

Electrochemical Behaviour of Molybdenum(VI) and Tungsten(VI) Oxoanions and High-Temperature Electrochemical Synthesis of Molybdenum and Tungsten Carbides*

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The possibility of realizing multielectron processes of tungsten electroreduction from dimeric forms in the narrow potential range and of controlling process potential by means of melt acid-base properties is shown. Conditions of bringing together the reduction potentials of carbon dioxide and dimeric forms have been found. It has been shown that the direct electrochemical synthesis of molybdenum and tungsten carbides under excessive carbon dioxide pressure is possible in principle.

Refractory metal carbides can be successfully produced as fine powders by high-temperature electrochemical synthesis (HTES) from ionic melts. This method may compete with other known methods for the synthesis of fine powders, and be of interest in powder metallurgy [1–3].

The possibility of obtaining carbide powders by electrolysis in molten media was first reported by *Andrieux* and *Weiss* [4]. They produced powders of molybdenum and tungsten carbides by the electrolysis of the $\text{Na}_2\text{B}_2\text{O}_7\text{—Na}_2\text{CO}_3\text{—LiF—MO}_3$ melt (M is Mo or W). The further development of HTES method was primarily associated with the selection of new bath compositions [5–9]. The fact is noteworthy that in all cases the molten mixtures invariably contained a carbonate, fluoride, and boride component, that are aggressive and difficult to separate from the deposit.

However, it was impossible to effect electrosynthesis in practice due to the complexity of the process and the lack of clear ideas of electrode processes involving refractory metal and carbon compounds. It was not until the late 1970s that certain ways of solving the problem of refractory metals carbides HTES began to show thanks to works of *Baraboshkin*, *Delimarskii*, *Ivanovskii*, *Shapoval*, *Senderoff*, *Brenner*, and *Mellors* [10–16] in the field of theory and practice of refractory metals and nonmetals electroplating.

Analysis of literature data on carbonate ion electroreduction from ionic melts [17, 18] showed that the electrochemically active species (ECAS) is carbon dioxide, which is formed by thermal dissociation of CO_3^{2-} . This fact together with the known method [17] for producing amorphous carbon by electrolysis of chloride—carbonate melts under excessive carbon dioxide pressure led us to the idea that carbides can

be obtained from nonaggressive tungstate—chloride melts under excessive carbon dioxide pressure.

Shapoval et al. [19] showed theoretically and experimentally for the first time that the necessary condition for effecting carbides HTES from ionic melts is the closeness of potentials of carbon and refractory metal deposition from different ionic (molecular) species. To confirm that this approach is correct, the electrochemical behaviour of each carbide component must be studied (determination of discharge potential range, partial currents, the mechanism of electrode processes, and the methods of decreasing the difference between discharge potentials).

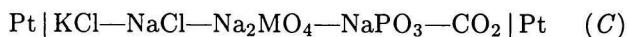
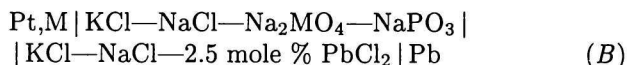
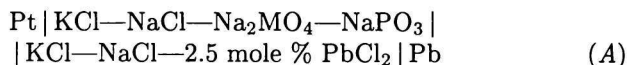
The electrochemical behaviour of CO_2 in the KCl—NaCl—CO_2 melt was studied by us earlier [20]. In a pure chloride melt potentials of Mo and W deposition from oxoanions are by 0.6–0.8 V more negative than the potential of C deposition from carbon dioxide. To bring them into coincidence, strong acceptors of oxygen ions (for example PO_3^-) must be added to the melt.

Therefore, the aim of this study was to determine conditions for carrying out multielectron processes of molybdenum and tungsten deposition and the simultaneous electroreduction of molybdenum, tungsten, and carbon dioxide as well as to develop on this basis basically new method for the HTES of fine molybdenum and tungsten carbide powders.

EXPERIMENTAL

We studied the effect of PO_3^- metaphosphate ions on the electrochemical behaviour of oxoanions W(VI) and Mo(VI) at 1023 K in the following systems

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where M is Mo or W.

Lead reference electrode was half-element $\text{KCl—NaCl—2.5 mole \% PbCl}_2 | \text{Pb}$ separated from electrolyte by the asbestos partition. To contact with the liquid lead the tungsten wire was used. In the cell denoted B the left electrode was a piece of Mo or W hung on a platinum wire.

Two electrochemical methods were used: voltammetry and potentiometry. The voltammetric investigation of systems (A) and (B) with half-immersed electrodes was carried out in cells with reagents and on devices described in Ref. [21], and that of system (C) with reagents and on devices described in Ref. [20]. EMF of systems (A) and (B) was measured with high-resistance voltmeters. Sodium dimolybdate and ditungstate were obtained by fusing oxide and oxosalt in an equimolar ratio at 1173 K and tested by the X-ray diffraction method.

RESULTS

Electrochemical Behaviour of Mo(VI) and W(VI) Oxoanions in Chloride—Metaphosphate Melts

Molybdate and tungstate ions MO_4^{2-} are not ECAS's in chloride melt as supporting electrolyte (Fig. 1, curve 2). When PO_3^- ions are added to tungstate—chloride melts two waves appear in voltammograms (Fig. 1, curve 3) at potentials of $-(0.1\text{—}0.2)$ V and $-(0.3\text{—}0.5)$ V against a $\text{Pb} | \text{Pb}^{2+}$ reference electrode. An increase of PO_3^- concentration within the limits of the $0.01 < [\text{PO}_3^-]/[\text{MO}_4^{2-}] < 0.18$ ratio leads to an increase in the second-wave current, the first-wave potentials and currents being unchanged (Fig. 1, curve 4). The dependence of the second-wave current on NaPO_3 concentration is rectilinear (Fig. 2). The product of potentiostatic electrolysis at the above potentials is molybdenum or tungsten powder.

An increase in acid additive concentration above $[\text{PO}_3^-]/[\text{MO}_4^{2-}] > 0.18$ leads to an increase in the first-wave current, a stretching of the second wave along the potential axis and then to its bifurcation (Fig. 1, curve 5). The product of potentiostatic electrolysis at the specified NaPO_3 concentrations is a mixture of powders of Mo (W) and its phosphides.

Cyclic voltammograms ($\Delta E^{C-A} = 0.550\text{—}0.630$ V $\gg 0.047$ V = $3.2RT/6F$) and the dependence of the second-wave half-peak potential on electrode polar-

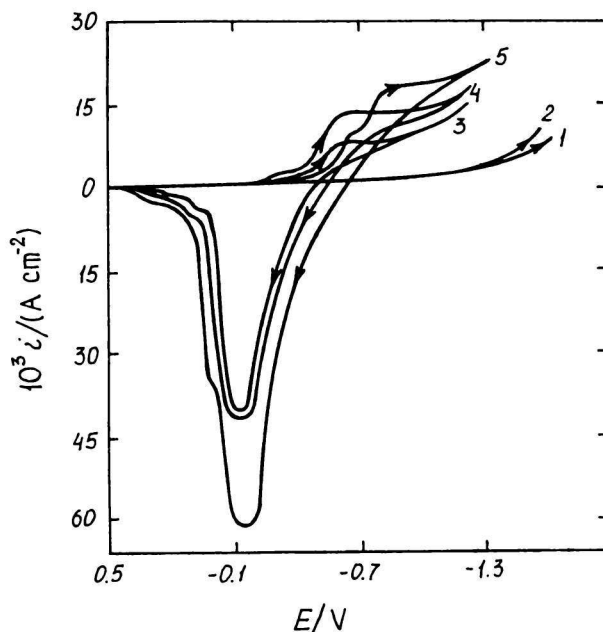


Fig. 1. Voltammograms of K,Na/Cl melt (1), with 5×10^{-4} mol cm^{-3} Na_2WO_4 (2) and after successive addition of NaPO_3 4×10^{-5} mol cm^{-3} (3), 6×10^{-5} mol cm^{-3} (4), and 1×10^{-4} mol cm^{-3} (5). $T = 1023$ K, cathode — Pt, polarization rate -0.1 V s^{-1} .

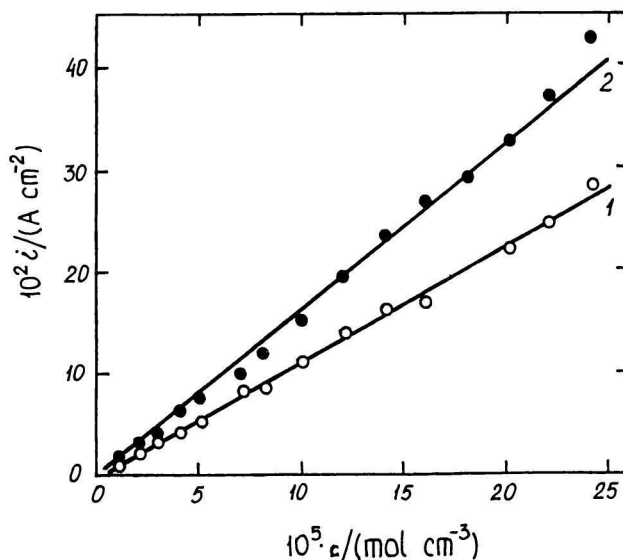


Fig. 2. Dependence of wave of limiting current of $\text{W}_2\text{O}_7^{2-}$ (1) and $\text{Mo}_2\text{O}_7^{2-}$ (2) electroreduction on NaPO_3 concentration in K,Na/Cl melt. $T = 1023$ K.

ization rate indicate the electrode process to be irreversible.

To understand the essence of processes occurring on the cathode in these rather complicated systems we tried to model them. We studied the electrochemical behaviour of PO_3^- , PO_4^{3-} , $\text{M}_2\text{O}_7^{2-}$ anions and

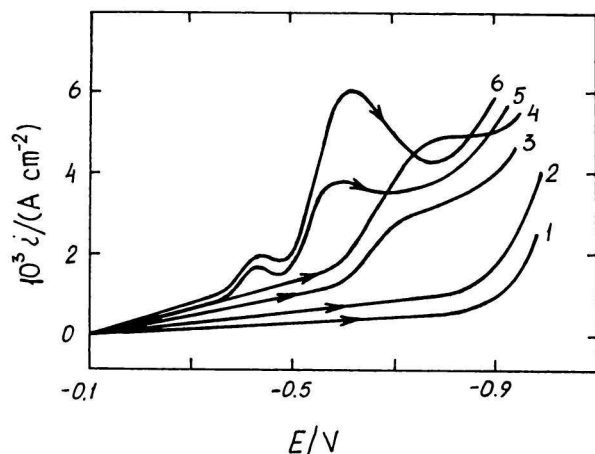
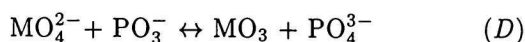


Fig. 3. Voltammograms of K,Na/Cl melt (1), with 1×10^{-4} mol cm^{-3} Na_3PO_4 (2) and after successive addition of NaPO_3 and Na_2WO_4 1×10^{-5} mol cm^{-3} NaPO_3 (3), 5×10^{-5} mol cm^{-3} NaPO_3 (4), 5×10^{-4} mol cm^{-3} Na_2WO_4 (5), and 7.5×10^{-4} mol cm^{-3} Na_2WO_4 (6). $T = 1023$ K, cathode - Pt, polarization rate - 0.1 V s^{-1}

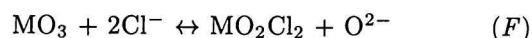
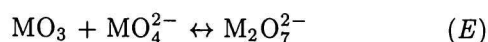
MO_2Cl_2 , MOCl_4 molecules in a chloride melt since they are involved in electrode processes.

Our assumption that dimeric ionic forms take part in electrode processes under consideration is based on the following evidence. *Raksha* [22] showed that addition of NaPO_3 to a pure tungstate melt leads to a shift of tungsten electrode potential from -1.8 to -1.0 V. It is at -1.0 V that $\text{W}_2\text{O}_7^{2-}$ ions are discharged. Their existence was proved in Refs. [23, 24] dealing with studying the ionic composition of a tungstate melt by both electrochemical and high-temperature X-ray diffraction methods.

The PO_3^- reduction wave potentials in a chloride melt as supporting electrolyte (Fig. 3, curves 3 and 4) are by 50–100 mV more negative than the second-wave potential in a molybdate(tungstate)—chloride melt. The product of potentiostatic electrolysis at the specified potentials is phosphorus. At a concentration ratio of $[\text{PO}_3^-]/[\text{MO}_4^{2-}] < 0.18$ the electrolysis of molybdate(tungstate)—metaphosphate—chloride melts gives neither phosphorus nor refractory metal phosphide. This indicates a practically complete shift of acid-base equilibrium to the right



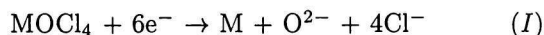
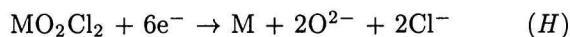
The second product of the reaction (D) - orthophosphate anion PO_4^{3-} gives no electroreduction waves in a chloride melt (Fig. 3, curve 2). MO_3 oxide formed is unstable in chloride melt at a temperature above 773 K and interacts with electrolyte anions according to one of the following schemes



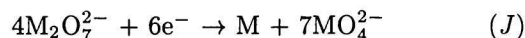
Sodium dimolybdate (ditungstate) is electroactive in chloride melt as supporting electrolyte and gives a reduction wave at potentials corresponding to the second waves in molybdate(tungstate)—chloride melts in the presence of metaphosphate ion. It should be noted that some excess of MO_4^{2-} in the melt is needed for dimeric forms stabilization. The product of the potentiostatic electrolysis of this system is molybdenum (tungsten).

When MO_3 is added to a chloride melt at a temperature above 773 K gaseous oxochlorides of refractory metal are formed. Voltammograms taken just after MO_3 addition correspond to the first-wave potentials of voltammograms for the $\text{KCl-NaCl-Na}_2\text{MO}_4\text{-NaPO}_3$ system (Fig. 1). As a result of oxochloride gas evolution the heights of these waves decrease in due course.

On the basis of the foregoing it can be suggested that the first wave of voltammograms for the $\text{KCl-NaCl-Na}_2\text{MO}_4\text{-NaPO}_3$ systems should be attributed to the discharge of oxochlorides formed by reactions (F) and (G)

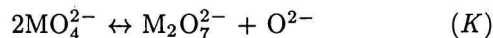


and the second wave to the discharge of dimolybdate (ditungstate) ions formed by reaction

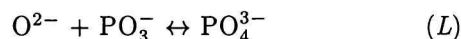


Electrochemical Behaviour of Platinum-Oxygen and Mo (W) Electrodes

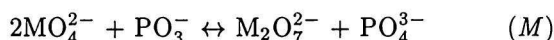
The mechanism of ECAS formation is explained in terms of ideas of the existence of acid-base equilibria in the investigated melts. When there are no PO ions, an equilibrium shifted to the left exists in the melt



Addition of the acid species PO_3^- leads to bounding of oxygen ions by the reaction



or to the overall reaction



A decrease of O^{2-} ions activity by addition of PO_3^- ions to molybdate(tungstate)—chloride melts is seen

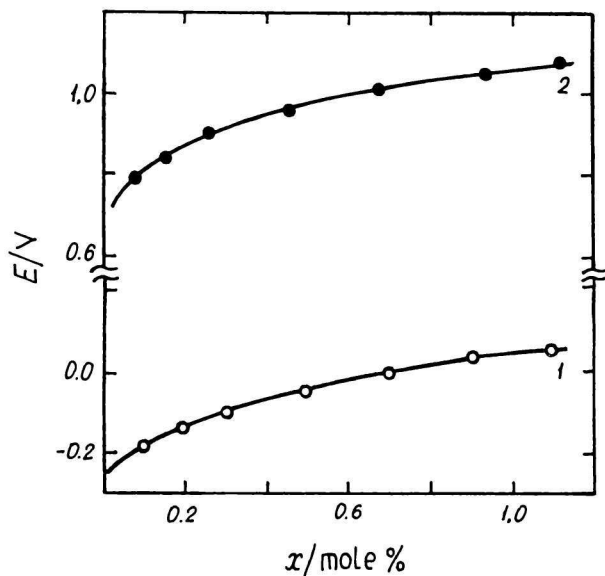


Fig. 4. Dependence of potentials of platinum-oxygen electrode on NaPO_3 concentration in K,Na/Cl melt with $3.5 \times 10^{-4} \text{ mol cm}^{-3} \text{ Na}_2\text{MoO}_4$ relatively to Pt,O|KCl-NaCl , $3.5 \times 10^{-4} \text{ mol cm}^{-3} \text{ Na}_2\text{MoO}_4$ (1) and Pb|Pb^{2+} (2) reference electrodes.

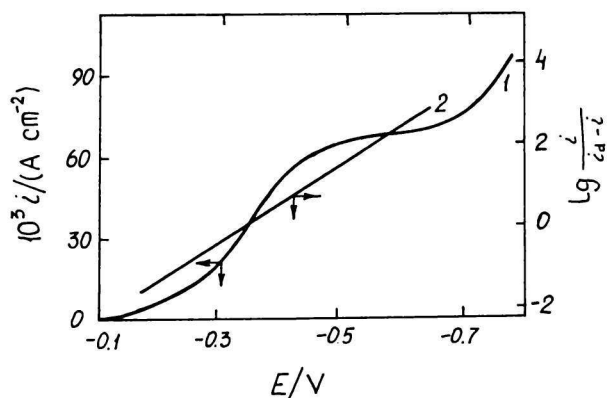


Fig. 5. Polarization of molybdenum electrode (1) and its analysis in logarithmic coordinates (2) in the KCl-NaCl melt, $5 \times 10^{-4} \text{ mol cm}^{-3} \text{ Na}_2\text{MoO}_4$ and $2 \times 10^{-4} \text{ mol cm}^{-3} \text{ NaPO}_3$ melt. $T = 1023 \text{ K}$.

from the dependence of equilibrium potentials of oxygen electrode on NaPO_3 concentration (Fig. 4). Additions of NaPO_3 shift it towards more positive values, *i.e.* decrease the oxygen activity in the melt (as follows from reaction (L)).

In the $\text{KCl-NaCl-Na}_2\text{MoO}_4\text{-NaPO}_3$ melts there is a noticeable corrosion of refractory metal. For example, it is $12.2\text{--}15.3 \text{ g m}^{-2} \text{ h}^{-1}$ at Na_2MoO_4 and NaPO_3 concentration of $1.75 \times 10^{-4} \text{ mol cm}^{-3}$ and $6 \times 10^{-4} \text{ mol cm}^{-3}$, respectively. The corrosion potential shifts towards more positive values with increasing NaPO_3 concentration. The number of electrons calculated from the $dE/d \lg \{c\}$ relation is $0.5\text{--}0.7$, which

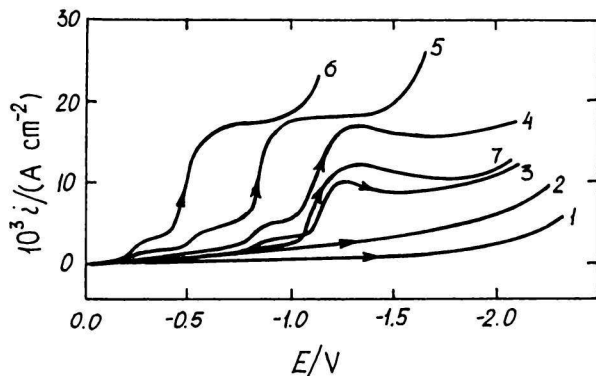


Fig. 6. Voltammograms of K,Na/Cl melt (1), with $5 \times 10^{-4} \text{ mol cm}^{-3} \text{ Na}_2\text{MoO}_4$ (2), and with $2.5 \times 10^{-4} \text{ mol cm}^{-3} \text{ NaPO}_3$ (3), under different carbon dioxide pressures in the system, $5 \times 10^5 \text{ Pa}$ (4), $10 \times 10^5 \text{ Pa}$ (5), $12 \times 10^5 \text{ Pa}$ (6), and $1 \times 10^5 \text{ Pa}$ (7). $T = 1023 \text{ K}$, cathode - Pt, polarization rate - 0.1 V s^{-1} .

is much less than 1.5 according to eqn (J).

Mo and W deposit in these melts with a noticeable overpotential (Fig. 5). Polarization curves analysis in the semilogarithmic coordinates $E, \lg(i/i_d - i)$ gives a number of d electrons transferred in the electrode process, which is much less than six (2.2–3.1). This confirms the irreversible character of electroreduction process.

Coelectroreduction of Carbon Dioxide and Dimeric Forms

Voltammograms for the coelectroreduction of CO_2 and $\text{M}_2\text{O}_7^{2-}$ in a chloride melt acidified by PO_3^- anion show, in the case of CO_2 atmosphere formation, an increase in the current of the already existing $\text{M}_2\text{O}_7^{2-}$ discharge wave (Fig. 6, curves 4–6). No extra waves were found and coexisting species are discharged in the melt at the same potentials as the individual ones, that is at potentials of $(-1.0\text{--}1.1) \text{ V}$ against platinum-oxygen reference electrode. Decrease of CO_2 pressure leads to the reproduction of initial picture of $\text{M}_2\text{O}_7^{2-}$ electroreduction both for current and for potential (Fig. 6, curve 7). The observed shift of waves along the potential axis (Fig. 6, curves 5 and 6) after increase of CO_2 pressure is coupled with the change of the reference electrode function from platinum-oxygen function to the platinum-carbonate one [19, 20].

The observed increase in $\text{M}_2\text{O}_7^{2-}$ and CO coelectroreduction wave current with CO_2 pressure in the system coincides quantitatively with the current of CO_2 reduction at a corresponding pressure (Table 1). The experimental data are in good agreement with the currents calculated theoretically from the equation

$$I = n(\text{Mo})\nu(\text{Mo})Fj(\text{Mo}) + n(\text{C})\nu(\text{C})Fj(\text{C}) \quad (1)$$

where $n(\text{Mo})$, $n(\text{C})$ are the numbers of electrons in-

Table 1. Partial Currents, Currents of Coelectroreduction of CO_2 and $\text{Mo}_2\text{O}_7^{2-}$, and Products of the Electrolysis of the $\text{KCl}-\text{NaCl}-\text{Na}_2\text{MoO}_4$ ($c = 5 \times 10^{-4} \text{ mol cm}^{-3}$)— NaPO_3 ($c = 2.5 \times 10^{-5} \text{ mol cm}^{-3}$) System under Different Pressures of Carbon Dioxide over the Melt (Polarization Rate 1 V s^{-1})

Pressure of CO_2 , $10^5 \cdot p/\text{Pa}$	0	1	2.5	5	7.5	10
Coelectroreduction currents of $\text{Mo}_2\text{O}_7^{2-}$ and CO_2 , $10^{-3} \cdot i/(\text{A cm}^2)$	17.4	18.6	20.0	22.0	23.5	25.0
Electroreduction current of CO_2 in K,Na/Cl melt, $10^{-3} \cdot i/(\text{A cm}^2)$		1	2.3	4.5	7.0	9.0
Partial electroreduction current of CO_2 , $10^{-3} \cdot i/(\text{A cm}^2)$,		1.2	2.6	4.6	6.1	7.6
$I(\text{CO}_2) = I(\text{total}) - I(\text{Mo}_2\text{O}_7^{2-})$						
Electrolysis products at -1.2 V	Mo	Mo	Mo^+ , Mo_2C	Mo_2C^+ , Mo	Mo_2C	Mo_2C

Table 2. Dependence of Phase Composition of Cathode Product Obtained by the Electrolysis of the $\text{KCl}-\text{NaCl}-\text{Na}_2\text{WO}_4$ ($x = 5 \text{ mole \%}$)— NaPO_3 ($x = 0.75 \text{ mole \%}$) Melt on Carbon Dioxide Pressure in Electrolyzer ($E = 2.5 \text{ V}$, $T = 1023 \text{ K}$)

Pressure $10^5 \cdot p/\text{Pa}$	0	2.5	5.0	7.5	10	15	17
Phase composition of products	W	W, W_2C	W, W_2C	W_2C , WC	W_2C , WC	WC, W_2C	WC*

*Single-phase powders of molybdenum carbide contain up to 4 mass % of free carbon.

involved in the discharge of $\text{M}_2\text{O}_7^{2-}$ and CO_2 , $\nu(\text{Mo}) = 2$, $\nu(\text{C}) = 1$ are the stoichiometric coefficients of interaction between products, $j(\text{Mo})$ and $j(\text{C})$ are the discharge currents of $\text{M}_2\text{O}_7^{2-}$ ions and CO_2 . Thus, a partial CO_2 electroreduction current of $5.8 \times 10^{-3} \text{ A cm}^{-2}$ is theoretically required for a partial $\text{M}_2\text{O}_7^{2-}$ electroreduction current of $17.4 \times 10 \text{ A cm}^{-2}$ in Mo_2C electrolysis. The total CO_2 and $\text{M}_2\text{O}_7^{2-}$ coelectroreduction current must be in this case 23.2 A cm^{-2} . Such conditions are attained in a CO_2 pressure range of $(7.5-10) \times 10^5 \text{ Pa}$.

Voltammograms for the coelectroreduction of CO_2 and $\text{W}_2\text{O}_7^{2-}$ in a chloride melt acidified by the PO_3^- anion show the following picture in the case of CO atmosphere generation. The CO_2 discharge potential is almost by 300 mV more positive than $\text{W}_2\text{O}_7^{2-}$ discharge potential. This results in the fact that at low carbon dioxide pressures in the cell the CO_2 and $\text{W}_2\text{O}_7^{2-}$ coelectroreduction conditions are not attained, and tungsten is reduced on carbon that has already deposited on cathode. When the excessive CO_2 pressure is increased, $\text{W}_2\text{O}_7^{2-}$ wave shifts towards positive values, and at pressure of $17 \times 10^5 \text{ Pa}$ the CO_2 and $\text{W}_2\text{O}_7^{2-}$ electroreduction waves merge into one wave stretched along the potential. Decrease of CO_2 pressure leads to the reproduction of initial picture of $\text{W}_2\text{O}_7^{2-}$ electroreduction both for current and for potential.

HTES of Molybdenum and Tungsten Carbide Powders under an Excessive Carbon Dioxide Pressure

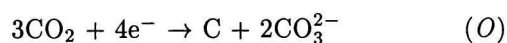
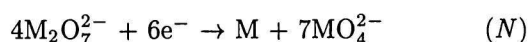
The electrochemical investigations described in the above section allowed us to purposively use the above electrolytes for the electrochemical synthesis of molybdenum and tungsten carbides. We carried out potentiostatic and galvanostatic electrolysis of the investigated melts. The cathodic product of electrolysis fell on the bottom of the crucible. After cooling down, the

melt was broken off from the body of the electrolyte, boiled in a dilute HCl solution and decanted several times with distilled water. The washed off product was identified by chemical and X-ray phase analysis. Potentiostatic electrolysis conditions were used to study the effect of CO_2 pressure in the system and the concentration of oxygen ion acceptors on the phase composition of the product.

To obtain the Mo_2C carbide phase, a CO_2 pressure of not under $7.5 \times 10^5 \text{ Pa}$ must be generated in the electrolyzer. At a less pressure the carbide product is contaminated by molybdenum and at higher pressure by free carbon (Table 1).

Electrolysis of a halide—tungstate melt at different basicities and CO_2 pressures showed that the single-phase WC product can be obtained at high gas pressures $p(\text{CO}_2) > 17 \times 10 \text{ Pa}$ (Table 2). The cathode current density ($i(c)$) varied during electrolysis within the limits of $(5-30) \times 10^2 \text{ A m}^{-2}$. The optimal composition of the electrolyte used was $x/\text{mole \%}$: $\text{NaCl} - 47.25-55.0$; $\text{KCl} - 47.25-55.0$; $\text{Na}_2\text{WO}_4 - 5.0-10.0$; $\text{NaPO}_3 - 0.5-2.0$; carbon dioxide pressure - $(16-17) \times 10 \text{ Pa}$. The NaPO_3 composition range $0.5-2.0 \text{ mole \%}$ is explained by the following. If the NaPO_3 composition is over 2 mole %, the product contains tungsten and tungsten semicarbide. If the NaPO_3 mole fraction is under 0.5 mole %, the product contains free carbon.

The HTES of molybdenum and tungsten carbides from molybdate(tungstate)—metaphosphate—chloride melts under an excessive CO_2 pressure may be schematically represented as follows



where $x = 1, 2$.

The effect of $i(c)$ on the composition of products

and on their specific surface area was studied for the KCl—NaCl—5 mole % Na₂WO₄—0.75 mole % NaPO₃ electrolyte at a CO₂ pressure of 17×10^5 Pa. The single-phase product WC was obtained at 1023 K and current densities of $(5\text{--}20) \times 10^2$ A m⁻². In this current density range, a dependence of the specific surface area of the synthesized powders W₂C and their fineness on cathode current density is observed. At $i(c) = 5 \times 10^2$ A m⁻² the specific surface area and particle size of carbide powder were 10 m² g⁻¹ and 2—5 μm, respectively. An increase of $i(c)$ up to 20×10^2 A m⁻² leads to an increase of powder surface area to 25 m² g⁻¹ and to a diminishing in powder grain size to 0.5 μm. Electrolysis at $i(c) > 20 \times 10^2$ A m⁻² yields a powdered mixture of tungsten semi- and monocarbide and tungsten as cathodic product. The electrolysis product at $i(c) < 5 \times 10^2$ A m⁻² was a mixture of tungsten semicarbide and carbon. The rate of WC deposition in the current density range under study is $(2\text{--}4) \times 10^{-1}$ g A⁻¹ h⁻¹, and the current efficiency is up to 60 %.

A single-phase powder of tungsten monocarbide WC was obtained at optimal $i(c) = 1 \times 10^3$ A m⁻² in a temperature range of 973—1073 K. We took an attempt to lower the temperature of electrosynthesis. To do this, we used low-melting electrolytes of the composition (in mole %): 58LiCl—42KCl ($T(f) = 633$ K) and 34NaCl—66CsCl ($T(f) = 769$ K) as solvent melts. The electrolysis of the above electrolytes containing Na₂WO₄ and NaPO₃ in a $[\text{PO}_3^-] = 0.2[\text{WO}_4]$ ratio under a CO₂ pressure of 15×10^5 Pa at 773—873 K yielded a mixture of lower valence tungsten oxides and carbon as cathodic product. X-Ray phase analysis at 923 K showed the presence of the WC carbide phase in the above mixture. It is evident that the chemical interaction between W and C discharge products started at temperatures not under 923—973 K.

The proper choice of electrode materials is an important prerequisite for a successful HTES. Glassy carbon or graphite is most expedient to be used as anodic material since oxygen ion oxidizing on the anode interacts with the anode to form carbon dioxide, in which the process takes place. As a cathodic material tungsten, nickel, graphite, and glassy carbon were tested. At $i(c) = 6 \times 10^2$ A m⁻², a mixture of tungsten carbide powders and the metal itself was obtained on a completely immersed tungsten and nickel cathodes. The cathodic product on a graphite and glassy carbon electrodes consisted of one phase — tungsten monocarbide — at a pressure of 17×10^5 Pa. However, the loosening of graphite cathode makes it less convenient material due to the contamination of the product by carbon.

The agreement between the experimental and tabulated interplanar spacing and relative line intensity values identified unambiguously the WC phase. The lattice parameters of WC powder were calculated on an attachment to the diffractometer N26-ChA (Zeiss,

Jena) using a standard lattice parameter computation program. Synthesized WC powder has a hexagonal lattice with the following parameters: $a = 2.8973 \times 10^{-10}$ m², $\Delta a = 0.00414 \times 10^{-10}$ m², $c = 2.8381 \times 10^{-10}$ m², $\Delta c = 0.00885 \times 10^{-10}$ m².

The shape and the size of cathode deposit particles were determined with a transmission electron microscope. Two types of particles are characteristic of powders WC — layered, loose conglomerations of 10—20 μm size and individual needle crystals of 0.5—1 μm size. The specific surface area of WC powders, determined by the method of thermal desorption of argon from the He—Ar mixture on a “Khrom-31” chromatograph is 10—25 m² g⁻¹.

The results of chemical analysis of cathodic single-phase products, which was carried out by the methods reported in [25], are

Element w/mass %	W	C(total)	C(pure)	C(bound)
	86.9 + 1	7.4 + 0.5	2.2 + 0.2	5.2

According to the data the W-fixed C ratio corresponds to the stoichiometric compound WC. Auger spectra were taken for powdered WC deposits (on a IUMP-10C Auger microprobe). The presence of the carbide phase WC and oxygen, which was not bound to a chemical compound and apparently adsorbed during air drying of the powder, was shown.

The absence of oxygen peak from Auger spectrograms after 20 min long ionic etching to a depth of 200×10^{-10} m indicates the adsorbed nature of oxygen.

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