon for 0.5-0.7

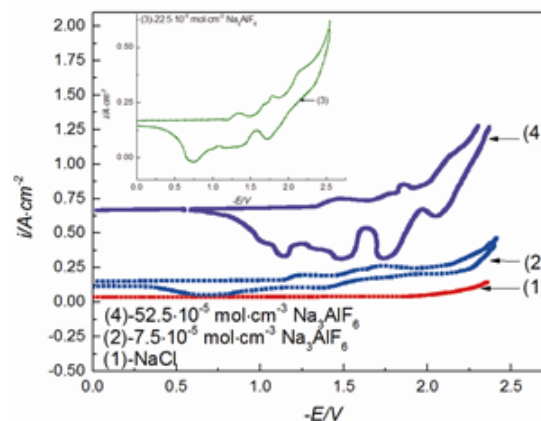


Fig. 2 Cyclic voltammograms obtained at $T=1173\text{ K}$ with $0.1\text{ V}\cdot\text{s}^{-1}$ polarization rate for NaCl (1) and NaCl with different additions of Na_3AlF_6 (2,3,4); cathode was Pt (1,2) and glassy carbon-GC (3,4).

V. Values of depolarization of boron and silicon deposition onto tungsten and molybdenum are no more than 200 mV.

Therefore, the synthesis of chromium, tungsten, and molybdenum borides and silicides is possible only in the kinetic mode. To manage this kind of synthesis, one should know about peculiarities of process of electrodeposition of components forming silicide or boride. Features of electrodeposition of chromium, molybdenum, and tungsten from melts of different composition are described in detail by us in [44]. As for silicon and boron, it was necessary, using available data [45-48], to find out their electrochemical behavior in selected systems.

Systems for the synthesis were selected on the base of the results of thermodynamic analysis, and also on the base of the following considerations. Since the synthesis of Cr, Mo and W metals borides and silicides takes place in reaction diffusion mode, it will be carried out at relatively high temperatures (above 1123 K). Halide systems are not suitable for industrial use in this case due to the high volatility and thermal instability of the components (fluorosilicates and fluoroborates). Consequently, the most suitable are oxide compounds of silicon and boron, namely SiO_2 and B_2O_3 , because silicon in elementary form is hardly deposited from its oxyanion forms SiO_3^{2-} and SiO_4^{4-} .

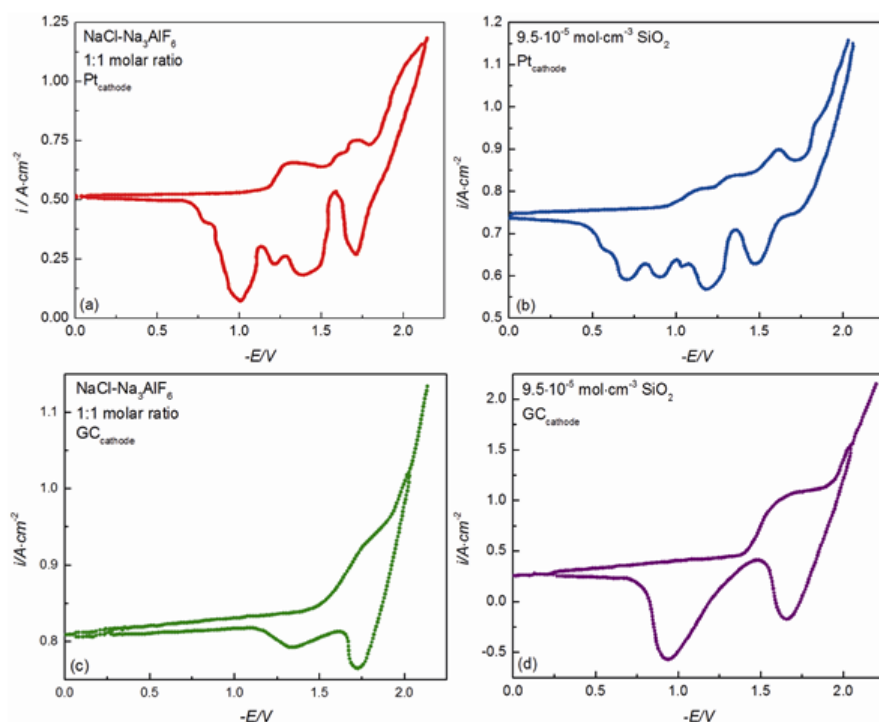


Fig. 3 Cyclic voltammograms obtained on the melts of $\text{NaCl-Na}_3\text{AlF}_6$ (a,c) and on $\text{NaCl-Na}_3\text{AlF}_6$ with different additions of SiO_2 (b,d); $T=1173\text{ K}$, polarization rate $0.1\text{ V}\cdot\text{s}^{-1}$

The use of melts of alkali metal fluorides as solvents for SiO_2 and B_2O_3 is also not possible since these salts convert SiO_2 and B_2O_3 to higher fluorides.

It seems to us that the most suitable solvent for oxides of silicon and boron can be $\text{NaCl-Na}_3\text{AlF}_6$ melt, because, unlike the alkali metal fluorides the fluoride ion is bound here to a stable complex $[\text{AlF}_6]^{3-}$. Oxides of silicon and boron in this melt are stable and dissolve in a sufficient amount of it. Furthermore, this system, as shown in [39], is suitable for electrodeposition of chromium, molybdenum, and tungsten.

Theoretical backgrounds of ESMS

Electroreduction of Si (IV) and B (III) against the molten $\text{NaCl-Na}_3\text{AlF}_6$ (1:1 molar ratio)

The most detailed studies of processes of electrochemical reduction of silicon dioxide in molten cryolite are published in literature [44,45]. The measurement of potential versus time in $\text{Na}_3\text{AlF}_6\text{-SiO}_2$ melt [45] has shown that the electroreduction at a nickel cathode includes a *weak* predissociation of complex to the active state followed by four-electron process of Si^{4+} discharge:



The authors of [44] have measured potential versus time for $\text{Na}_3\text{AlF}_6\text{-AlF}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ melt using platinum cathode at 1173 K. The presence of several waves on the $E(t)$ curves enabled the authors to conclude that the electroreduction of Si (IV) has several stages with intermediate formation of compounds with silicon in lower oxidation degree.

It is known that silicon and aluminum are fairly active elements to form various alloys with platinum. When using platinum as the cathode for electrochemical measurements in these systems, the main process can be overlapped by alloy formation processes, so the interpretation of measurement results is difficult. In addition, a focused selection of components for electrochemical synthesis is not possible without knowledge of the potentials of silicon deposition. Presented in [44] potentials of silicon deposition are significantly

different from those calculated by us using thermodynamic values (see above). Therefore, we have attempted to search indifferent material, and to obtain new information on the electrochemical behavior of Si (IV) in $\text{NaCl-Na}_3\text{AlF}_6$ melt with its help. Figure 2 shows the current-voltage dependences of the molten sodium chloride with sequential addition of cryolite.

Small additions of Na_3AlF_6 (less than 1.0 wt.%) lead to the appearance of three waves at the potentials -1.2, -1.5, and -1.7 V. At higher concentrations of cryolite, fourth wave appears at a potential -2.0 V. These data suggest that the platinum electrode is indifferent only above -1.2 V. The observed waves are associated with the processes of the alloy formation and of the immediate deposition of aluminum from $[\text{AlF}_6]^{3-}$. Quite a different picture is observed during the polarization of the GC cathode (Fig. 3c). In this case, the region of potentials at which the electrode is indifferent in the $\text{NaCl-Na}_3\text{AlF}_6$ system is expanding significantly. Isolation of SiO_2 reduction wave at a platinum cathode is not possible. However, at GC cathode, well-reproducible wave of electroreduction of silicon (IV) is observed which potential is close to the thermodynamic potential of silica decomposition. Potentiostatic electrolysis at this potential gives the cathode deposit consisting of free silicon.

Figure 4 shows the volt-ampere dependences for $\text{NaCl-Na}_3\text{AlF}_6$ (1:1 molar ratio) melt with sequential addition of SiO_2 . Reduction wave appears at a potential -1.6 — -1.9 V and is characterized by the following features: the wave is stretched along the potential axis; limiting current is not clearly expressed; on the reverse dependences $i(E)$, two peaks of dissolution of the cathodic cycle product are found. At SiO_2 concentration less than 1 wt.%, limiting current increases in direct proportion to the concentration of SiO_2 (fig. 5). On this basis, one can conclude that the SiO_2 solubility in molten $\text{NaCl-Na}_3\text{AlF}_6$ (1:1) is about 1.0 wt.%. It can be assumed that the dissolution of SiO_2 in the $\text{NaCl-Na}_3\text{AlF}_6$, as in pure cryolite [41,45-47], is connected with complex oxyfluorides formation.

Analysis of the current-voltage relationships in a semilogarithmic coordinate system $\lg[i/(i_d - i)] = f(E)$ shows that the slope of the experimental lines described by dependences $i(E)$ is 0.087-0.108. It is more than for four-

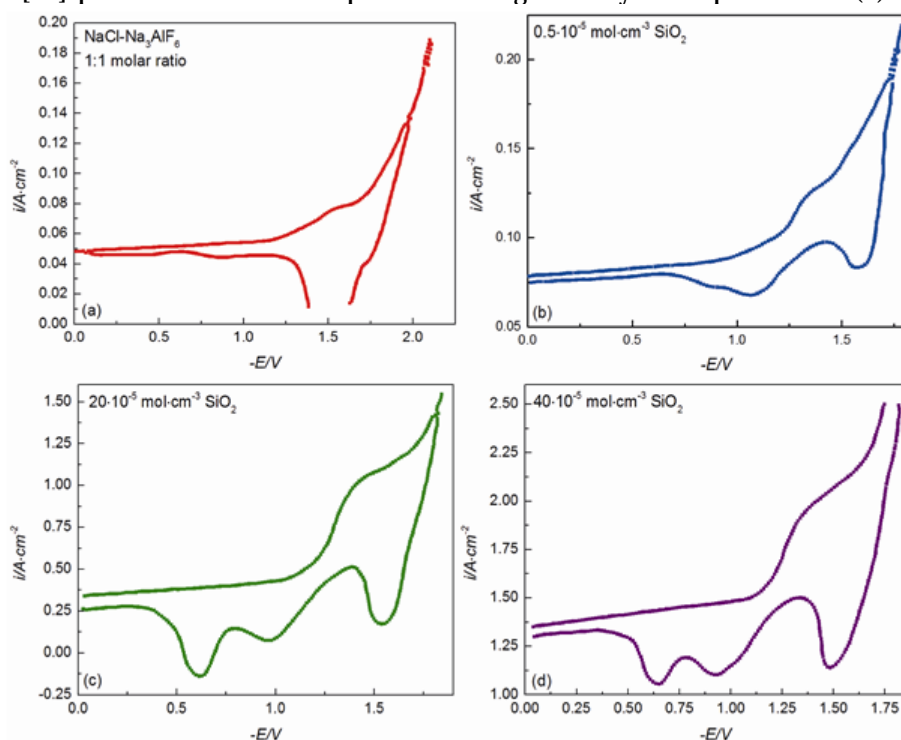


Fig. 4 Voltammograms of $\text{NaCl-Na}_3\text{AlF}_6$ (a), containing different concentration of SiO_2 (b,c,d) at $T=1173\text{K}$; polarization rate $0.1 \text{ V}\cdot\text{s}^{-1}$ and GC cathode.

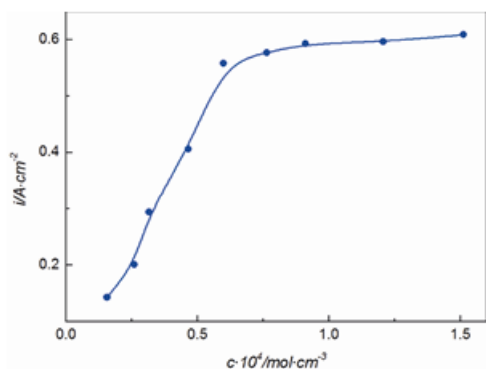
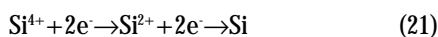


Fig. 5 Dependence of current of electroreduction of Si (IV) in the NaCl-Na₃AlF₆ (1:1 molar ratio) melt on concentration of SiO₂ at T=1173 K; polarization rate 0.1 V·s⁻¹, GC cathode

electron process ($2.3RT/(nF)=0.058$). Slope of polarization curves of silicon electrode in coordinates $\lg i(\eta)$ ($n=2.5-3.2$) is also higher than for four-electron reversible process. These experimental facts, as well as the presence of two peaks at the anodic dissolution curves, allow to judge about the possibility of reduction of the oxyfluoride complex in NaCl-Na₃AlF₆ melt in several stages:



When K₂SiF₆ is added instead of SiO₂, the current-voltage dependences show one reduction wave stretched along the axis of the potentials from -1.5 to -2.0 V (fig. 6). At high concentrations, there is a tendency to the wave bifurcation. On the curves of dissolution of the cathodic cycle product, there are two waves. The limiting current of K₂SiF₆ electroreduction increases in direct proportion to the concentration of fluorosilicate.

The slope of the current-voltage curves in semilogarithmic coordinates $\lg [i/(i_d - i)] = f(E)$ is also greater than for the reversible four-electron process. Thus, electroreduction of K₂SiF₆ against NaCl-Na₃AlF₆ melt, as well as oxyfluoride complexes, can be represented by the equation (21).

The results of voltammetric measurements in the NaCl-Na₃AlF₆-SiO₂ system allowed us to make the reasonable selection of conditions of electrodeposition of silicon. For this purpose, the molten composition NaCl-Na₃AlF₆-SiO₂ was used (the content of SiO₂ was 0.5-1.0 wt.%) at 1173 K. With low current density (1-8)·10⁻² A·cm⁻², light gray fine crystalline silicon coating was deposited. Coating deposition rate within the specified current density range was 10-40 microns per hour, and the current yield of silicon as a coating was 70-80%. The silicon coatings were deposited onto the samples of GC, graphite, nickel, copper, molybdenum, tungsten, and steel 3. At current densities greater than 0.2 A·cm⁻², fine silicon powder was deposited.

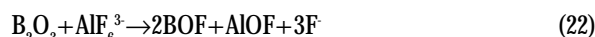
Thus, the use of GC as a cathode material allows to obtain more reliable results for Si(IV) electroreduction against the chloride-cryolite melt. It is shown that Si(IV) electroreduction proceeds irreversibly in at least two stages. Silicon was obtained both in the form of fine powders and in the form of coatings.

Analysis of the literature data for electrodeposition of boron from ion melts has shown that, for the electrochemical production of elemental boron, molten halides of alkali metals and mixtures thereof, containing potassium fluoroborate or boron oxide were mainly used [42,43]. As in the case of silicon, the thermal instability of the fluoroborate ion against alkali metal halides, taking into account features of the task (electrosynthesis of borides of chromium, molybdenum, and tungsten in the

kinetic mode), led us to consider the use of NaCl-Na₃AlF₆ melt as a solvent for boron oxide. The electrochemical behavior of boron against this melt has not been studied previously. Therefore, to realize the electrosynthesis of VI-B group metals borides, it was necessary to find out peculiarities of the electrochemical behavior of boron against the cryolite-chloride melt.

Figure 6 presents volt-ampere dependences for NaCl-Na₃AlF₆ (1:1 molar ratio) melt with sequential addition of boron oxide. Small additions of boron oxide lead to the appearance of reduction wave at a potential -1.5 — -1.9 V versus platinum-oxygen electrode. The height of the wave increases with increasing concentration of B₂O₃ in the melt; however, it is not possible to establish a quantitative relationship.

Waves are extended along the potential axis. Appearance of the cyclic voltammograms indicates irreversible nature of the charge transfer step. Moreover, with boron oxide concentration increase, the irreversibility degree of the process is also increasing. Product of potentiostatic electrolysis at potential -1.7 — -1.9 V is dispersing powder of amorphous boron. We did not attempt to determine the detailed mechanism of electroreduction of B₂O₃. Based on the current-voltage measurements data, process of electroreduction can be schematically represented as follows:



The electrochemical behavior of the molten NaCl-Na₃AlF₆ system under the joint presence of tungstate (molybdate, chromate) of sodium and silicon oxide (boron oxide)

Comparison of potentials of electrodeposition of tungsten and molybdenum from chloride-cryolite melt containing sodium tungstate and molybdate with potentials of

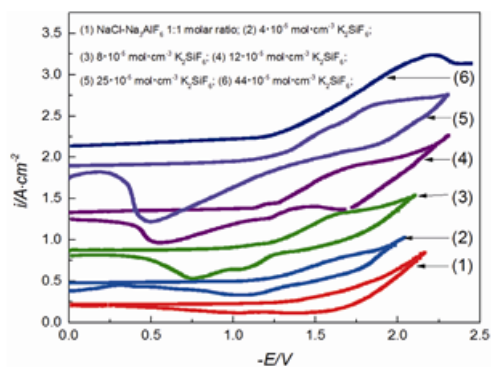


Fig. 6 Voltammograms of NaCl-Na₃AlF₆ (1) melt containing K₂SiF₆ in various concentration (2-6) at T=1123 K with the polarization rate 0.1 V·s⁻¹ on GC cathode

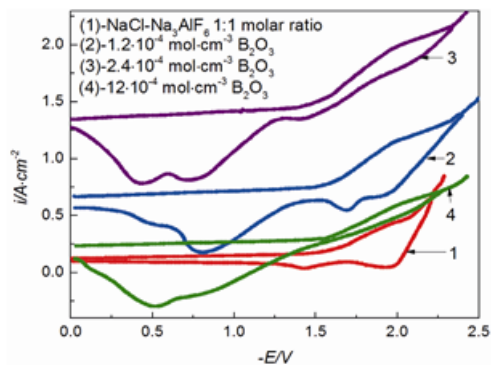


Fig. 7 Voltammograms of NaCl-Na₃AlF₆ (1) melt containing B₂O₃ in various concentration at T=1173 K with polarization speed 0.1 V·s⁻¹ at GC cathode

electroreduction of boron and silicon oxyfluoride complexes allows assuming that the joint electroreduction of oxyfluoride complexes of these metals cannot be realized. Figure 8 and 9 show the current-voltage dependences for chloride-cryolite melt with the co-presence of sodium tungstate and oxides of silicon and boron. As expected, there are two waves. The first wave corresponds to the process of electroreduction of oxyfluoride complex of tungsten to metal tungsten [39], and the second - to the electroreduction of oxyfluoride complexes of silicon (boron) to free silicon (boron). The difference of half-wave potentials is 0.7-0.8 V. A similar pattern is observed in the presence of sodium molybdate or chromate, with the only difference being that the potential of electroreduction of oxyfluoride complexes of molybdenum and chromium, for 150-200 and 250-300 mV higher than that of tungsten, respectively. One more difference is the fact that, during the potentiostatic electrolysis at potentials of electroreduction of refractory metals oxyfluoride complexes, tungsten, molybdenum, and chromium oxide (III) are deposited, respectively. These data confirm once again that the electro-synthesis of silicides and borides will occur in the kinetic mode.

ESMS of chromium, molybdenum and tungsten, metals borides and silicides

Electrochemical synthesis of powders of molybdenum and tungsten silicides from molten salts

Thermodynamic analysis and voltammetric electro-synthesis of

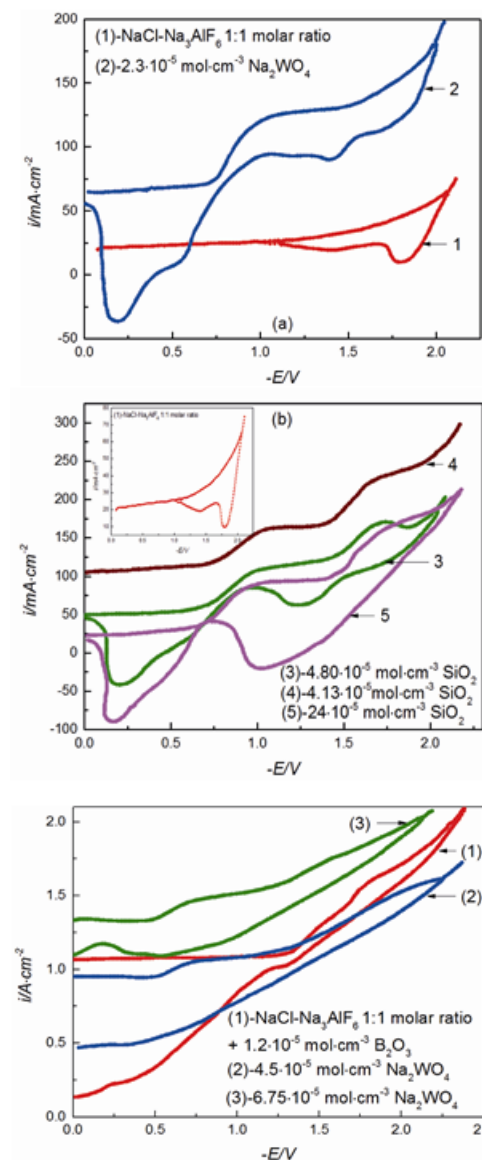


Fig. 8 Voltammograms of NaCl-Na₃AlF₆ (background) melt containing (a) Na₂WO₄ and (b) SiO₂ in various concentration at T=1173 K with polarization rate 0.1 V·s⁻¹ at GC cathode.

Fig. 9 Voltammograms of NaCl-Na₃AlF₆ melt containing B₂O₃ (1-3), and Na₂WO₄ (2,3) at T=1173 K with the polarization rate 0.1 V·s⁻¹ on GC cathode

silicides and borides can be done only in the kinetic mode. Hence, the following sequence of steps of electro-synthesis of silicides and borides of tungsten and molybdenum is appropriate:

- deposition of more electropositive component (tungsten or molybdenum);
- deposition of the second component (silicon or boron) on the surface of previously deposited tungsten or molybdenum;
- the reaction diffusion of silicon or boron into the metal-salt aggregate with formation of silicide and boride phases of different composition up to the higher borides and silicides MSi₂ and MB₄.

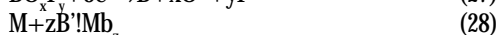
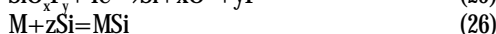
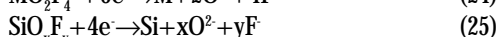
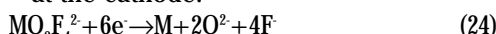
The duration of the first stage of the synthesis depends on the amount of refractory metal in the system and on the cathode current density. To obtain tungsten or molybdenum in the form of fine powder, the current density should be maximized. The second stage begins with the deposition of the electropositive component.

Synthesis of borides or silicides was realized only under the condition that the powders of tungsten or molybdenum are deposited on the cathode as a metal-salt aggregate of such size and shape that allow it to be persistent on the cathode without destruction. In case of scaling of metal (Mo or W) powders down to the bottom of the electrolyzer, components are not in contact, and the synthesis does not occur.

By the traditional way, borides and silicides of tungsten and molybdenum was prepared at the 1373-1673 K; and electro-synthesis at 1123-1273 K. The energy gain (and, therefore, the reduction of synthesis temperature) is provided by interaction of fine powders of tungsten, molybdenum, silicon, or boron deposited at the cathode.

Optimization of the process of electro-synthesis of borides and silicides consisted in determination of the concentration ratios, current densities, temperatures, duration of the process etc. The process of obtaining of borides and silicides can be described by the following electrochemical and chemical equations:

- at the cathode:



- at the anode:



Electro-synthesis of silicides of molybdenum and tungsten was carried out in the molten mixture NaCl-Na₃AlF₆-Na₂MO₄-SiO₂ (M=Mo,W). Selecting the concentration ratios of components guided by the following considerations: according to [46,47], silica has limited solubility (8.82 wt.% at 1283 K) in the cryolite melt. The addition of sodium chloride to cryolite reduces the melting point of the mixture and the solubility of SiO₂. In the eutectic melt containing 68.5 wt.% NaCl and 31.5 wt.% Na₃AlF₆ (T=1010 K), the solubility of silica is 1.0 wt.%. The maximum content of molten cryolite in binary system NaCl-Na₃AlF₆ allowing to carry out electrolysis at 1173 K is 70 wt.%. The solubility of SiO₂ in the melt of such composition is approximately 2.0 wt.%.

Therefore, in the selected area of the binary NaCl-Na₃AlF₆ system (from eutectic up to 70 wt.% of Na₃AlF₆), SiO₂ solubility determines the necessary concentration of sodium tungstate (molybdate) to obtain silicides of stoichiometric composition. Melt components concentration range, wt.%: NaCl:29.0-67.5, Na₃AlF₆:31.0-67.0, Na₂MO₄:0.5-2.0, SiO₂:1.0-2.0. With the NaCl

concentration more than 67.5 wt.%, SiO_2 solubility in the melt is less than 1.0 wt.%. Thus, the concentration of Na_2MoO_4 for the silicides MoSi_2 and WSi_2 formation should be less than 0.5 wt.%, i.e. the process becomes inefficient. If the Na_3AlF_6 concentration is more than 67.0 wt.%, the melt is liquefied above 1173 K and the synthesis should be carried out at a temperature above 1223 K with decrease of metal salt aggregate stability when temperature raise. Furthermore, the higher the cryolite content in melt is, the more complicated cleaning process of synthesis product is to be used, and the more aggressive and less practical melt becomes.

Choosing concentration of oxosalts of refractory metal, first stage of electrosynthesis must be taken into account. The first stage is formation of metal-salt aggregate, and the deposition of silicon begins with the deposition of oxosalt of refractory metal. Therefore, the higher the oxosalt concentration is, the longer time (with $i=\text{const}$) is necessary for formation of metal-salt aggregate. This metal-salt aggregate grows large. Accordingly, the ability of sediment to be hold at the cathode (the stability of the aggregate) decreases, and complete conversion of the deposited molybdenum and tungsten into silicides is not achieved.

Therefore, with Na_2MoO_4 content in the melt over 2.0 wt.%, free tungsten and molybdenum are present in the final product. If the concentration of Na_2MoO_4 is less than 0.5 wt.%, free silicon appears in the final product. At even lower Na_2MoO_4 concentrations, silicon-aluminum alloys are obtained. Temperature and current density are essential for electrosynthesis. At temperatures below 1123 K, the completeness of interaction between Mo (W) and Si is not achieved. At temperatures above 1223 K, metal-salt aggregate stability decreases, and silicides are not formed.

At the optimum composition of the melt, pure silicides MoSi_2 (WSi_2) are obtained with the current density 0.5-1.2 $\text{A}\cdot\text{cm}^{-2}$ for MoSi_2 and 0.5-1.5 $\text{A}\cdot\text{cm}^{-2}$ for WSi_2 . With the current density below 0.5 $\text{A}\cdot\text{cm}^{-2}$, the desired product is contaminated by free molybdenum or tungsten. With the current density above 1.2 $\text{A}\cdot\text{cm}^{-2}$, double silicide $\text{Mo}(\text{Al},\text{Si})_2$ phase appears in molybdate containing melt. In tungsten containing melts, with the current density above 1.5 $\text{A}\cdot\text{cm}^{-2}$, silicon-aluminum alloy is obtained in addition to WSi_2 . Within the range 0.5-1.5 $\text{A}\cdot\text{cm}^{-2}$, with an increase of the current density, specific surface area of obtained silicides of molybdenum and tungsten is also increased ($S_{\text{sp}}=5-15 \text{ m}^2\cdot\text{g}^{-1}$).

Using Tesla BS-300 scanning electron microscope, the shape and size of the MoSi_2 powder particles were studied. These particles are characterized by presence of weakly adherent conglomerates with average size 0.5-2.0 microns.

Since the silicides are formed in the reaction diffusion mode, the duration of the process must substantially influence the composition of the products obtained. The data presented in table. 4 show the dependence of the phase composition of the cathode deposits on the electrolysis time for electrolytes of the optimum composition, temperature, and current density.

Similar dependence of the phase composition on the electrolysis duration is observed in the $\text{NaCl}-\text{Na}_3\text{AlF}_6-\text{Na}_2\text{WO}_4-\text{SiO}_2$ system (table 5). Thus, the optimal duration of electrolysis is 45-50 min. Chemical analysis of the electrolyte after electrolysis for 45-50 min has shown that tungsten, molybdenum, and silicon is extracted from melt almost completely. To conduct the process further, it is necessary to add tungstate (molybdate) of sodium and silica to the melt.

To obtain disilicides of molybdenum and tungsten in the pure form, metal-salt precipitate is leached with hot 10%

Table 4

THE DEPENDENCE OF PRODUCT COMPOSITION ON MOLIBDATE CONCENTRATION AND ELECTROLYSIS TIME FROM NaCl (49.0WT.%) - Na_3AlF_6 (49.0 WT.%) - Na_2MoO_4 (1.0 WT.%) - SiO_2 (1.0 WT.%) SYSTEM AT $T=1173 \text{ K}$, $I=1.0 \text{ A}\cdot\text{cm}^{-2}$

Time/min	Current density/ $\text{A}\cdot\text{cm}^{-2}$	Composition
10	1.0	Mo
20	1.0	Mo, Mo_3Si_5
30	1.0	Mo_3Si_5 , MoSi_2
45	1.0	MoSi_2
60	1.0	MoSi_2 , Si

Table 5

THE DEPENDENCE OF PRODUCT COMPOSITION ON TUNGSTATE CONCENTRATION AND ELECTROLYSIS TIME FROM NaCl (48.5 WT.%) - Na_3AlF_6 (48.5 WT.%) - Na_2WO_4 (2.0 WT.%) - SiO_2 (1.0 WT.%) SYSTEM

Time/min	Current density/ $\text{A}\cdot\text{cm}^{-2}$	Composition
10	1.0	W
20	1.0	W
30	1.0	W, W_3Si_5
45	1.0	W, W_3Si_5
60	1.0	W_3Si_5 , WSi_2
90	1.0	WSi_2

solution of sulfuric acid with the subsequent washing with distilled water, filtration, and drying.

Free silicon is not removed thus. To remove silicon from silicides, precipitate was treated with 10% sodium hydroxide at 353-363 K during 1-1.5 h. The yield of molybdenum silicide was 0.2-0.3 $\text{g}\cdot\text{A}^{-1}\cdot\text{h}^{-1}$, and of tungsten silicide: 0.3-0.45 $\text{g}\cdot\text{A}^{-1}\cdot\text{h}^{-1}$.

If melts electrolysis is carried out to deposit molybdenum disilicide at higher current densities, deposition of $\text{Mo}(\text{Al},\text{Si})_2$ takes place. Components concentration range in melt are as follows, wt. %: NaCl :28.5-67.5, Na_3AlF_6 :31.0-68.5, Na_2MoO_4 :0.5-1.5, SiO_2 :1.0-1.5. If the Na_2MoO_4 content in melt is over 1.5 wt. %, molybdenum disilicide and metal molybdenum are present in the final product. If the concentration of sodium molybdate is less than 0.5 wt.%, free silicon appears in the final product; and, at even lower concentrations, silicon-aluminum alloys are obtained. Of great importance for the process of obtaining dual silicide has a current density (table 6).

Electrochemical synthesis of molybdenum and tungsten borides

Electrochemical synthesis of tungsten and molybdenum borides was carried out in the molten $\text{NaCl}-\text{Na}_3\text{AlF}_6-\text{Na}_2\text{MoO}_4-\text{MoO}_3-\text{B}_2\text{O}_3$ ($\text{Na}_2\text{B}_4\text{O}_7$) mixture.

In these systems, depending on the composition and parameters of electrolysis, both individual phases of refractory metal and its higher boride MB_4 and mixtures of these phases including M_2B , MB , M_2B_3 . Optimization of the process of borides electrosynthesis lies in determination of the mode of obtaining of higher boride MB_4 having the most valuable physical and mechanical properties. As in the case of the silicides synthesis, the molten $\text{NaCl}-\text{Na}_3\text{AlF}_6$ (1:1 molar ratio) mixture was used as solvent for oxides

Table 6

THE DEPENDENCE OF PRODUCT COMPOSITION ON MOLIBDATE CONCENTRATION AND ELECTROLYSIS TIME FROM NaCl(49.0 WT.%) - Na₃AlF₆(49.0 WT.%) - Na₂MoO₄(1.0 WT.%) - SiO₂(1.0 WT. %) SYSTEM AT T=1173 K

Current density/A·cm ⁻²	Composition	Specific surface area/m ² ·g ⁻¹
1.2	MoSi ₂ , traces of Mo(AlSi) ₂	-
1.3	Mo(AlSi) ₂ , traces of MoSi ₂	11.3
1.7	Mo(AlSi) ₂	14.3
2.0	Mo(AlSi) ₂	15.2
2.5	Mo(AlSi) ₂ , silumins	-

Table 7

THE DEPENDENCE OF PRODUCT COMPOSITION ON TUNGSTATE CONCENTRATION AND ELECTROLYSIS TIME FROM NaCl(39.5 WT.%) - Na₃AlF₆(39.5 WT.%) - WO₃(1.0 WT.%) - B₂O₃(20.0 WT. %) SYSTEM AT T=1223 K, U=4.0 V

Time/min	Tension/V	Composition
5	4.0	W
10	4.0	W, WB
20	4.0	W, WB, W ₂ B ₅
30	4.0	WB, W ₂ B ₅ , WB ₄
45	4.0	WB ₄

and oxalates of refractory metal and boron. Unlike SiO₂, boron oxide and borax are readily soluble in the molten mixture. Choosing a concentration of oxide and oxosalt of refractory metal, it is necessary to take into account the first stage of electrosynthesis, when the deposition of tungsten and molybdenum takes place to form the metal-salt deposit. Boron deposition begins as oxide and oxosalt of refractory metal form. The optimum concentration of the oxide and oxosalt of refractory metal is 0.75-1.5 wt.%. At higher concentrations, due to the instability of metal-salt aggregate, complete boriding of deposited refractory metal are not achieved. We have investigated the effect of the concentration of boron oxide and borax on the composition of cathodic deposits. The appearance of boride phase in the cathode deposit begins with the content of boron oxide or borax in the melt 5 wt.%. With increase of the concentration of boron oxide (borax), the amount of boride phases in the cathode deposit increases. Within the range of B₂O₃ and Na₂B₄O₇ concentrations 10-20 wt.%, complete boriding of refractory metal with formation of higher boride phase MoB₄ or WB₄.

Of great significance during the electrosynthesis of borides, the temperature is. With T < 1073 K, complete interaction between Mo (W) and B is not achieved. Above 1223 K, stability of metal-salt aggregate decreases and borides are not formed. Electrosynthesis of molybdenum and tungsten borides were carried out in potenti- and galvanostatic modes. It turned out that these modes are not equal for this process. In the galvanostatic mode, the

true current density value is known only in the initial period since cathode surface area changes substantially during the electrolysis. In most cases, potentiostatic mode was used since it is the voltage (potential) which determines the course of the reactions and controls the nature of the deposition reaction. If the anode material is graphite, and the cell voltage U is < 2.5 V, the cathode deposit is composed mainly of metallic tungsten or molybdenum. Provided U = 2.5-3.5 V, the mixture of different phases of M, M₂B, MB, and M₂B₅ is formed. If U = 3.5-4.5 V, the cathode deposit consists of higher boride MB₄.

As in case of silicides electrosynthesis, process duration significantly affect the composition of the cathode deposit. Data presented in the table. 7 show the dependence of the phase composition of cathodic deposits on the duration of electrolysis in electrolytes of optimal composition at optimum temperature and cell voltage.

Similar dependence of the deposit phase composition on the electrolysis time is observed in the NaCl-Na₃AlF₆-Na₂MoO₄-B₂O₃ system (table 8). The optimal duration of electrolysis to produce MB₄ phases is 45-60 min. Generally, the process of electrosynthesis of molybdenum and tungsten borides is determined by the following interrelated parameters: the composition of the electrolyte, the cell voltage, the duration of electrolysis, and the temperature. The optimum values of these parameters are as follows: the composition of the melt (wt.%): NaCl:39.25-44.5, Na₃AlF₆:39.25-44.5, Na₂MoO₄ (MO₃):1.0-1.5, Na₂B₄O₇

Table 8

THE DEPENDENCE OF PRODUCT COMPOSITION ON MOLIBDATE CONCENTRATION AND ELECTROLYSIS TIME FROM NaCl-Na₃AlF₆-Na₂MoO₄-B₂O₃(20 WT.%) SYSTEM AT T=1173 K, U=4 V.

C/wt.%	t/min					
	5	10	15	30	45	60
1.5	Mo	Mo	Mo, MoB ₂ , Mo ₂ B ₅ , Mo ₂ B	Mo, MoB ₂ , MoB, Mo ₂ B ₅	Mo, Mo ₂ B, MoB	Mo ₂ B ₅ , MoB ₄
1.0	Mo	Mo ₂ B	Mo, Mo ₂ B, MoB, Mo ₂ B ₅	MoB, Mo ₂ B ₅ , MoB ₄	MoB ₄	
0.75	Mo	Mo, Mo ₂ B	MoB, Mo ₂ B ₅ , MoB ₄	Mo ₂ B ₅ , MoB ₄	MoB ₄	
0.50	Mo	Mo, Mo ₂ B, MoB	MoB, Mo ₂ B ₅ , MoB ₄	MoB ₄	MoB ₄	

C/wt. %	t/min			
	5	15	30	60
0.5	Cr ₃ Si, Si	Cr ₃ Si, CrSi ₂	CrSi ₂	CrSi ₂ , Si
1.0	Cr ₃ Si	Cr ₃ Si, Si	Cr ₃ Si, CrSi ₂	CrSi ₂ , Si

Cr _x Si _y	T/K	
	973	1173
Cr ₃ Si ₂	-3391	-6597
Cr ₂ Si	-65572	-89650
CrSi	-15938	-21166
CrSi ₂	-39868	-46619

Table 9
THE DEPENDENCE OF PRODUCT COMPOSITION ON CHROMATE CONCENTRATION AND ELECTROLYSIS TIME FROM KCl-KF-K₂SiF₆ (25.0 WT.%) - SiO₂ (1.0 WT.%) - K₂CrO₄ SYSTEM AT T=1173 K, U=3-4 V

Table 10
VALUES OF ΔG (KJ/MOLE) OF REACTIONS
Cr₂O₃ + Si → Cr_xSi_y + SiO₂

(B₂O₃):10-20; the cell voltage 3.5-4.5 V, electrolysis duration 45-50 min, the temperature of the process 1173-1223 K.

Chemical analysis of the electrolyte after the electrolysis has shown that the tungsten and molybdenum are extracted almost completely from the melt. To conduct the electrolysis process further, the addition of the refractory metal oxide or oxosalt is required.

For pure tungsten and molybdenum borides obtaining, it is necessary to carry out all the operations described above for the silicides. The yield of single-phase products MoB₄ and WB₄ is 0.2-0.3 g·A⁻¹·h⁻¹ and 0.3-0.45 g·A⁻¹·h⁻¹, respectively. The specific surface area of fine powders of MoB₄ and WB₄ is 5-15 m²·g⁻¹.

Electrochemical synthesis of borides and silicides of chromium

Initially, high-temperature electrochemical synthesis of chromium silicides was carried out in the molten KCl-Na₃AlF₆-K₂CrO₄-SiO₂ mixture. Current-voltage dependences include reduction waves of oxyfluoride complexes of Cr and Si at the potentials -0.7 — -0.9 and -1.6 — -1.9 V, respectively. Depending on the electrolyte composition and electrolysis parameters, phases Cr₂O₃, higher silicide CrSi₂, silicide Cr₃Si in mixture with aluminum compounds were obtained.

In order to optimize obtaining process of chromium silicides, high-temperature electrochemical synthesis was carried out in the KCl-KF-K₂SiF₆-K₂CrO₄ system. On the current-voltage dependences of this system, there are also reduction waves of oxyfluoride complexes of Cr and Si at significantly different potentials. Depending on the electrolyte composition and electrolysis parameters, both individual phases Cr₂O₃, Cr₃Si, and CrSi₂ and mixtures of these phases with low silicon content were obtained (table 9). Choosing concentrations of CrO₄²⁻ and SiO₂ (K₂SiF₆), one must take into account that, during the first stage of electrolysis, aggregate is formed comprising Cr₂O₃ and salts, which begins to siliconize as deposition of refractory metal proceeds. Unlike high-temperature electrochemical synthesis of borides and silicides of molybdenum and tungsten, in this case, one of the components is precipitated not in elementary form but in the oxide form, and the other component is the reducing agent for this oxide.

Thermodynamic calculations for silicon thermic reduction were not done previously [1]. Analysis of the reactions of Cr₂O₃ with Si using reference data [42,43] in order to obtain different silicides (Cr₃Si, CrSi, CrSi₂) and oxidation of Si to SiO or SiO₂ (table 10) has shown that

the formation of higher silicide CrSi₂ occurs through the stages of formation of lower silicides. In the high-temperature electrochemical synthesis conditions (973-1173 K) most thermodynamically favorable process is Cr₃Si and CrSi₂ silicides formation and oxidation of Si to SiO₂. Experimental data (table 9) show that the process of silicon thermic reduction of Cr₂O₃ depends on several factors, among which, a crucial role is played by the temperature and process duration.

At the current-voltage dependences of the joint electroreduction in molten NaCl-Na₃AlF₆-K₂CrO₄-B₂O₃ systems, reduction waves are observed at significantly different potentials: -0.7 — -0.9 and -1.4 — -1.7 V, respectively. At the first stage of the electrochemical synthesis, chromium is deposited in the form of Cr₂O₃, interacting with the boron deposited during the second stage of electrolysis to form borides. Electrochemical synthesis of chromium borides was carried out in molten NaCl-Na₃AlF₆-K₂CrO₄-B₂O₃ mixture. Depending on the composition of the melt and electrolysis parameters, both individual phases Cr₂O₃, Cr₃B, CrB, CrB₄ and mixtures thereof were obtained (table 11). The yield of single-phase product CrB₄ was 0.14-0.21 g·A⁻¹·h⁻¹. Fine powders have specific surface area 10-20 m²·g⁻¹. Thermodynamic calculations for boron thermic reduction of Cr₂O₃ were not performed as reference data for chromium borides are missing.

Generally, the process of chromium borides high-temperature electrochemical synthesis is determined by the following interrelated parameters: the composition of the electrolyte, the cell voltage, temperature, and the duration of electrolysis. The optimum composition of the melt is as follows, wt. %: NaCl:39.25-44.5, Na₃AlF₆:39.25-44.5, K₂CrO₄:1.0-1.5, B₂O₃:10.0-20.0. The optimal parameters of electrolysis are following: the cell voltage 3.5-4.5 V, the temperature 1173-1223 K, duration of electrolysis 45-60 min, current density 1.0-1.8 A·cm⁻².

Chemical analysis of the electrolyte after the electrolysis has shown that the chromium is removed virtually completely from the melt. To carry out the electrolysis process further, the addition of potassium chromate is required.

Conclusions

We systematized the well-known electrolytes for the high-temperature electrochemical synthesis of powders of silicides and borides compounds of chromium, molybdenum and tungsten metals, according to the classes of synthesized compounds. We also described the results

Table 11
THE DEPENDENCE OF PRODUCT COMPOSITION ON CHROMATE CONCENTRATION AND ELECTROLYSIS TIME FROM
NaCl-Na₃AlF₆-B₂O₃ (10 wt.%) -K₂CrO₄ SYSTEM AT T=1173 K, U=3.5 V

C/wt.%	t/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

of recent investigations into the ionic melts electrochemical synthesis.

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