Russian Chemical Reviews **64** (2) 125–132 (1995)
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UDC 541.135; 546.26

Modern problems in the high-temperature electrochemical synthesis of the compounds of Group IV – VI transition metals

V I Shapoval, V V Malyshev, I A Novoselova, Kh B Kushkhov

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Abstract. The present state of research in the field of high-temperature electrochemical synthesis of the carbides, borides, and silicides of Group IV – VI metals in ionic melts is reviewed. Modern problems in electrochemical synthesis and possible future developments are discussed. The results of recent studies of high-temperature electrochemical synthesis are reported. The bibliography includes 103 references.

I. Introduction

An increasing interest in the development of new and effective methods of preparing high-melting compounds (the carbides, boride, and silicides of Group IV – VI metals) has been stimulated by the ever increasing number of applications of these compounds in modern technology. A comparative analysis of currently available methods of synthesis of quasimetallic high-melting compounds (QHC) showed that the high-temperature electrochemical synthesis (HES) in ionic melts,[1] though inadequately investigated to date, is one of the most promising methods.

The HES of quasimetallic high-melting compounds is based on multielectron processes leading to the electrodeposition of metals and nonmetals from ionic melts.[2–4] Lack of information on the theoretical basis and on the controlling principles of both the multielectron processes and the HES had initially prevented the practical application of electrosynthesis methods. This explains the original lack of interest in these methods. However, the systematic data on the multielectron processes leading to the deposition of high-melting metals and nonmetals obtained during the last two decades have provided a scientific basis and understanding which have stimulated an increasing interest in the problems of HES.[2,5–21]

V I Shapoval, V V Malyshev, I A Novoselova Institute of General and Inorganic Chemistry of the Ukrainian National Academy of Sciences, prosp. Palladina 32/34, 252680 Kiev, Ukraine. Fax (7-044) 444 30 70
Kh B Kushkhov Department of Physical Chemistry, Kabardino-Balkarsk State University, ul. Lenina 34, 260017 Nal'chik. Fax (7-866) 222 15 85

Received 7 July 1994
Uspekhi Khimii **64** (2) 133–141 (1995); translated by J I Carasso

II. Methods of high-temperature electrochemical synthesis

1. Variants of the method of high-temperature electrochemical synthesis

The high-temperature electrochemical synthesis of QHC is based on the simultaneous or the sequential generation of multielectron electrochemical reactions resulting in the formation and deposition of the required product (carbide, boride, silicide) on the cathode. It should be noted that the presence of electronic conduction in the deposited compound is a necessary condition for the realisation of electrochemical synthesis.

There are two methods of achieving HES.[1] In the first variant the molten electrolyte contains one of the components in a molecular or an ionic form which is discharged on the electrode (consisting of the other component). The species to be discharged is either a compound of carbon, silicon, or boron which can be reduced to the elemental state on a high-melting metal cathode (electrochemical carbidisation,[22,23] silicidation,[24,25] boridation[26–28]) or an oxyanion of a high-melting metal which is reduced to the metal on a graphite cathode.[29,30] All these processes are slow even at relatively high temperatures, and they yield only compounds of variable composition in the form of coatings.

In the second variant the electrolyte contains both components, which are discharged simultaneously or sequentially on an indifferent electrode: the discharge products can then react chemically. Both theoretically and practically this variant seems more promising than the first, because it allows QHC of the required composition to be produced, either as coatings or as finely divided powders, simply by varying the electrolysis conditions (composition and temperature of the electrolyte, and current density).

2. Synthesis of the carbides of high-melting metals

The electrochemical synthesis of molybdenum and tungsten carbides was first reported by Andrieux and Weiss,[31] who obtained powders of the carbides by electrolysing a melt of composition $LiF-NaBO_2-Na_2CO_3-MO_3$ (where M = Mo, W). The stoichiometric composition of the deposited powders depended on the $[CO_3^{2-}]:[MO_3]$ concentration ratio.

The further development of the HES of carbides involved the choice of new electrolyte compositions. The conditions used in the synthesis of high-melting metal carbides are shown in Table 1. It is noteworthy that in every case the molten mixtures invariably contained fluoride, borate, or carbonate components. The high-melting metal was introduced as an oxide or as an alkali metal oxy-salt.

Table 1. Electrochemical systems and conditions for the HES of the carbides of high-melting metals.

Electrolyte	Component with high-melting metal	Component with carbon	Electrolysis parameters		T/K	Cathodic product	Ref.
			U/V	$10^{-2}i_k$/A m^{-2}			
$LiF-NaBO_2$	WO_3, MoO_3	Na_2CO_3	3		1050–1100	WC, W_2C (Mo_2C)	31
$NaF-KF-Na_2B_4O_7$	Na_2MoO_4	Na_2CO_3		86	1300	Mo_2C	32
$NaCl-NaF-NaOH-B_2O_3$, ($NaBO_2$, $Na_2B_4O_7$)	Na_2WO_4	Graphite anode		10–150	1300	WC	33
$NaF-KF-Na_2B_4O_7$	Ta_2O_5, Nb_2O_5	Na_2CO_3	0.3–0.8		1100	TaC, NbC	34
$LiF-NaF-KF$	K_2TaF_7	K_2CO_3	0.4–0.9		1023–1073	Ta_2C	34
$NaF-KF$ $LiF-NaF$ $LiF-KF$ $LiF-NaF-KF$	K_2TiF_6, R_2HfF_6, K_2ZrF_6, K_2NbF_7, K_2TaF_7, K_2CrF_6 K_3MoCl_6	K_2CO_3	1.5		973–1023	Cr, Mo, W, Nb, Ta, Ti, Zr, Hf carbides	35–41
$LiF-NaF-KF$	Na_2WO_4 or tungsten anode	K_2CO_3	1.0–1.5	2–7	973–1023	W_2C	39, 40, 45
$LiF-KF$	K_2SiF_6	Li_2CO_3		3–5		SiC	45
$LiF-NaBO_2$	K_2SiF_6	Na_2CO_3		3–5		SiC	45

An interesting method of preparing metal carbides was disclosed in an American patent.[33] Its most important feature is the omission of carbonate ions from the melt, using a dissolvable graphite anode as the source of carbon. However, the potential use of this method is limited by anodic effects on the carbon electrode and by the corrosiveness of the molten medium.

In an attempt to extend the method[33] to other carbides it was noted[36] that if the fluorides were thoroughly dried the graphite anodes did not lose mass, and no carbides were formed. This was attributed[36] to the fact that carbon can react electrochemically with the melt only in the presence of water, and therefore a variant of the HES of carbides based on the Mellors–Senderoff method was proposed.[41–49] The following are its most characteristic features: the electrolyte contains only fluoride anions; the proportion of alkali metal cations varies from 15% to 75% of the total number of cations; the melt does not contain complex formers.

These requirements are satisfied by the ternary LiF–NaF–KF eutectic. By adding potassium carbonate and oxides or halides of the high-melting metal to it, Stern and coworkers[35–40] obtained coatings of the carbides of Group IV–VI metals. However, it is doubtful whether the carbonate ion and the fluoride complexes K_2TaF_7, K_2NbF_7, K_2CrF_6, K_2TiF_6, K_2ZrF_6, and especially K_3MoCl_6 are compatible and can coexist with a LiF–NaF–KF melt. Indeed, in a later paper[44] Stern describes only the preparation of tungsten carbide using Na_2WO_4.

It has been reported[45] that silicon carbide (SiC) can be deposited electrolytically from a $NaF-KF-K_2SiF_6-Li_2CO_3$ melt in the form of powders, coatings, or dendrites.

Only one attempt to develop theoretical foundations for the electrochemical synthesis of carbides has been reported.[36] However, the mechanism of these processes was not discussed in sufficient depth.

3. Synthesis of the silicides of high-melting metals

The HES of silicides was first achieved by Dodero,[46] who synthesised the silicides of titanium, zirconium, and chromium by the electrolysis of molten mixtures of Na_2SiF_6 and K_2SiF_6 with the oxides and fluorides of titanium, zirconium, and chromium.

$TiSi_2$ was synthesised by the electrolysis of an $NaCl-KCl-K_2SiF_6-K_2TiF_6$ melt.[47] These workers[47] studied the cathodic processes involved in the deposition of $TiSi_2$ from chloride–fluoride melts.

The electrodeposition of Group IV–VI silicides from a melt containing a eutectic mixture of alkali metal fluorides, silicon (in the form of potassium silicofluoride), and the high-melting metal (in the form of its fluoride) has been described in a patent.[48] A more detailed description of the electrodeposition of tantalum silicide coatings has also been published.[49]

The conditions used in the preparation of the silicides of high-melting metals are summarised in Table 2.

4. Synthesis of the borides of high-melting metals

In 1929 Andrieux[50] described the preparation of borides by the electrolysis of molten fluorides and oxides of alkali and alkaline earth metals containing the oxides of boron and of a high-melting metal. He synthesised 17 borides, including TiB_2, ZrB_2, TaB_2, NbB_2, VB_2, and CrB_2. According to Andrieux and Barletty[51] the oxides of the high-melting metal and boron are reduced by the lithium, magnesium, or calcium initially deposited at the cathode.

More recently Andrieux and Weiss[52] reported the preparation of MoB and WB by the electrolysis of mixtures of the fluorides, oxides, and borates of alkali and alkaline earth metals containing the oxide of the transition metal.

Table 2. Electrochemical systems and conditions for the HES of the silicides of high-melting metals.

Electrolyte	Component with high-melting metal	Component with silicon	U/V	T/K	Cathodic product	Ref.
Na_2SiF_6 (K_2SiF_6)	TiO_2, ZrO_2, Cr_2O_3, fluorides Ti, Zr, Cr	Na_2SiF_6 (K_2SiF_6)	1.9–2.1	1273	$TiSi_2$, $ZrSi_2$ $CrSi_2$	46
$NaCl-KCl$	K_2TiF_6	K_2SiF_6	1.3–1.5	973	$TiSi_2$	47
$LiF-KF$	K_2TaF_7	K_2SiF_6	1.2	1023	$TaSi_2$, $TiSi_2$, $ZrSi_2$	48, 49
$NaF-KF$	K_2TiF_6					
$LiF-NaF-KF$	K_2ZrF_6					

Table 3. Electrochemical systems and conditions for the HES of the borides of high-melting metals.

Electrolyte	Component with high-melting metal	Component with boron	Electrolysis parameters		T/K	Cathodic product	Ref.
			U/V	$10^{-2} i_k$/A m^{-2}			
$M_xO_y - M_xF_y$ (M is an alkali or alkaline earth metal)	M_zO_y (M′ is a metal of Groups IV–VI)	B_2O_3	3–10	30–100	1223–1273	TiB_2, ZrB_2, NbB_2, TaB_2, Mo_2B_5, Cr_xB_y, WB	50, 51
$M_xO_y - M_xF_y$	M'_zO_y	MBO_2			1223–1323	MoB, WB	52
$CaB_4O_7 - CaF_2$	Cr_2O_3	B_2O_3			1273–1372	Cr_3B_4, CrB Cr_5B_3, Cr_2B	53
$LiBO_2 - NaBO_2$	TiO_2 $(Li, Na)_2TiO_3$	$LiBO_2$ $NaBO_2$		4–40	1123–1223	TiB_2	54–57
$Na_2B_4O_7$	M_2O_5 ($NaMO_3$, Na_2MO_6) M = V, Nb, Ta	$Na_2B_4O_7$ (B_2O_3)		0.2–20	1073–1273	M_3B_2, MB, (M = V, Nb, Ta)	58
$NaCl - KCl$	K_2TiF_6 (K_2ZrF_6)	KBF_4		10–20	973–1023	TiB_2 (ZrB_2)	59
MF	Ti (anode)	BF_3 (gas) B (anode)		1–50	810–1033	TiB_2	60
$LiF - KF$	K_2TiF_6 TiF_3	KBF_4		1–20	943–1073	TiB_2	62
$MBO_2 - MF$	TiO_2	B_2O_3			1073–1173	TiB_2	63
$NaCl - Na_3AlF_6 - - Na_2CO_3$	TiO_2	$Na_2B_4O_7$		1.5×10^4	1273	TiB_2	64, 65
$NaCl - Na_3AlF_6 - - NaOH - NaF$	$ZrSiO_4$ (ZrO_2)	$Na_2B_4O_7$		120–240	1025	ZrB_2	63, 64
$Na_3AlF_6 - NaOH$	HfO_2	$Na_2B_4O_7$		150	1323	HfB_2	65
$LiF - NaF - KF$	K_2ZrF_6 (ZrF_4)	B_2O_3		0.5–10	1023	ZrB_2	66
$K_2ZrF_6 - KBF_4$	ZrO_2	B_2O_3		10–20	873	ZrB_2	67
KF	WO_3 (MoO_3)	KBF_4			1173–1273	W_2B_5, WB (Mo_2B_5, MoB)	68

The synthesis of a series of chromium borides of different composition has also been reported.[53] These compounds were obtained by gradual changes in the Cr_2O_3 content of the fluoride–borate melts.

The HES of borides was subsequently developed in three directions: electrolysis from purely oxide melts, from purely halide melts, and from mixed oxide–halide melts. The conditions used in the preparation of the borides of high-melting metals are summarised in Table 3.

Pure oxide melts were studied by Schlain and coworkers[54–57] in the preparation of coatings of titanium boride. They used melts of alkali and alkaline earth metal borides with added titanium oxide. Titanium or sintered TiB_2 were used as anodes. The TiB_2 anode offered more stable electrolysis conditions. The rate of deposition of the coatings was between 20 and 220 μm h^{-1}.

A method of preparing coatings of vanadium, niobium, and tantalum borides has been disclosed.[58] The authors suggest the use of a purely oxide melt based on borates: the bath was made of graphite or heat-resistant steel, the anode was the body of the bath or an electrode made of graphite, heat-resistant steel, or an alloy of vanadium, niobium, or tantalum.

Another patent[59] claims the electrodeposition of titanium and zirconium diborides (though the method is equally applicable to other borides) from the fluoride–chloride melt $NaCl - KCl - K_2TiF_6(K_2ZrF_6) - KBF_4$. A method of preparing coatings of TiB_2 by the electrolysis of molten salts using a soluble anode or an anode of pure boron in the presence of BF_4^- ions (introduced as gaseous BF_3 has also been disclosed.[60] The composition of the bath must include an alkali metal fluoride. A method of depositing TiB_2 coatings on various items by the electrolysis of $LiF - KF - K_2TiF_6 - TiF_3 - KBF_4$ melts has been developed.[61]

The electrosynthesis of tantalum boride from the chloride–fluoride melt $KCl - K_2TaF_7 - KBF_4$ has been achieved,[62] and an attempt has been made to identify the mechanism of the process. A mixture of tantalum mono- and diboride or only one of these borides could be obtained by varying the composition of the electrolyte, the anodic current, and the cell voltage.

An analysis[63] of the current–voltage curves for the electrolytic dissociation of TiO_2 and B_2O_3 showed that the direct deposition of the boride TiB_2 from a fused borate–fluoride bath is the primary process. Substantial depolarisation of the cathodic process through the formation of TiB_2 is possible.

Another patent[64] proposes a method of synthesising the borides ZrB_2 and TiB_2 from melts of sodium chloride, fluoride, borate, and carbonate. A detailed description of the electrolytic preparation of metal diborides from their oxides and ore concentrates has also been given.[65]

A method of preparing zirconium diboride from a fluoride–oxide melt has been patented.[66] ZrF_4 can replace K_2ZrF_6 as the source of zirconium. Zirconium diboride has been prepared also from a fluoride–oxide melt containing only zirconium and boron components.[67] In this case the process is controlled by the concentration of B_2O_3 in the melt, and at high current densities metallic zirconium is deposited as well as the diboride.

Aleonard[68] extended Marion's method (described by Hagenmüller[53]) to the preparation of molybdenum and tungsten borides. He also used fluoride–oxide melts.

III. Modern problems in high-temperature electrochemical synthesis

An analysis of the state of problems in the HES of quasimetallic high-melting compounds has shown that (as a rule) electrosynthesis is carried out by a purely empirical choice of melt composition and of experimental conditions. The very small number of publications (approximately thirty) devoted to this problem is noteworthy.

Most of these publications dealt with the HES of titanium and zirconium borides, titanium silicides, and molybdenum and tungsten carbides. There are also a few unrelated papers on the preparation of tungsten and molybdenum borides, and of compounds of Group V metals. No information at all is available on the electrosynthesis of molybdenum and tungsten silicides, and of three-component high-melting compounds. However, in the whole of this work no reference can be found to the mechanism and to the controlling principles of the HES processes, without which the practical exploitation of the method is severely limited.

Because of these limitations studies in depth have been pursued in our laboratories during the past 15 years: their aim has been to create theoretical foundations for the HES and for the principles underlying the realisation and control of multielectron reactions, and to explain their mechanism. The following problems were formulated in order to achieve these objectives:

(1) to develop a thermodynamic basis for the high-temperature electrosynthesis of QHC, and to use it to identify possible variants and regimes of the electrosynthesis and to choose the components for the synthesis;

(2) to establish the mechanism of the electrolytic reduction of large complex anions of high-melting metals and nonmetals, and to develop the principles underlying the realisation and control of multielectron processes;

(3) to develop methods of approximating and identifying the conditions for reconciling the potentials of different processes for the deposition of the components;

(4) to define methods for controlling the form (powders, or coatings) of the cathodic deposits.

Table 4. Electrochemical systems and conditions for the HES of multicomponent high-melting compounds.

Electrolyte	Component with high-melting metal	Component with nonmetal	Electrolysis parameters		T/K	Cathode product	Ref.
			U/V	$10^{-2}i_k$/A m^{-2}			
KCl–NaCl–Na_3PO_4	Na_2WO_4 (Na_2MoO_4)	CO_2	2.5	5–20	1023	WC (Mo_2C)	79
KCl–NaCl–NaF	WO_3 ($Na_3WO_3F_3$)	CO_2	1.9	5–20	1023	WC (W_2C)	79
Na_2WO_4	Li_2WO_4	Li_2CO_3	1.8	100–170	1073–1173	WC	81
	Li_2MoO_4	Li_2CO_3	1.7	100–170	1073–1173	Mo_2C	81, 82
NaCl–LiF	Na_2MoO_4 (Na_2WO_4)	Na_2CO_3		100–1000	1073	Mo_2C (W_2C)	83, 84
KCl–KF	K_2CrO_4	K_2SiF_6 (SiO_2)	3–4		1173	Cr_3Si, $CrSi_2$	85, 89
NaCl–Na_3AlF_6	Na_2MO_4 (M = Mo, W)	SiO_2	3–4	1000	1173	M_3Si_5, MSi_2 (M = Mo, W)	86, 87
	K_2CrO_4	B_2O_3	3–4	100–300	1173	Cr_2B, CrB, CrB_4	89
	Na_2MO_4 (MO_3) (M = Mo, W)	$Na_2B_4O_7$ (B_2O_3)	3.5–4	100–300	1173	MoB_4, WB_4	90
NaCl–KCl–NaF	$TiCl_3$	KBF_4		50–150	963–1123	TiB_2	91, 92
	K_2ZrF_6	KBF_4		30–120	963–1123	ZrB_2	91
NaCl–KCl	K_2TaF_7	KBF_4		5–20	973–1023	TaB_2	95
NaCl–KCl–NaF	K_2TaF_7	K_2SiF_6		200–400	1073–1173	Ta_2Si_5	96
$Na_2B_4F_7$	Fe–M anode (M = V, Nb, Ta)	$Na_2B_4O_7$		2	1173	VB, NbB_2, TaB_2	97
NaCl–Na_3AlF_6	Na_2MO_4 (M = Mo,W)	SiO_2		130–250	1173	$M(Al,Si)_2$	98
KCl–NaCl–$MgCl_2$	Na_2MoO_4	$CoCl_2$	1.0–1.1		1023	Co_3Mo	101
KCl–NaCl–$NaPO_3$	Na_2MoO_4	$CoCl_2$ ($NiCl_2$)	1.1		1023	Co_3Mo (Ni_3Mo)	101
KCl–NaCl	Na_2MoO_4 $Na_2Mo_2O_7$	$CoCl_2$ ($NiCl_2$)	1.1		1023	Co_3Mo (Ni_3Mo)	101
	Na_2WO_4 $Na_2W_2O_7$	$CoCl_2$ ($NiCl_2$)	1.1–1.2		1023	Co_3W (NiW)	102
KCl–NaCl–NaF	$Na_3WO_3F_3$	$CoCl_2$	1.2		1023	Co_3W	102
KCl–NaCl–$MgCl_2$	Na_2MoO_4	CO_2 $CoCl_2$	1.3		1023	Co_6Mo_6C, Mo_2C	101
KCl–NaCl–$NaPO_3$	Na_2MoO_4	CO_2, $CoCl_2$	1.2		1023	Co_6Mo_6C, Mo_2C	101
KCl–NaCl	Na_2WO_4 $Na_2W_2O_7$	CO_2, $CoCl_2$	1.3		1023	W_2C, WC Co_3W_3C	102
	Na_2WO_4 $Na_2W_2O_7$	PO_2 $NiCl_2$	1.2		1023	W_2C, WC Ni_6W_6C	102
KCl–NaCl–NaF	WO_3	CO_2, $CoCl_2$	1.1		1023	Co_3W_3C	102
	WO_3	CO_2, $NiCl_2$	1.1		1023	WC, W_2C, Ni_6W_6C	102

The high-temperature electrochemical synthesis of QHC can take place in two regimes: the thermodynamic (or quasi-equilibrium) or the kinetic regime. According to a theoretical analysis of the electrochemical preparation of alloys[5] the thermodynamic regime is established when the deposition potential of the components are similar ($\Delta U \leqslant 0.2$ V). Under these conditions the composition of the alloy is independent of the current density over a wide range. In the opposite case ($\Delta U > 0.2$ V) we meet the kinetic regime, and the composition of the alloy is independent of the potential difference. In order to deposit carbides, borides, and silicides with a greater interaction energy the range of values of the potential for the thermodynamic regime is increased by G_f/zF, where G_f is the Gibbs free energy of formation of the QHC from the elements in their standard state; z is the total number of electrons contributing to the electrosynthesis of the QHC (for Mo_2C this number is $z = 16$).

The thermodynamic foundations of the HES of quasimetallic high-melting compounds and of the choice of systems for the synthesis were established by an analysis of the equilibrium potentials (voltages) for the decomposition of various compounds of high-melting metals of Groups IV–VI and of nonmetals (C, B, Si) at high temperatures (900–1200 K), using thermodynamic data obtained for these compounds.[69,70] Bartlett and Johnston[71,72] carried out a similar analysis of electrochemical processes involving the carbonate ion and carbon dioxide.

A comparison of the temperature dependences of the deposition potentials of the Group IV–VI metals and of carbon, boron, and silicon shows that those of the high-melting metals of Group IV are similar to those of boron and silicon, with a corresponding similarity between the deposition potentials of the high-melting metals of Group VI and carbon. Under these conditions the electrolysis can be carried out in the thermodynamic regime. The electrochemical synthesis of the carbides of Group VI metals and of the borides and silicides of Group VI metals is possible only in the kinetic regime, because in these systems the deposition potentials are markedly different.

A comparative study of the results obtained in studies of the elecrochemical reduction of the oxy-anions of high-melting metals and nonmetals in chloride, chloride, fluoride, and oxide melts having different acid–base properties has revealed three mechanisms for the formation of electrochemically active species:[2,3,73] the cationisation of an anion with formation of cationised species, the breakdown of an oxy-anion with formation of oxide–halide complexes, and the formation of dimeric complexes.

By constructing electrochemically active species of different structure and composition we can generate conditions enabling multielectron electrochemical processes to be realised. This approach allows us to control the rate of formation of these species in multielectron systems and the potential of the charge transfer reaction, to reconcile the potentials of different processes, and to achieve the HES of quasimetallic high-melting compounds.

Problems arising in the electrochemical synthesis of quasimetallic high-melting compounds are currently being studied by workers from various countries.[4,34,39,44,94]

The results of those workers, and those obtained by the present writers, on the electrochemical synthesis of quasimetallic high-melting compounds from various salt systems are discussed below. The compositions of the systems examined, the experimental conditions, and the compositions of the products in the HES of carbides, silicides, and borides, and also of double carbides, are shown in Table 4.

IV. High-temperature electrochemical synthesis of multicomponent high-melting compounds

1. Synthesis of molybdenum and tungsten carbide powders under an excess pressure of carbon dioxide

The potential application of the HES method can be extended by using carbon dioxide (whose concentration in the melt can be controlled by an excess pressure) as a source of carbon for the synthesis. This allows us to produce a buffer molten electrolyte based on low-melting alkali metal chlorides and having prescribed acid–base properties [cationised[74] $\{M_x^{2+}[M'O_4^{2-}]\}^{2x-2}$, dimeric[75,76] $M'_2O_7^{2-}$, fluoride oxide[77] $M'O_2F_4^{2-}$ (where M′ = Mo; W, M = Li^+, Ca^{2+}, Mg^{2+}, Al^{3+})], and to obtain a direct electrochemical synthesis of carbides in the presence of an excess pressure of carbon dioxide. The effects of the electrolyte composition, of the CO_2 pressure over the melt, of the temperature, of the cathodic current density, and of the design and materials of the electrodes on the phase composition and on the properties of the carbide powders thus obtained have now been established.[74,76] The reactions which provide the foundations of the HES and the special technological features of the process have been described.[74,78] We have developed a new design of electrolysis cell which can be used at 973–1073 K and under an excess pressure of CO_2 of up to 2×10^6 Pa. The specific surface of the powders was 6–10 $m^2\ g^{-1}$. The rate of deposition of WC in an NaCl–KCl–Na_3PO_4 electrolyte was 0.2–0.4 g $A^{-1}\ h^{-1}$ with a current yield of up to 56%; in a KCl–NaCl–NaF electrolyte the corresponding parameters were 0.35–0.52 g $A^{-1}\ h^{-1}$ and up to 75% respectively (see Table 4).[79]

2. Synthesis of highly dispersed powders of molybdenum and tungsten carbides from oxide melts

The low solubility of CO_2 in halide oxide melts allows us to work at low current densities (i_k) and to produce particles with diameters of 2–5 μm. Smaller particles (< 2 μm) can be obtained in tungstate–molybdate–carbonate oxide melts by increasing i_k. The electrolytic reduction of the CO_3^{2-}, MoO_4^{2-}, and WO_4^{2-} ions in a melt of Na_2WO_4 takes place at low potentials.[75,79] This allows their simultaneous reduction, and therefore also the HES of the carbides. The specific surface of the powders is 10–20 $m^2\ g^{-1}$, the yield of product is 0.71 g $A^{-1}\ h^{-1}$, and the current yield is 93%–97%.

Graphite or vitreous carbon are used most effectively as anode material; nickel as cathode material. Highly dispersed powders often contain up to 5–7 mass% of free carbon and sorbed oxygen. Annealing the synthesised molybdenum and tungsten carbide powders in activated hydrogen almost completely eliminates the free carbon (from 7 to 0.1 mass%) and lowers the oxygen content by an order of magnitude (from 5 to 0.2–0.3 mass%).[80] The crystal lattice parameters of the monocarbide WC prepared in this way ($a = 2.906 \pm 0.003$; $c = 2.837 \pm 0.006$ Å) coincide with the accepted values.

3. Electrodeposition of molybdenum and tungsten carbide coatings from oxide and halide oxide melts

One advantage of HES over other methods of synthesis is its suitability for the production of coatings. The electrodeposition of Mo_2C coatings was achieved[75,79] from the purely oxide melt Na_2WO_4–Li_2MoO_4–Li_2CO_3. In this system the MoO_4^{2-} and CO_3^{2-} ions can be reduced simultaneously by electrolytic reduction. The experimental melts are stable, nontoxic, and nonhygroscopic, and do not require a protective atmosphere. Continuous oxides were obtained at 1073–1223 K and current densities between 10^2 and 10^3 A m^{-2}. The rate of deposition of the coating was 5–20 μm h^{-1}, the current yield of the product was up to 60%, its thickness was up to 50 μm (see Ref. 81).

The main shortcoming of oxide melts is the high concentration of tungsten and molybdenum. A eutectic NaCl–LiF melt was used in order to lower the concentration, and the deposition potentials of molybdenum, tungsten, and carbon were

determined for this medium.[82,83] The deposition potential of molybdenum from MoO_4^{2-} was 200 mV higher than the deposition of tungsten from WO_4^{2-}, and almost equal to the deposition potential of carbon from CO_3^{2-}. This accounts for the possibility of depositing coatings of Mo_2C and W_2C. The crystallisation of WC as a continuous coating could not be achieved. The rate of deposition of W_2C and Mo_2C was up to 10 μm h^{-1}, the current yield as a coating was up to 40%, the thickness up to 20 μm. The microhardness of Mo_2C was 1800–1900, that of W_2C ws 2900–3100 kg mm^{-2}.

An interesting study[84] of the effect of silver ions on the electrodeposition is relevant to the control of the structure of tungsten carbide coatings prepared from halide–oxide melts. It was established that the addition of 10^{-3} mol% of AgCl to a melt of the LiCl–KCl eutectic containing K_2CO_3 and K_2WO_4 produces [at $i_k = (2-50) \times 10^2$ A m^{-2}] hexagonal crystals of the carbides W_2C and WC instead of the needles and dendrites obtained in the absence of AgCl.

4. Synthesis of chromium, molybdenum, and tungsten silicides from halide–oxide melts

A thermodynamic analysis combined with voltammetric measurements showed that the HES of the silicides of Group VI metals can be achieved only in the kinetic regime, in which the more electropositive component (Cr_2O_3, Mo, W) is deposited first, and the other component (Si) is next deposited on its surface.[85–88] The diffuse reaction path leads to the formation of silicides of various compositions, up to the highest (MSi_2).

The $KCl-KF-K_2SiF_6-K_2CrO_4$ system has been used for the high-temperature electrochemical synthesis of chromium silicides. Depending on the composition and on the electrolysis parameters both individual phases (Cr_3Si and $CrSi_2$) and mixtures of these phases (with a small amount of free silicon) could be obtained.[85,89]

The electrochemical synthesis of molybdenum and tungsten silicides has been achieved in a molten chloride–cryolite mixture containing molybdate (or tungstate) and silica.[86,87] The HES is strongly influenced by the temperature and by the current density. Below 1123 K the reaction of the molybdenum (or tungsten) with the silicon does not go to completion, and at higher temperatures (>1223 K) the stability of the metallic salt deposit decreases. When $i_k < 5.6 \times 10^3$ A m^{-2} the product is contaminated by free metal, and when $i_k > 1.2 \times 10^3$ A m^{-2} a phase of the double silicide $(Al,Si)_2M$ appears (where M = Mo, W). The specific surface of the powders is 5–15 m^2 g^{-1}, the particle size is 0.5–2.0 μm, the rate of deposition of $MoSi_2$ is 0.2–0.3, that of WSi_2 is 0.3–0.45 g A^{-1} h^{-1}.

5. Synthesis of chromium, molybdenum, and tungsten borides from halide–oxide melts

The large difference between the electrodeposition potentials of chromium,[85] molybdenum,[86] and tungsten[87] from a chloride–cryolite melt containing sodium chromate (molybdate, tungstate) and the deposition potentials of the oxide fluoride complexes of boron[89] from the same systems, which can be as high as 0.7–0.8 V, suggests that the HES of the chromium, molybdenum, and tungsten borides can be carried out only in the kinetic regime. The electrochemical synthesis of chromium borides was achieved from a chloride–cryolite melt containing chromate and boron oxide.[89] Depending on the composition of the melt and on the electrolysis parameters both the individual phases (Cr_2B, CrB, CrB_4) and their mixtures could be obtained. The yield of the single-phase product CrB_4 was 0.14–0.21 g A^{-1} h^{-1}, the specific surface was 8–17 m^2 g^{-1}.

The electrochemical synthesis of molybdenum and tungsten borides was achieved from a molten chloride–cryolite mixture containing molybdenum (or tungstate) or molybdenum (or tungsten) oxide, and borax (or boric oxide).[90] The synthesis process was optimised by establishing the regimes leading to the production of the single-phase higher boride MB_4, which offers the most valuable physical and mechanical properties. At concentrations of B_2O_3 and $Na_2B_4O_7$ between 10 and 20 mass% complete boridation of the high-melting metal is observed, with formation of the MoB_4 and WB_4 phases. The yield of these products is 0.2–0.3 and 0.3–0.45 g A^{-1} h^{-1} respectively, and the specific surface of both powders is 5–15 m^2 g^{-1}.

6. Synthesis of titanium, zirconium, and hafnium borides from halide melts

The possible use of chloride and chloride–fluoride melts (containing not more than 10 mass% of fluoride) for the HES of titanium and zirconium borides has been studied.[91] It was found that the formation of MB_2 on the cathode (where M = Ti, Zr) is accompanied by a substantial energy effect [?overpotential. (Ed. of Translation)] of 0.32 for TiB_2 and 0.38 V for ZrB_2 (at 973 K). The potentials at which the synthesis takes place depend on the difference between the reduction potentials of the components, i.e. on the form of the electrically active species. In the BCl_3-TiCl_4, MBF_4-MTiF_6, $MBF_4-M_2TiF_6$, BCl_3-ZrCl_4, MBF_4-ZrCl_4, and $MBF_4-M_2ZrF_6$ systems (in a melt of KCl–NaCl) the difference between the deposition potentials of the high-melting metal and of boron is not more than 0.2 V. The HES conditions are chosen by varying the cation/anion composition of the electrolyte. By changing the electrolysis parameters we can obtain titanium and zirconium diboride powders having surface areas between 1×10^3 and 5×10^4 m^2 kg^{-1}, or continuous coatings up to 20 μm thick (see Table 4). The quality of the coatings is improved by carrying out the process in the refining regime with a MB_2 anode. The mechanism of the cathodic processes taking place during the HES of titanium diboride has been examined in detail.[92]

It was found[93] that the HES of hafnium diboride is possible only in the thermodynamic regime. In addition to the waves produced by the electrolytic reduction of the complexes of tervalent boron with quadrivalent hafnium, a wave at potentials more positive than the discharges of BF_4^- and HfF_6^{2-} by 0.1 and 0.35–0.4 V respectively was observed in a voltammetric study of the $NaCl-KCl-KBF_4-K_2HfF_6$ system. It was tentatively attributed to complex species: heteronuclear complexes produced by the interaction of the complexes of hafnium(IV) and boron(III). Coatings of hafnium diboride having a microhardness of 3200 ± 250 kg mm^{-2} were produced in this study.

7. Synthesis of the borides and silicides of vanadium, niobium, and tantalum from halide melts

It has been shown[94] that the borides of Group V metals can be prepared by HES from chloride–fluoride melts. Thermodynamic calculations led to the conclusion that the borides of the vanadium subgroup are characterised by a kinetic synthesis regime from chloride and fluoride melts. The conditions and regime for the synthesis of TaB_2 from chloride–fluoride melts and the potential regions for the deposition of tantalum, boron, and tantalum diboride have been determined[95] as a function of the activity of the fluoride ion in the melt. It was concluded from voltammetric measurements that conditions consistent with the thermodynamic synthesis regime can be achieved by varying the anion composition of the electrolyte (see Table 4).

The conditions and the regime of the synthesis of powdered Ta_5Si_3 from chloride–fluoride melts and the deposition potentials of Ta, Si, and Ta_5Si_3 have been determined[96] as a function of changes in the acid–base properties of the melt. It was concluded from voltammetric measurements that the thermodynamic synthesis regime applies in this case.

The electrodeposition of the borides of elements in the VA subgroup is described in a patent.[97] The method combines the following procedures: preparation of the borate melt, saturation of the melt with compounds of the elements from the VA subgroup by anodic dissolution of Fe–M alloy anodes (where M = V, Nb, Ta), and cathodic treatment of the articles to be coated. VB, NbB_2, and TaB_2 coatings were produced.

8. Electrochemical synthesis of the double silicides of molybdenum (or tungsten) and aluminium

When chloride–cryolite melts are electrolysed to deposit the disilicides of molybdenum and tungsten increasing the current density produces deposits of the double disilicides $M(Al, Si)_2$, where M = Mo, W.[98] If the chloride–cryolite melt contains more than 1.5 mass% of Na_2MO_4 the product contains molybdenum (or tungsten) disilicide and metallic molybdenum (or tungsten). If the concentration of Na_2MO_4 is less than 0.5 mass% some free silicon appears in the product, and in the concentration range $0.5 < [Na_2MO_4] < 1.5$ mass% silicon–aluminium alloys are formed. Depending on the current density the specific surface of the disilicide powders lies in the range 11.3–15.2 $m^2\ g^{-1}$ (see Table 4).

9. Synthesis of two-component intermetallic compounds based on molybdenum(tungsten) and cobalt(nickel)

Construction materials and coatings based on the high-coercivity wear and corrosion resistant W–Co, W–Ni, Mo–Co, and Mo–Ni alloys have recently stimulated wide interest. They are usually prepared by electrodeposition from aqueous solutions.[99] However, this method has several shortcomings: the concentration of nonmetals (O_2, N_2, H_2) in the final product is high, the rate of deposition is low ($i_k \leqslant 1 \times 10^3$ A m^{-2}), and alloys of constant composition cannot be obtained. The use of melts avoids these shortcomings.

Nickel and cobalt are much more noble (electropositive) than molybdenum and tungsten. Furthermore, to achieve the HES of intermetallic compounds based on molybdenum(tungsten) and cobalt we must find a method of bringing their deposition potentials closer together, and conditions compatible with their simultaneous discharge. This can be done by controlling the electrolytic reduction potential of the $[MO_4^{2-}]$ anions through acid–base interactions. We used the cationisation of the oxide complexes $\{M'_x[MoO_4^{2-}]\}^{2x-2}$ (where $M' = Ba^{2+}$, Ca^{2+}, Mg^{2+}), which are decomposed with formation of dimeric [75,76] and halide oxide complexes.[100] In the case of the Mg^{2+} cation it is possible to superpose the electrolytic reduction waves of Co^{2+} and $\{Mg_x[MoO_4^{2-}]\}^{2x-2}$ and to bring the deposition potentials of cobalt and tungsten to within 300 mV of each other (see Refs 100 and 102). Better results were obtained for the decomposition of $[MO_4^{2-}]$, in which the corresponding processes can be exactly superposed.[101,102]

These studies led to the choice of three systems for the synthesis of binary alloys based on molybdenum and two systems for tungsten alloys (see Table 4).

10. Synthesis of three-component hard alloy compositions

In powder metallurgy cobalt and nickel powders, which act as a binder component, are added to the charge when articles of molybdenum or tungsten carbide are made by hot pressing. This fact, and other unique properties of the ternary alloys, stimulated the search in the $WO_3–CO_2–CoCl_2$ system[102] for conditions which allow the simultaneous electrodeposition of carbon, tungsten(molybdenum), and cobalt(nickel), aimed at the HES of binary carbides. From the results of a study[103] of the electrolytic reduction of CO_2 dissolved in halide melts under an excess pressure systems for testing the possibility of bringing together the deposition waves of carbon from CO_2, of cobalt(nickel) from the $[MCl_4]^{2-}$ complex, and of molybdenum(tungsten) from various complex ionic forms were chosen. The simultaneous deposition of three components [carbon, molybdenum(tungsten), and cobalt(nickel)] was realised in systems with differences in discharge potential not greater than 200 mV. In the latter case the CO_2 acts not only as a source of carbon but also as an acidic additive which shifts the molybdenum(tungsten) deposition potential towards more positive values.

The compositions of the liquid electrolytes and the conditions for the synthesis are summarised in Table 4. In all the systems potentiostatic electrolysis is applied, at the potentials corresponding to the simultaneous deposition of the three components. A pure binary carbide was obtained only in one system. The yield of the single-phase product Co_3W_3C is 0.4–0.6 g $A^{-1}\ h^{-1}$, the particle size is 0.3–1.0 μm. Evidently the composition of the three-component alloy and its purity are determined by several factors: the ratio of the partial currents of the reacting components, the energetics of their interaction, and the possibility of parallel reactions between two components. The latter reactions are responsible for the presence of impurities of high-melting metal carbides.

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