SYNTHESIS FUNCTIONAL AND CONSTRUCTIONAL NANOMATERIALS ON A BASIS CARBIDE TUNGSTEN, MOLYBDENUM AND METALS OF A TRIAD OF IRON IN IONIC MELTS

H. B. Kushkhov, M. N. Adamokova, V. A. Kvashin, and A. L. Kardanov
Kabardino-Balkar State University, ul. Chernyshevskogo 173, Nalchik, 360004 Russia
e-mail: hasbikushchov@yahoo.com

Abstract—Single and cyclic voltammetry is used to study the electrode processes that occur during electrochemical synthesis of hard-alloy compositions based on tungsten carbide and an iron triad metal in tungstate and tungstate-carbonate Na$_2$WO$_4$–Li$_2$WO$_4$–Li$_2$CO$_3$ (5.0–22.0 wt %) melts. The conditions of bringing the electroprecipitation potentials of tungsten, carbon, and an iron triad metal into coincidence are determined.

INTRODUCTION

Methods for producing fine-grained alloys in a nanocrystalline state, where the particle sizes do not exceed 40 nm, are being actively developed [1–4]. The most promising method of forming nanostructured materials with a low sintering temperature and high strength properties (due to a fine-grained structure) is the use of nano- and submicrocrystalline carbides as alloy components [5, 6]. Plasmachemical synthesis is one of the most widely used chemical methods for producing highly dispersed nitride and carbide powders [7, 8]. The synthesis of a fine-grained tungsten carbide powder using an arc plasma generator was described in [9]. The authors of [10] considered a low-temperature gas-phase synthesis of a WC nanopowder; this is a two-step process, which includes tungsten reduction in the form of a powder from tungstic acid salts and subsequent carbonization of tungsten in a CO-containing gas mixture. A simpler one-step process of synthesizing a nanocrystalline disperse WC carbide was described in [11]. The modern technologies of producing nanocomposite WC–Co mixtures include the following sequential operations: precipitation from colloidal solutions, cryogenic spraying and drying, and carbothermic reduction. For example, an effective method for producing nanocrystalline tungsten carbide and cobalt compositions used to manufacture hard alloys is based on the coprecipitation of WC and Co precursors from colloidal solutions [12, 13]. This technology was patented as a spray conversion process (SCP) [14]. An almost ideal version of a mechanochemical synthesis, which is combined with the formation of a nanocomposite mixture, was described in [15]. An analysis of available data demonstrates that nanostructured hard-alloy WC–Co compositions can be synthesized by various methods and that the most efficient methods are based on the use of a WC–Co nanomixture rather than only nanostructured tungsten carbide.
One of these promising methods is high-temperature electrochemical synthesis of hard-alloy compositions based on tungsten carbide and an iron triad metal. At present, high-temperature electrochemical synthesis of tungsten carbides is performed in the following two fields: in the first field, a carbonate ion is used as a carbon source; in the second field, carbon dioxide is used. The contribution of the Ukrainian school of Shapoval and Kushkhov to the development of electrochemical synthesis of carbides should be emphasized in designing more efficient electrolytes for the manufacture of carbides having no hard-to-dissolve borates and fluorides of alkali metals [16–19]. High-temperature electrochemical synthesis is based on the multielectron electrochemical reactions of precipitation of hard-alloy components from an ionic melt. A necessary synthesis condition consists in bringing the electroprecipitation potentials of tungsten, carbon, and an iron triad metal into coincidence. The purpose of this work is to study the electrochemical behavior of a Na2WO4–Li2WO4–MWO4 (M = Ni, Co, Fe) melt and the possibility of combined electroprecipitation of an iron triad metal, tungsten, and carbon from oxide melts.

EXPERIMENTAL

We studied the I–V characteristics and the combined electroprecipitation of tungsten, carbon, and an iron triad metal by single and cyclic voltammetry using a PARSTAT 2273 potentiostat–galvanostat with a computer control system. As base electrolytes, we used tungstate Na2WO4 and tungstate–carbonate Na2WO4–Li2WO4–Li2CO3 (5.0–22.0 wt %) melts. Individual salts were preliminarily resolidified and then melted in an atmosphere of purified and dried argon. The sodium and lithium tungstates used as a base electrolyte had special purity grade and were preliminarily dried at a temperature of 573 K. The quality of the base electrolyte was determined by measuring the residual polarographic currents. The experiments were carried out in a three-electrode cell. As an indicator electrode, we applied a half submerged needle platinum electrode; as an anode, we used a platinum plate. A quasi-reversible platinum electrode served as a reference electrode. X-ray diffraction analysis of cathode precipitates was performed on a DRON-6 X-ray diffractometer using CuKα radiation at a wavelength of 1.54051 Å. X-ray diffraction patterns were recorded in the angular range Θ = 10°–90° at a step of 2° per minute with a diffraction angle measurement accuracy of 0.005°. To refine the lattice parameters, we repeatedly recorded some diffraction lines at a rate of 0.5°/min. The exposure time was 1 s. An elemental analysis of cathode precipitates was performed on a MAKS-GV X-ray fluorescence elemental analyzer. To determine the free carbon content in samples, we used a Multi EA 2000 CS carbon analyzer.
RESULTS AND DISCUSSION

Figure 1a shows the I–V characteristic of a Na2WO4–Li2WO4–NiWO4 melt. The introduction of the first nickel tungstate portions into the base electrolyte of sodium tungstate leads to the appearance of a small peak of a nickel ion reduction wave at a potential of −(0.5–0.6) V with respect to the platinum–oxygen reference electrode (Fig. 1a, curves 2–7). As is seen from Fig. 2 (curve 1), an increase in the nickel tungstate concentration leads to a linear increase in the current density to a concentration of $3.0 \times 10^{-4}$ mol/cm$^3$. As the nickel tungstate concentration increases, the concentration dependence of the current density of the NiWO$_4$ electroreduction peak ceases to be linear, which is explained by reaching the limiting nickel tungstate solubility in sodium tungstate and reaching the equilibrium

$$
\text{NiWO}_4 + \text{Na}_2\text{WO}_4 \leftrightarrow \text{NiO} + \text{Na}_2\text{W}_2\text{O}_7. \quad (1)
$$

As follows from the studies of the solubility of nickel tungstate in sodium tungstate, the maximum nickel tungstate concentration achievable in the given melt is about $3.0 \times 10^{-4}$ mol/cm$^3$, which corresponds to 2.5-3.0 wt %. X-ray diffraction analysis of the cathode precipitates of potentiostatic electrolysis at the potential of the end of the Ni ion electroreduction wave (−0.7 V) demonstrates the presence of only metallic nickel (Fig. 3a). We then introduced lithium tungstate into the melt to study electrochemically active W particles, namely, ions cationized by lithium ions. As is seen from Fig. 1b (curves 5, 6), the introduction of lithium tungstate leads to the appearance of a W electroreduction wave at a potential of −(1.6–1.8) V with respect to the platinum–oxygen reference electrode. The difference in the nickel and tungsten precipitation potentials in this melt is about 1.0 V. An increase in the lithium tungstate concentration to 40 mol % does not decrease the difference between the Ni and W precipitation potentials; however, an apparent shift in the entire I–V characteristic toward a positive potential region is observed, which is caused by a change in the potential of the platinum–oxygen reference electrode. X-ray diffraction analysis of the cathode precipitates formed at a potential of −(1.6–1.8) V reveals the presence of metallic Ni, W, and NiW alloy (Fig. 3b). Similarly to the study of the combined electroreduction of tungsten and nickel ions, we should first determine the solubility of cobalt tungstate in sodium tungstate in order to analyze the mechanism of combined W and Co electroprecipitation. To determine the solubility of cobalt tungstate in sodium tungstate, we also used cyclic voltammetry. The dependence of the current density of the CoWO$_4$ electroreduction on the CoWO$_4$ concentration is linear up to a concentration of $3.0 \times 10^{-4}$ mol/cm$^3$ (2.5–3.0 wt %; see Fig. 2, curve 2). The electroreduction potential of cobalt ions against the background of sodium tungstate is −(0.5–0.8) V. As is seen from the I–V characteristics (Fig. 1c), the mechanism of cobalt electroreduction against the background of sodium tungstate is irreversible, which is indicated by the shape of the I–V characteristics (which are
extended along the potential axis) and by the difference between the cathode and anode peak potentials (200–300 mV). X-ray diffraction analysis of the products of potentiostatic electrolysis at a potential of –0.7 V demonstrates the presence of metallic cobalt (Fig. 3c). An addition of lithium tungstate leads to the appearance of a tungsten ion reduction wave as a result of the formation of electrically active particles at a potential of –(1.5–1.7) V with respect to the platinum–oxygen reference electrode. Thus, excess lithium ions lead to both a shift in the I–V characteristics
Fig. 1. I–V characteristics of (a) Na$_2$WO$_4$–Li$_2$WO$_4$ melt in which NiWO$_4$ is gradually added and a Na$_2$WO$_4$ melt containing (b) NiWO$_4$ and Li$_2$WO$_4$, (c) CoWO$_4$ and Li$_2$WO$_4$, and (d) FeWO$_4$ and Li$_2$WO$_4$. Pt cathode, the polarization rate is 0.1 V/s, T = 1173 K. (a) C(NiWO$_4$) × 10^{-4}, mol/cm$^3$: (1) 0, (2) 0.5, (3) 1.5, (4) 2.0, (5) 3.0, (6) 3.5, and (7) 4.0. (b) C(NiWO$_4$) × 10^{-4}, mol/cm$^3$: (1) base curve, (2) 2.0, (3) 3.0, and (4–6) 4.0; C(Li$_2$WO$_4$), mol/cm$^3$: (1–4) 0, (5) 20.0, and (6) 40.0. (c) C(CoWO$_4$) × 10^{-4}, mol/cm$^3$: (1) base curve, (2) 0, (3) 1.0, and (4) 2.0; C(Li$_2$WO$_4$), mol/cm$^3$: (1) 0 and (2–4) 40.0. (d) C(FeWO$_4$) × 10^{-4}, mol/cm$^3$: (1) base curve, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 6.0, and (7) 8.0; C(Li$_2$WO$_4$), mol/cm$^3$: (1–7) 0, (8) 20.0, and (9) 40.0.

Fig. 2. Electroreduction peak current of (1) NiWO$_4$ or (2) CoWO$_4$ vs. the NiWO$_4$ or CoWO$_4$ concentration, respectively.

toward a positive potential range with respect to the base curve and a small (~100 mV) shift in the tungsten and cobalt precipitation potentials toward each other (Fig. 1c). The tungsten reduction current height increases with the lithium ion concentration, which is related to an increase in the concentration of electrically active particles, namely, tungsten ions cationized by lithium ions [Li$_x$WO$_4$]$^{x-2}$ (where x ≥ 2). X-ray diffraction analysis of the cathode precipitates formed at a potential of −(1.5–1.7) V demonstrates the presence of metallic W and Co$_7$W$_6$ and Co$_3$W intermetallics (Fig. 3d). The cyclic voltammetry study of the solubility of iron tungstate in a sodium tungstate melt demonstrates a higher solubility of iron tungstate in this melt (up to 1.0 × 10^{-3} mol/cm$^3$, or up to 8 wt%) as compared to nickel or cobalt tungstate (Fig. 5a). The iron ion electroreduction potential in a sodium tungstate melt is −(1.1–1.2) V with respect to the platinum–oxygen reference electrode. However, as the FeWO$_4$ concentration increases above 3.0 × 10^{-4} mol/cm$^3$, the second wave appears in I–V characteristics at a potential of −(1.2–1.4) V. As follows from the electroreduction potential of this peak, it can belong to electrically active W$_2$O$_7^{2-}$ particles (Fig. 5a, curves 6–8). The effect of excess lithium tungstate on the tungsten electroreduction processes in this melt is similar to those in the electrolytic systems with nickel and cobalt tungstates: the I–V characteristics shift toward a positive
potential range by 250–300 mV, and the electroreduction potentials of iron ions and electrically active tungsten particles move toward each other (Fig. 1d; curves 8, 9). The dependence of the current density of the FeWO$_4$ electroreduction peak on the FeWO$_4$ concentration is linear up to a concentration of $3.0 \times 10^{-4}$ mol/cm$^3$ (2.5–3.0 wt %). X-ray diffraction analysis of the cathode precipitates formed at a potential of $-(1.5–1.7)$ V demonstrates the presence of metallic W and Fe. Based on an analysis of the I–V characteristics of a tungstate melt containing the tungstate of an iron triad metal, we assume that the equilibrium in the reactions

$$\text{Na}_2\text{WO}_4 + \text{NiWO}_4 \leftrightarrow \text{Na}_2\text{W}_2\text{O}_7 + \text{NiO},$$
$$\text{Na}_2\text{WO}_4 + \text{CoWO}_4 \leftrightarrow \text{Na}_2\text{W}_2\text{O}_7 + \text{CoO},$$
$$\text{Na}_2\text{WO}_4 + \text{FeWO}_4 \leftrightarrow \text{Na}_2\text{W}_2\text{O}_7 + \text{FeO}$$

shifts toward the formation of ditungstate W$_2$O$_7^{2-}$ ions when going from nickel tungstate to iron tungstate. W$_2$O$_7^{2-}$ ions are reduced at potentials close to the reduction potential of iron ions $-(1.5–1.7)$ V, which explains the appearance of metallic tungsten in the cathode product during the electrolysis of a Na$_2$WO$_4$-FeWO$_4$ melt, in contrast to the Na$_2$WO$_4$-NiWO$_4$ and Na$_2$WO$_4$–CoWO$_4$ systems. As shown above, the cathode precipitate in the last case consists of metallic Ni and Co. Since the tungstates of the iron triad metals are relatively expensive and their synthesis is difficult, it is interesting to study the electrochemical behavior of the chlorides of Fe, Co, and Ni, which are available and cheaper as compared to their tungstates, in a tungstate melt. The results obtained demonstrate that the I–V characteristics of the chlorides and tungstates of Fe, Co, and Ni in a tungstate melt are similar, which is seen from the I–V characteristics shown in Figs. 4a, 4b, and 5b. Based on these data, we applied the chlorides of Fe, Co, and Ni for electrochemical synthesis of hard-alloy compositions based on tungsten carbide and an iron triad metal. Using the results of studying combined electroreduction of tungsten, carbon, and iron (cobalt, nickel) ions, we tried to perform electrochemical synthesis of double W–Fe(Co, Ni)–C carbides in molten systems (mol %) 51.0 Na$_2$WO$_4$–34.0 Li$_2$WO$_4$–15.0Li$_2$CO$_3$–MCl$_2$ (1.5×10$^{-4}$ mol/cm$^3$), 48.9 Na$_2$WO$_4$–32.6 Li$_2$WO$_4$–18.5 Li$_2$CO$_3$–MCl$_2$ (1.5×10$^{-4}$ mol/cm$^3$), and 46.8 Na$_2$WO$_4$–31.2 Li$_2$WO$_4$–22.0 Li$_2$CO$_3$–MCl$_2$ (1.5×10$^{-4}$ mol/cm$^3$). Electrolysis was carried out in a potentiostatic mode at low (1.0–2.0 A/cm$^2$), growing (1.0–8.0 A/cm$^2$), and high (8.0–12.0 A/cm$^2$) current densities. Table 1 presents the results of X-ray diffraction analysis and chemical analysis performed to determine the free carbon content. It follows from the data in Table 1 that 15.0 mol % is a sufficient Li$_2$CO$_3$ concentration in the 51.0 Na$_2$WO$_4$–34.0 Li$_2$WO$_4$–Li$_2$CO$_3$–MCl$_2$ (1.5×10$^{-4}$ mol/cm$^3$).
Fig. 3. X-ray diffraction patterns of the cathode precipitate formed upon potentiostatic electrolysis from a (a, b) Na₂WO₄–NiWO₄ or (c, d) Na₂WO₄–CoWO₄ melt. The cathode is made of a platinum plate, $S = 2.7 \text{ cm}^2$, $T = 1173 \text{ K}$, and the potential is $-0.7 \text{ V}$. Diffraction lines (a) (1) Ni; (b) (1) W, (2) Ni, and (3) NiW; (c) (1) Co; and (d) (1) W, (2) Co₇W₆, and (3) Co₃W.

(M = Fe, Co, Ni) system at a current density of 1.0-2.0 A/cm², 18.5 mol % is a sufficient Li₂CO₃ concentration in the 48.9 Na₂WO₄–32.6 Li₂WO₄–Li₂CO₃–MCl₂
(1.5×10⁻⁴ mol/cm³) system at a current density of 1.0–8.0 A/cm², and 22.0 mol % is a sufficient Li₂CO₃ concentration in the 46.8 Na₂WO₄–31.2 Li₂WO₄–Li₂CO₃–MCl₂ (1.5×10⁻⁴ mol/cm³) system at a current density of 8.0–12.0 A/cm². These results are supported by X-ray diffraction analysis (DRON-6 diffractometer) and an analysis for a total carbon content (multi EA 2000 CS). Using an elemental fluorescence Spektroscan MAKS-GV analyzer, we analyzed the W and M (M=Fe, Co, Ni) contents in binary tungsten and iron triad metal carbides in the samples produced by potentiostatic electrolysis in molten systems (mol %) 51.0 Na₂WO₄–34.0 Li₂WO₄–15.0 Li₂CO₃–MCl₂ (1.5×10⁻⁴ mol/cm³), 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–MCl₂ (1.5×10⁻⁴ mol/cm³), and 46.8 Na₂WO₄–31.2 Li₂WO₄–22.0 Li₂CO₃–MCl₂ (1.5×10⁻⁴ mol/cm³). The results of electron-probe fluorescence analysis of the binary tungsten carbides are given in Table 2.

**Fig. 4.** I–V characteristics of a Na₂WO₄ melt containing (a) NiCl₂ or (b) CoCl₂. Pt cathode, polarization rate is 0.1 V/s, and T =1173 K. (a) C(NiCl₂) . 10⁻⁴, mol/cm³: (1) base curve, (2) 1.0, (3) 2.0, and (4) 4.0. (b) C(CoCl₂) . 10⁻⁴, mol/cm³: (1) base curve, (2) 2.0, (3) 4.0, and (4) 6.0, and (5) 8.0.
Fig. 5. I–V characteristics of a Na₂WO₄ melt (a) added gradually by FeWO₄ and containing (b) FeCl₂. Pt cathode, polarization rate is 0.1 V/s, and T = 1173 K. (a) C(FeWO₄) × 10⁻⁴, mol/cm³: (1) base curve, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 6.0, (7) 8.0, and (8) 10.0. (b) C(FeCl₂) × 10⁻⁴, mol/cm³: (1) base curve, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 5.0, (7) 6.0, (8) 7.0, (9) 9.0, and (10) 1.3 × 10⁻³ mol/cm³.

Table 1. Results of X-ray diffraction analysis and analysis for the free carbon content in the binary tungsten carbides produced by potentiostatic electrolysis of a Na₂WO₄–Li₂WO₄–Li₂CO₃ (15.0, 18.5, 22.0 mol %)–MCl₂ (1.5 × 10⁻⁴ mol/cm³; M = Ni, Co, Fe) in the current density range 1.0–12.0 A/cm².
Table 2. Results of electron-probe fluorescence analysis of the binary tungsten carbides produced by potentiostatic electrolysis of a Na₂WO₄–Li₂WO₄–Li₂CO₃ (15.0, 18.5, 22.0 mol %)–MCl₂ (1.5×10⁻⁴ mol/cm³; M = Fe, Co, Ni) in the current density range 1.0–12.0 A/cm²

| Electrolyte composition, mol % | Current density, A/cm² | Bath voltage, V | Total carbon, % | Phase composition |
|-------------------------------|------------------------|-----------------|-----------------|------------------|
| 51.0 Na₂WO₄–34.0 Li₂WO₄–15.0 Li₂CO₃–FeCl₂ (1.5×10⁻⁴ mol/cm³) | 1.0–2.0 | 2.0–4.5 | 9.283 | WC, Fe₆W₆C |
| 51.0 Na₂WO₄–34.0 Li₂WO₄–15.0 Li₂CO₃–CoCl₂ (1.5×10⁻⁴ mol/cm³) | 1.0–2.0 | 2.0–4.5 | 7.136 | WC, Co₆W₆C |
| 51.0 Na₂WO₄–34.0 Li₂WO₄–15.0 Li₂CO₃–NiCl₂ (1.5×10⁻⁴ mol/cm³) | 1.0–2.0 | 2.0–4.5 | 6.025 | WC, NiCₓ, NiW |
| 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–FeCl₂ (1.5×10⁻⁴ mol/cm³) | 1.0–8.0 | 2.0–4.5 | 10.16 | WC, Fe₆W₆C |
| 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–CoCl₂ (1.5×10⁻⁴ mol/cm³) | 1.0–8.0 | 2.0–4.5 | 6.834 | WC, Co₆W₆C |
| 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–NiCl₂ (1.5×10⁻⁴ mol/cm³) | 1.0–8.0 | 2.0–4.5 | 8.874 | WC, NiCₓ, NiW |
| 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–CoCl₂ (1.5×10⁻⁴ mol/cm³) | 8.0–12.0 | 2.0–4.5 | 3.748 | WC, Co₆W₆C |
| 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–NiCl₂ (1.5×10⁻⁴ mol/cm³) | 8.0–12.0 | 2.0–4.5 | 4.662 | WC, Co₆W₆C |
| 48.9 Na₂WO₄–32.6 Li₂WO₄–18.5 Li₂CO₃–NiCl₂ (1.5×10⁻⁴ mol/cm³) | 8.0–12.0 | 2.0–4.5 | 3.645 | WC, Co₆W₆C |
| 46.8 Na₂WO₄–31.2 Li₂WO₄–22.0 Li₂CO₃–FeCl₂ (1.5×10⁻⁴ mol/cm³) | 8.0–12.0 | 2.0–4.5 | 5.1 | WC, Fe₆W₆C |
| 46.8 Na₂WO₄–31.2 Li₂WO₄–22.0 Li₂CO₃–CoCl₂ (1.5×10⁻⁴ mol/cm³) | 8.0–12.0 | 2.0–4.5 | 5.4 | WC, Co₆W₆C, Co₆W₆C |
| 46.8 Na₂WO₄–31.2 Li₂WO₄–22.0 Li₂CO₃–NiCl₂ (1.5×10⁻⁴ mol/cm³) | 8.0–12.0 | 2.0–4.5 | 8.255 | WC, NiCₓ, NiW |

| No. | Hard-alloy composition based on the carbide of | Current density, A/cm² | W, % | M (Fe, Co, Ni), % | C, % |
|-----|----------------------------------------------|------------------------|------|------------------|------|
| 1   | tungsten and iron                             | 1.0–2.0                | 86.335 | 0.038           | 9.283|
| 2   |                                              | 1.0–8.0                | 89.798 | 0.042           | 10.16|
| 3   |                                              | 8.0–12.0               | 94.87  | 0.040           | 5.19 |
| 4   | tungsten and cobalt                           | 1.0–2.0                | 91.576 | 1.288           | 7.136|
| 5   |                                              | 1.0–8.0                | 90.834 | 2.332           | 6.834|
| 6   |                                              | 8.0–12.0               | 84.190 | 2.320           | 13.49|
| 7   | tungsten and nickel                           | 1.0–2.0                | 90.787 | 3.188           | 6.025|
| 8   |                                              | 1.0–8.0                | 88.763 | 2.363           | 8.874|
| 9   |                                              | 8.0–12.0               | 86.086 | 5.739           | 8.255|
As it has been shown in the work [20] lithium carbonate in a tungstate melt is reduced at potential - (1.0-1.3) V. Therefore, for electrochemical synthesis of double molybdenum and tungsten carbides, management of the factors influencing for speed of allocation of carbon is required. In the researched system the concentration of Li$_2$CO$_3$ is a such factor.

At addition of lithium carbonate (fig. 6, a curve 2 and fig. 7) in tungstate-molybdate melts Na$_2$WO$_4$-Li$_2$WO$_4$ (20.0 wt %)-Li$_2$MoO$_4$ (5.0 wt %) a wave of carbonate-ions reduction coordinated with cationic of lithium is appear in the field of positive potentials - (1.1-1.3) V(fig. 7).

With increasing of lithium carbonate concentration (fig. 6, a curve 3) these waves merge in one joint carbon, molybdenum and tungsten deposition wave stretched on an axis of potentials.

At addition of lithium carbonate in tungstate-molybdate melts the form of the anodic dissolution of cathode product wave changes too. A wave of carbon dissolution is observed at potentials - (0.250-0) V with the wave of metal phase dissolution.

Proceeding from our researches on joint electroreduction of tungsten, molybdenum and carbon ions we carried out the electrochemical synthesis of double tungsten and molybdenum carbides from tungstate-molybdate-carbonate melts (a mol %) (45.0-55.0) Na$_2$WO$_4$-(30.0-37.0) Li$_2$WO$_4$-(1.0-5.0) Li$_2$MoO$_4$-(7.0-21.0) Li$_2$CO$_3$. The electrolysis was carried out at cathode current density (1.0-2.5) A/sm$^2$ with nickel cathode in graphite crucible (MPG-7) at temperature 1173 K.
The results of the electrolysis products analysis are given in Table. 3. The basic opportunity of double molybdenum and tungsten carbides synthesis by electrolysis of melted Na$_2$WO$_4$-Li$_2$WO$_4$-Li$_2$MoO$_4$-Li$_2$CO$_3$ system is follow. Thus, the concentration of molybdate and a lithium carbonate in melts are important, but their parity is more important. Besides that, the phase structure of cathode deposits are changes with increase in electricity quantity.

Fig. 6. I–V characteristics of a Na$_2$WO$_4$ melt Na$_2$WO$_4$ - Li$_2$WO$_4$ (20.0 wt %) - Li$_2$MoO$_4$ (20.0 wt %) at consecutive addition Li$_2$CO$_3$, mol %: 1 - 0, 2 - 5.0; 3 - 20.0. Pt cathode, polarization rate is 0.1 V/s, and T = 1173 K.
Fig. 7. I–V characteristics of melt Na$_2$WO$_4$ - Li$_2$WO$_4$ (20.0 wt %) - Li$_2$MoO$_4$ (20.0 wt%) - Li$_2$CO$_3$ (5.0 wt%) at various potentials, 1 - 1.8; 2 - 2.0; 3 - 2.3. Pt cathode, and T = 1173 K.

Table 3

Results of X-ray diffraction analysis of products electrolysis fused systems Na$_2$WO$_4$-Li$_2$WO$_4$-Li$_2$MoO$_4$-Li$_2$CO$_3$ at 1173 K

| Electrolyte composition, mol % | Current density, A/cm$^2$ | Duration electrolysis, min | Phase composition |
|-------------------------------|--------------------------|----------------------------|-------------------|
| 55.2 Na$_2$WO$_4$             | 2.4                      | 10                         | W$_2$C, Mo$_2$C   |
| 36.8 Li$_2$WO$_4$             | 2.3                      | 20                         | WC, MoC, W$_2$C, Mo$_2$C |
| 1.0 Li$_2$MoO$_4$             |                          |                            |                   |
| 7.0 Li$_2$CO$_3$              |                          |                            |                   |
| 55.2 Na$_2$WO$_4$             | 2.0                      | 30                         | W$_2$C, Mo$_2$C, W, Mo |
| 50.4 Na$_2$WO$_4$             | 1.9                      | 30                         | W$_2$C, Mo$_2$C   |
| 33.6 Li$_2$WO$_4$             | 1.8                      | 60                         | WC, MoC, W$_2$C, Mo$_2$C |
| 2.0 Li$_2$MoO$_4$             |                          |                            |                   |
| 14.0 Li$_2$CO$_3$             |                          |                            |                   |
| 50.4 Na$_2$WO$_4$             | 2.0                      | 70                         | W$_2$C, Mo$_2$C, W, Mo |
| 45.6 Na$_2$WO$_4$             | 2.0                      | 80                         | W, Mo             |
| 30.4 Li$_2$WO$_4$             | 2.0                      | 30                         | W$_2$C, Mo$_2$C   |
| 3.0 Li$_2$MoO$_4$             | 2.0                      | 50                         | W$_2$C, Mo$_2$C   |
| 21.0 Li$_2$CO$_3$             | 1.6                      | 70                         | W$_2$C, Mo$_2$C   |
CONCLUSIONS

By electrolysis of tungstate-carbonate melt containing iron triad metal ions, we carried out the electrochemical synthesis of hard-alloy compositions based on tungsten carbide. The processes of joint electrodeposition of tungsten, molybdenum, carbon ions and iron triad metal ions are carried out in tungstate-molybdate-carbonate melts. The structures of cathode deposits are established too.

REFERENCES

1. A. I. Gusev, “Nanocrystalline State Effects in Compact metals and Compounds,” in Nanocrystalline Materials: Production Methods and Properties (UrO RAN, Yekaterinburg, 1998), pp. 5–9.
2. A. I. Gusev and A. A. Rempel, in Nanocrystalline Materials (Nauka, Moscow, 2000), pp. 13–19.
3. A. I. Gusev and A. A. Rempel, “Nonstoichiometric Transition Metal Carbides as Alternative Hard Materials,” in Nanocrystalline Materials (Cambridge Intern. Science Publ., Cambridge, 2004), pp. 256–263.
4. A. I. Gusev, in Nanomaterials, Nanostructures, and Nanotechnologies (Fizmatlit, Moscow, 2005), pp. 5–9.
5. S. Berger, R. Porat, and R. Rosen, “Nanocrystalline Materials: A Study of WC-based Hard Metals,” Prog. Mater. Sci. 42, 311–320 (1997).
6. A. I. Gusev and A. S. Kurlov, “Hard Alloys Today and Tomorrow,” Metally Evrazii 2, 42–45 (2005).
7. T. N. Miller, Neorg. Mater. 15, 557 (1979).
8. T. Ya. Kosolapova, G. N. Makarenko, and D. P. Zyatkевич, “Plasmachemical Synthesis of Refractory Compounds,” Zh. VKhO im. Mendeleeva 24, 328–333 (1979).
9. Yu. V. Blagoveshchenskii, E. A. Danilkin, T. P. Egorikhina, and V. I. Terekhov, in Proceedings of the IV All_Russia Conference on Physical Chemistry of Ultradispersed Systems, Moscow, Russia (MIFI, Moscow, 1998), p. 274.
10. L. Gao and B. H. Kear, “Nanostructure Tungsten Carbide Catalysts for Polymer Electrolyte Fuel Cells,” Nanostruct. Mater. 5, 555–563 (1995).

11. L. Gao and B. H. Kear, “Formation of Fine Intragranular Ferrite in Cast Plain Carbon Steel Inoculated by Titanium Oxide Nanopowder,” Nanomech. Material 9, 205–211 (1997).

12. L. E. McCandlish, B. H. Kear, and B. K. Kim, “Processing and Properties of Nanostructured WC–Co,” Nanostruct. Mater. 1, 119–123 (1992).

13. L. Wu, J. Lin, B. K. Kim, et al., in Proceedings of the 13th International Plansee Seminar, Ed. by H. Bildstein and R. Ekk (Metallwerk Plansee, Reutte, 1993), Vol. 3, pp. 667–678.

14. L. E. McCandlish, B. H. Kear, and S. J. Bhatia, US Patent 5352269, 1994.

15. M. A. Xueming and J. I. Gang, “Relative Effects of All Chemical Elements on the Electrical Conductivity of Metals and Alloys: An Alternative to Norbury–Linde Rule,” Alloys J. Compd., 245–247 (1996).

16. V. I. Shapoval, Yu. K. Delimarskii, and Kh. B. Kushkhov, “Kinetic Electroreduction Currents in KCl–NaCl Melts,” Elektrokhimiya 14 (8), 1141–1145 (1978).

17. V. I. Shapoval and Kh. B. Kushkhov, “Effect of the Li⁺ Cation on the WO₄²⁻ Electroreduction Kinetics in an Equimolar KCl–NaCl Melt,” Ukr. Khim. Zh. 45 (8), 698–701 (1979).

18. V. I. Shapoval and Kh. B. Kushkhov, “Mechanism of Formation of Electrochemically Active Particles during the Electroreduction of WO₄²⁻ in a KCl–NaCl Melt,” in Electrode Processes and Investigation Methods (Naukova Dumka, Kiev, 1978), pp. 165–169.

19. Kh. B. Kushkhov, L. M. Beroeva, M. N. Adamokova, and S. Dzh. Gonov, “Combined Electroprecipitation of Tungsten, Molybdenum, and Carbon from a Sodium Tungstate Melt at an Excess Carbon Dioxide Pressure,” in Proceedings of the XII Russian Conference on the Physical Chemistry and Electrochemistry of Ionic
Melts and Solid Electrolytes, Nal’chik, Russia (Kabard.-Balkar Gos. Univ., Nal’chik, 2001), Vol. 1, pp. 249–252.

20. Kushhov H.B., Malyshev V.V., Shapoval V. I. Electroreduction of carbonate-ions in tungsten melts. (Ukr. Khim. Zh. 54, №11, 1988), pp. 1155-1158.