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High-temperature electrochemical synthesis of carbides, silicides and borides of VI-group metals in ionic melts

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Abstract

Possible systems and conditions have been determined for the electrosynthesis of carbides, silicides and borides of chromium, molybdenum and tungsten on the basis of thermodynamic analysis of chemical and electrochemical reactions involved in high temperature electrochemical synthesis. Electrosynthesis of powdered molybdenum and tungsten carbides has been carried out under thermodynamic conditions from halide–oxide, under excess CO_2 pressure, and tungstate–molybdate–carbonate melts. Electrosynthesis of powdered silicides and borides of chromium, molybdenum and tungsten has been realized under kinetic conditions. Oxide and halide–oxide electrolytes have been developed for the electrodeposition of molybdenum and tungsten carbide coat ings.

1. Introduction

Among the novel methods for producing refractory compounds, high-temperature electrochemical synthesis (HES) from ionic melts is promising. This method allows the production time of powders and coatings of the above compounds to be considerably shortened and the process to be realized at the atomic level (at lower temperatures). It consists in carrying out simultaneous or sequential multielectron electrochemical reactions to give the metal and nonmetal, whose interaction results in the formation of the desired product (carbide, silicide or boride). This product is deposited on the cathode. At the time the present investigations were begun few papers had been published. The electrosynthesis of carbides [1–6], silicides [7–9], borides [1, 10–13] of group (IV–VI)A metals was carried out by empirical proportioning of the melt based on fluorides and by empirical selection of conditions for the process.

The goal of the present work was to develop fundamentals for the HES method and to create and effect new processes for electrosynthesis of the most useful compounds of group VIA metals with carbon, silicium and boron. The development is based on the thermodynamic analysis of chemical and electrochemical reactions [14–16] and the principles previously proposed for governing multielectron processes for the formation of metals and nonmetals [17, 18].

2. Thermodynamic aspects of HES

Electrochemical synthesis can be carried out in two regimes: ‘thermodynamic’ and ‘kinetic’. According to Baraboshkin [19], the thermodynamic regime takes place close to the standard potentials of the components. Under these conditions the alloy composition is independent of the current density over a wide range. For the electrodecomposition of metal alloys the author assumes a difference in deposition potential between the components of 0.2 V as a criterion. Otherwise, the kinetic regime takes place, and the alloy composition is independent of the difference in standard potential. Calculation of equilibrium decomposition potentials, E_p, for various compounds of group VIA metals and nonmetals (C, Si, B) within the 900–1200 K range provides thermodynamic substantiation of HES and selection of systems for the synthesis. The calculation is based on thermodynamic characteristics of the corresponding compounds. The equilibrium decomposition potential of a compound was calculated from the standard Gibbs energy for the decomposition reaction:

$$E_p = -\frac{\Delta G_T}{nF} \qquad (1)$$

where G_T is the standard Gibbs energy of the reaction of the compound decomposition into the corresponding components at temperature T, and n is the number of electrons involved in the redox reactions.

Table 1. Table containing selected pairs of compounds and regimes for the electrochemical synthesis of refractory compounds of group VI metals

No.	Temperature /K	Components for coelectro reduction	Decomposition potential differences /V
1	900	CO_2–WO_3	0.025
2	900	CO_2–WO_2Cl_2	0.038
3	900	CO_2–$MgWO_4$	0.145
4	900	Na_2CO_3–Na_2WO_4	0.145
5	900	$BaCO_3$–$CaWO_4$	0.024
6	900	CO_2–MoO_2	0.074
7	900	$BaCO_3$–$BaMoO_4$	0.009
8	900	CO_2–$MgMoO_4$	0.05
9	900	CO_2–MoO_2Cl_2	0.041
10	298	Na_2CO_3–Na_2MoO_4	0.053
11	298	Li_2CO_3–Na_2CrO_4	0.006
12	298	SiO_2–Na_2MoO_4	0.58
13	298	Na_2SiO_3–Na_2MoO_4	1.03
14	900	SiO_2–Na_2WO_4	0.37
15	900	Na_2SiO_3–Na_2WO_4	0.93
16	298	SiO_2–K_2CrO_4	0.53
17	900	B_2O_3–Na_2WO_4	0.23
18	298	B_2O_3–Na_2MoO_4	0.35
19	298	B_2O_3–Na_2CrO_4	0.56

In the calculation some assumptions are made. Nevertheless, the calculations determine decomposition potentials close to the real ones and allow the products of electrolysis to be predicted. Thermodynamic constants of electrochemically interesting compounds from reference-books [20, 21] were also used. Based on calculated data, pairs of compounds for carrying out HES were selected (Table 1). It is seen that the equilibrium potentials of deposition of metals and carbon from compounds of the same type are close to each other, and coelectrodeposition can be achieved under thermodynamic conditions. Unlike that of carbides, HES of silicides and borides of group VIA metals is possible only under kinetic conditions due to a considerable difference in deposition potential between the metals and silicium (boron).

3. Electrochemical synthesis of molybdenum and tungsten carbides under excess carbon dioxide pressure

We have previously shown the possibility of realizing coelectrodeposition of carbon dioxide and various electrochemically active ionic forms of molybdenum and tungsten – cationized $\{Me_x^{z+}[MO_4^{2-}]\}^{zx-2}$ [22], dimeric $M_2O_7^{2-}$ [23, 24] and fluoroxide $MO_2F_4^{2-}$ [25] ones, where Me is Li^+, Ca^{2+}, Mg^{2+}, Al^{3+}; M is Mo, W. This possibility has been assumed as a basis for the basically new method of synthesis of molybdenum and tungsten carbides by electrolysis of halide–oxide melts under excess carbon dioxide pressure. Reactions involved in the electrochemical synthesis have been described [22].

The synthesis was carried out in a cell fabricated from high temperature steel. The anode and cathode were semidipped plates of glassy carbon. The cathode product was shed to the bottom of a crucible. After cooling down the product was broken from the bulk electrolyte, boiled in a weak solution of hydrochloric acid and washed with distilled water.The product washed out was identified by chemical and X-ray phase analysis.

The cell design developed allows the electrolysis to be carried out in the 973–1073 K temperature range under an excess pressure of CO_2 up to 20×10^5 Pa. Thus the current parameters and concentration ratios were referred to the value of the rate of carbon electrodeposition at pressures from 15×10^5 to 20×10^5 Pa and $-(5.0–6.5) \times 10^{-3}$ A cm^{-2}. For the M_2C and MC phases to be formed the electroreduction currents of the refractory metal should be in the $(15.0–19.5) \times 10^{-3}$ and $(7.5–10.0) \times 10^{-3}$ A cm^{-2} ranges, respectively. Optimization of the HES process was therefore reduced to creation of acidity which provides the above rates of Mo and W deposition. It has been shown by experiment that a change in the excess pressure at a certain melt acidity affects the phase composition of the product (Table 2). Analysis of the data has shown that the electrolyte compositions II and IV are the most acceptable for HES of Mo and W carbides.

Table 2. Dependence of the phase composition of the cathodic product obtained by electrolysis of halide–tungstate melts on the pressure of carbon dioxide in the electrolyser at 1023 K

Pressure /(10^5 Pa) of CO_2	Phase composition of the product obtained from electrolytes			
	(1) KCl–NaCl–Na_2WO_4 /3 mol %–$MgCl_2$ /6 mol% U = 2.4 V, E_c = 1.4 V	(2) KCl–NaCl–Na_2WO_4 /5 mol %–$NaPO_3$ /0.7 mol % U = 2.5 V, E_c = 1.5 V	(3) KCl–NaCl–NaF /1 mol–WO_3 /3 mol % U = 1.9 V, E_c = 1.1 V	(4) KCl–NaCl–Na_2WO_4 /4 mol %–Na_2WO_7 /1 mol % U = 2.4 V, E_c = 1.4 V
0	W + MgO + $MgWO_4$	W	W	W
2.5	W + tracesW_2C + MgO	W + W_2C	W + W_2C	W + W_2C
5.0	W + W_2C + MgO	W + W_2C	W + W_2C + WC	W + W_2C
7.5	W_2C + WC + W + MgO	W_2C + WC + W	W + W_2C + WC	W_2C + WC
10.0	W_2C + WC + MgO	WC + W_2C	W_2C + WC	WC + W_2C
15.0	WC + W_2C + MgO	WC + W_2C	WC + W_2C	WC + W_2C
17.0	WC + MgO	WC*	WC*	WC*

* Monophases powders of tungsten carbide contain up to 4% free carbon.

At a cathode current density, i_c, of 5×10^{-2} A cm^{-2} the specific surface and particle size are 4 m^2 g^{-1} and 5 to 7 μm, respectively. An increase in i_c to 2×10^{-1} A cm^{-2} gives an increase in the specific surface from 6 to 8 m^2 g^{-1} and a decrease in the particle size from 3 to 2 μm. The WC deposition rate in electrolyte II is 0.2–0.4 g A^{-1} h^{-1}, current efficiency is up to 56%, whereas those in electrolyte IV are 0.35–0.52 g A^{-1} h^{-1} and up to 75%, respectively.

4. Electrochemical synthesis of fine powders of molybdenum and tungsten carbides from oxide melts

The employment of fine powders with a grain size of fractions of a micron allows the solution of problems concerning production of high strength ceramic and metal–ceramic materials. The low solubility of CO_2 in halide–oxide melts enables low current densities (0.1–0.2 A cm^{-2}) to be realized and particle size from 2 to 5 μm to be obtained. A decrease in the particle size with increasing i_c is possible in oxide tungstate–molybdate–carbonate melts.

The electroreduction of carbonate, molybdate and tungstate ions in the oxide Na_2WO_4 melt proceeds at closely spaced potential values [23, 26]. This allows coelectroreduction and HES of carbides to be carried out in the oxide melt. In such melts the phase composition of the product of electrolysis depends on the carbonate concentration (Table 3).

The conditions for tungsten carbide production are as follows: electrolyte composition (mol %): Li_2CO_3, 10–20; Li_2WO_4, 30–45; Na_2WO_4, the balance; $T = 1077$–1173 K; $i_c = 1.0$–1.7 A cm^{-2}. A change in the ratio of the components results in a corresponding change in the product composition; that is, the presence of W, WO_2 and free carbon impurities. The specific surface of the powders varies from 10 to 20 m^2 g^{-1}. Graphite or glassy carbon are the most useful anode materials, whereas nickel serves as cathode.

Tungsten carbide is obtained on the cathode as a cathode salt precipitate. After cooling down it is washed out with hot water. The product yield is between 0.68–0.71 g A^{-1} h^{-1}; current efficiency is between 93–97%.

The electrochemical synthesis of molybdenum carbide was carried out in an oxide electrolyte (mol %): Li_2MoO_4, 5–20; Li_2CO_3, 10–25; Na_2WO_4, 55–85. The process variables were the same. The current efficiency was 95–98%.

Table 3. Dependence of the phase composition of products obtained by electrolysis of the Na_2WO_4–Li_2WO_4 (40 mol %)–Li_2CO_3 system on Li_2CO_3 concentration (T = 1123 K)

Li_2CO_3 concentration	Electrolysis potential rel. Pt/O^{2-} /V	Phase composition of electrolysis products
0	1.9	W
1.0	1.9	$W + W_2C$
2.5	1.9	$W + W_2C + WC$
5.0	1.85	W_2C, WC
10.0	1.8	WC, W_2C
15.0	1.8	WC

Fine powders often contain up to 5–7 wt % free carbon and (surface) oxygen sorbed. This hinders compaction of the sintering of powders. Annealing in activated hydrogen allows complete removal of free carbon (from 7 to 0.1 wt %) and decrease in oxygen content by an order of magnitude (from 5 to about ~0.2–0.3 wt %) [27].

The lattice constants of monocarbide (a = 2.906 + 0.003 A, c = 2.937 + 0.006 Å) practically agree with literature data [28]. The morphology of the particles depends on the production conditions and varies over a wide range (Figure 1). Typical distribution of the particle size is as follows: 0.00–0.03 μm (20.44 wt %); 0.03–0.50 μm (39.54 wt %); 0.50–1.00 μm (60.28 wt %); 1.00–2.00 μm (68.29 wt %); 2.00–4.00 μm (100 wt %). Average grain size, d_{50} = 0.73 + 1.15 μm.

5. Electrodeposition of coatings of molybdenum and tungsten carbides from oxide and oxide–halide melts

An advantage of HES over other methods of synthesis is the possibility of producing coatings on various materials and articles.

Electroplating of molybdenum carbide was carried out from the oxide melt Na_2WO_4–Li_2MoO_4–Li_2CO_3. In this system coelectroreduction of MoO_4^{2-} and CO_3^{2-} ions is achieved [23, 26] as well as electrosynthesis of Mo_2C. The melts used are stable, nontoxic, nonhygroscopic, and do not require a protective atmosphere and special constructional materials for the electrolysis. Alundum or graphite crucibles serve as containers for the melt. The anode (in the case of alundum crucible) was molybdenum or graphite plates or rods.

Mo_2C coatings were formed with the following concentrations of Li_2MoO_4 and Li_2CO_3: 2.5–7.5 wt % and 2.5–10 wt %, respectively. Sound deposits were obtained at $T = 1073$–1223 K. At $T = 1073$ K powdered deposits were formed. The cathode current density was $(1$–$10) \times 10^{-2}$ A cm^{-2}. The rate of deposition of Mo_2C coatings over the i_c range varied from 5 to 20 μm h^{-1}. Coating current efficiency was up to 60%, and the thickness up to 50 μm. Photomicrographs of cross-sections for patterns with indentations from a microhardness test are shown in Figure 2.

The disadvantage of oxide melts is high concentrations of W and Mo. To decrease these, a solvent based on the NaCl–LiF eutectic mixture has been used. Regions of deposition potentials for Mo, W and C in this solvent have been determined [29, 30]. Molybdenum is formed from the MoO_4^{2-} ion at a potential 200 mV more positive than that of tungsten formation from the WO_4^{2-} ion and almost the same of carbon formation from CO_3^{2-}. This accounts for the possibility of depositing Mo_2C and W_2C coatings. It is almost impossible to achieve crystallization of WC as a sound deposit.

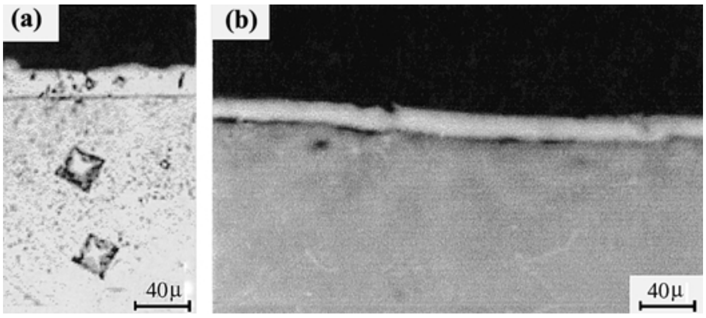

Fig. 1. Micrographs of sections of steel (a) and titanium (b) samples coated with molybdenum carbide with microhardness indents.

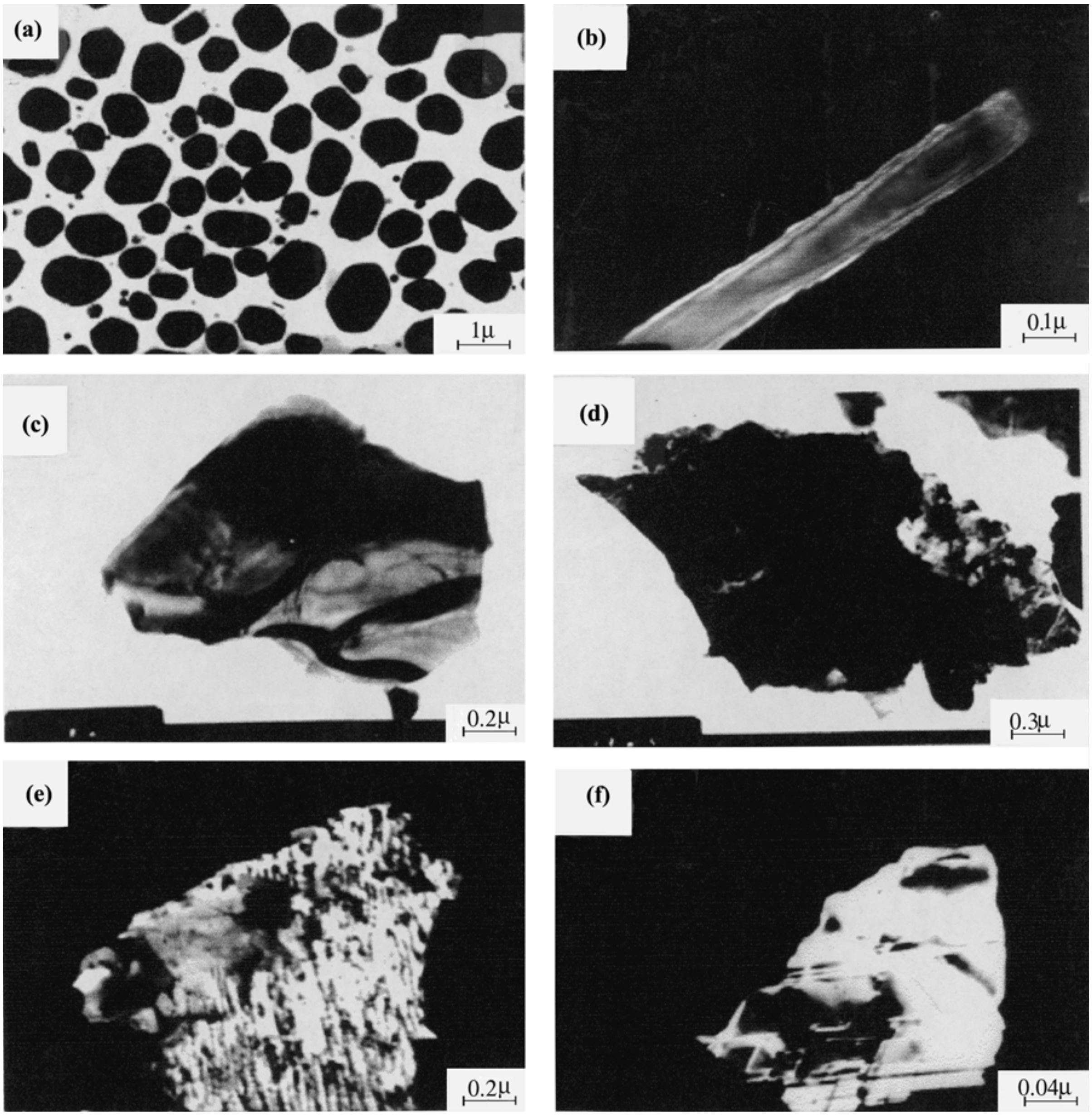

Fig. 2. Transmission electron micrographs of tungsten carbide powders: (a) disc-like single crystal particles; (b) uniaxial single crystal particles; (c) plate-like single crystal particles of irregular shape; (d) polycrystalline aggregates of single crystal particles; (e) and (f) layered aggregates of thin single crystal plates.

The effect of Na_2MoO_4, Na_2WO_4 and Na_2CO_3 concentrations on the composition of cathode products were studied (Table 4). Sound deposits were obtained at $T = 1073$–1173 K and $i_c = (2–15) \times 10^{-2}$ A cm^{-2}. The

Table 4. Composition of cathode deposits in the electrolysis of the NaCl–LiF (3:1 wt)–Na_2MO_4–Na_2CO_3 (M = Mo, W) systems at 1173 K and $i_c = 8 \times 10^{-2}$ A cm^{-2} (anode: graphite)

Concentration of components /wt %			Composition and nature of cathode deposits
Na_2MoO_4	Na_2WO_4	Na_2CO_3	
5.0	–	–	Coating, Mo
10.0	–	–	Nonadherent deposit, Mo, MoO_2
–	–	10.0	Amorphous carbon
5.0	–	1.5	Coating, Mo–Mo_2C
5.0	–	2.0–4.0	Coating, Mo_2C
5.0	–	4.0	Nonadherent deposit, Mo_2C–C
–	10.0	–	Coating, W
–	10.0	–	Nonadherent deposit, W, W_2C
–	5.0	0.2	Coating, W_2C–W
–	5.0	0.2–0.5	Coating, W_2C
–	5.0	1.0	Nonadherent deposit, WC–C

deposition rate was to 10 μm h^{-1}, current efficiency for the coatings was to 40% and the thickness up to 20 μm.

The microhardness of Mo_2C is 1800–1900 kgf mm^{-2} and that of W_2C is 2900–3100 kgf mm^{-2}. As a result of the electroplating the wear resistance of steel specimens increased five to ninefold, and their abrasion resistance four to six fold.

6. Electrochemical synthesis of chromium, molybdenum and tungsten silicides from halide–oxide melts

Thermodynamic analysis and voltammetric measurements [31–34] have shown that HES of silicides and borides of group VIA metals can be carried out only under kinetic conditions. The process involves the following sequential stages: (i) deposition of more electropositive component (Mo and W in the elementary form, Cr as Cr_2O_3); (ii) deposition of the other component on the surface of predeposited oxide or metal; and (iii) reaction diffusion of silicon or boron into the bulk metal–salt 'precipitate' to form silicide and boride phases of different compositions up to higher silicides and borides (MSi_2 and MB_4).

The electrosynthesis of chromium silicides was conducted in the KCl–KF–K_2SiF_6–K_2CrO_4 system. Both the individual phases Cr_2O_3, Cr_3Si and $CrSi_2$ and their mixtures with a small silicon content were obtained, depending on the composition and electrolysis variables (Table 5).

In the selection of CrO_4^{2-} and SiO_2 concentrations (K_2SiF_6) it should be taken into account that the Cr_2O_3-salt 'precipitate' is formed initially. This starts to be silicized as the refractory metal is generated. In contrast to the electrosynthesis of Mo and W carbides and borides, one of the components is deposited in non-elementary form, as an oxide, whereas the other component acts as a reducer for this oxide.

Table 5. Phase composition of products obtained by electrolysis of the KCl–KF 25 wt % K_2SiF_6–1 wt % SiO_2–K_2CrO_4 system (T = 900 K, U = 3–4 V)

K_2CrO_4 /wt %	Duration of electrolysis /min			
	5	*15*	*30*	*60*
0.5	Cr_3Si, Si	Cr_3Si, $CrSi_2$	$CrSi_2$	$CrSi_2$, Si
1.0	Cr_3Si	Cr_3Si, Si	Cr_3Si, $CrSi_2$	$CrSi_2$, Si

Table 6. Time dependence of the phase composition of electrolysis products for the NaCl–Na_3AlF_6–Na_2MoO_4–SiO_2 system (T = 1173 K, i_c = 1.0 A cm^{-2})

Melt composition /wt %	Duration of electrolysis /min				
	10	*20*	*30*	*45*	*60*
NaCl–49, Na_3AlF_6–49, Na_2MoO_4–1, SiO_2–1	Mo	Mo Mo_3Si_5	Mo_3Si_5 $MoSi_2$	$MoSi_2$	$MoSi_2$ Si

The electrosynthesis of molybdenum and tungsten silicides was carried out from the molten NaCl–Na_3AlF_6–Na_2MO_4–SiO_2 system (where M is Mo, W). The first stage of electrolysis involved the formation of the metal–salt 'precipitate'. The process of silicon decomposition started with the formation of an oxysalt of the refractory metal. When the temperature decreased below 1123 K, complete interaction between Mo (W) and Si did not occur. With increasing temperature (above 1223 K) the stability of metal–salt 'precipitate' decreases, and silicides are not formed. At the optimum composition of the melt, the pure binary silicides $MoSi_2$ and WSi_2 are obtained at $i_c = 0.5$–1.2 A cm^{-2} and $i_c = 0.5$–1.5 A cm^{-2}, respectively. At $i_c = 0.5$, the desired product had free metal impurity; at $i_c =$ 1.2 A cm^{-2}, the $(Al, Si)_2Mo$ phase of the binary silicide appeared in the molybdate-containing melt. The specific surface of the powders was 5–15 m^2 g^{-1}, and the particle size 0.5–2.0 μm. The yield of $MoSi_2$ was 0.2–0.3 g A^{-1} h^{-1}, and that of WSi_2 was 0.3–0.45 g A^{-1} h^{-1}.

Since silicides are formed under reaction diffusion conditions, the duration of the process markedly affects the composition of the products obtained (Table 6). For disilicides, MSi_2, to be obtained in the pure form, the cathode-salt 'precipitate' is leached with hot 10% solution of H_2SO_4. To remove silicon from the silicides, the deposit is treated with 10% NaOH solution, if necessary.

7. Electrochemical synthesis of chromium, molybdenum and tungsten borides from halide–oxide melts

Comparing the electrodeposition potentials of Cr [31], Mo [32] and W [33] from chloride–cryolite melts containing sodium chromate (molybdate, tungstate) with those of electroreduction of boron oxyfluoride

Table 7. Phase composition of electrolysis products for the NaCl–Na_3AlF_6–10 wt % B_2O_3–0.5 (1.0) wt % K_2CrO_4 system (T = 1123 K, U = 3 4 V)

Concentration /wt %	Duration of electrolysis /min				
	5	*15*	*30*	*45*	*60*
0.5	Cr_2B	Cr_2B, CrB	Cr_2B, CrB, CrB_4	CrB, CrB_4	CrB_4
1.0	Cr_2O_3, CrB_2	Cr_2B, CrB	CrB	CrB_4	CrB_4, B

Table 8. Dependence of phase composition of electrolysis product on process duration for the NaCl–Na_3AlF_6–MO_3–B_2O_3 (M–Mo, M) system (T = 1223 K, U = 4.0 V)

Melt composition /wt %	Duration of electrolysis /min				
	5	*10*	*20*	*30*	*45*
NaCl–39.5, Na_3AlF_6–39.5, MO_3–1.0, B_2O_3–20.0	M	M, MB	M, MB, M_2B_5	MB, M_2B_5, MB_4	MB_4

complexes [35], it can easily be concluded that it is impossible to achieve the coelectroreduction of metal and boron. The difference in potentials is to 0.7–0.8 V. These data provide evidence for the electrosynthesis of borides under kinetic conditions. The electrochemical synthesis of chromium borides was carried out from the molten NaCl–Na_3AlF_6–K_2CrO_4–B_2O_3 mixture. Both individual phases (Cr_2O_3, Cr_2B, CrB, CrB_4) and their mixtures were obtained depending on the melt composition and electrolysis parameters (Table 7). In contrast to HES of molybdenum and tungsten borides, Cr was deposited as Cr_2O_3, but not in elementary form, whereas B is the reducer of this oxide. The yield of the single-phase product of the composition CrB_4 was 0.14–0.21 g A^{-1} h^{-1}, the specific surface of powders was 8–17 m^2 g^{-1}. The electrochemical synthesis of molybdenum and tungsten was carried out from the molten NaCl–Na_3AlF_6–Na_2MO_4(MO_3)–B_2O_3($Na_2B_4O_7$) mixture. Optimization of the process consisted in the determination of conditions for producing higher borides MB_4, a compound with the most useful physico-mechanical properties. The optimum concentration of MO_3 or Na_2MO_4 amounted to 0.75–1.5 wt %. At higher concentrations, complete boration of the refractory metal deposited does not occur due to the instability of the metal–salt ‘precipitate’. In the 10–20 wt % range of B_2O_3 and $Na_2B_4O_7$ concentrations, complete boration of the refractory metal and formation of the MoB_4 and WB_4 phases occur.

Of essential importance in the electrosynthesis of borides is temperature. At $T = 1073$ K the interaction between Mo(W) and B does not go to completion, whereas at $T = 1123$ K the stability of the metal–salt ‘precipitate’ decreases, and borides are not formed.

It was noted that of potentiostatic and galvanostatic electrolysis, the former is preferable because it is potential that determines the course of the reactions and the nature of the deposition reaction. For the graphite anode and bath voltage $U = 2.5$ V, the cathode deposit consisted mainly of metallic molybdenum and tungsten. At $U = 2.5$–3.5 V, a mixture of various phases (M, M_2B, MB and M_2B_5) is obtained. At $U = 3.5$–4.5 V, the cathode deposit was higher boride MB_4.

The duration of the process in electrolytes of optimum composition, temperature and bath voltage exert a considerable effect on the composition of the cathode deposit (Table 8). For pure borides to be obtained it is necessary to conduct the procedures described above for silicides.

The yield of the single-phase products MoB_4 and WB_4 is 0.2–0.3 g A^{-1} h^{-1} and 0.3–0.45 g A^{-1} h^{-1}, respectively. The specific surface of the MoB_4 and WB_4 powders is 5–15 m^2 g^{-1}.

8. Conclusion

On the basis of the thermodynamic analysis of the chemical and electrochemical reactions that provide the foundation for high temperature electrochemical synthesis, possible variants, systems and conditions were determined for the electrosynthesis of carbides, silicides and borides of chromium, molybdenum and tungsten. Within the thermodynamic regime, the electrosynthesis of molybdenum and tungsten carbide powders was performed from halide–oxide melts under excess carbon dioxide pressure and from tungstate–molybdate–carbonate oxide melts. Within the kinetic regime the electrosynthesis of the powders of silicides and borides of chromium, molybdenum and tungsten was performed. Oxide and halide–oxide electrolytes were developed for electroplating with molybdenum and tungsten carbides.

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