

Management of composition cathodic products in the electrolysis of molybdenum-, tungsten- and carbon- bearing halogenide-oxide and oxide melts

Management der Zusammensetzung der kathodischen Produkte in der Elektrolyse von molybdän-, wolfram- und kohlenstoffhaltigen Halogenidoxiden und oxidischen Schmelzen

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It is shown that the cathode products of electrolysis of melts based on a eutectic mixture of sodium chloride and lithium fluoride as well as melts based on sodium tungstate in which dissolved oxides of molybdenum (VI) or tungsten (VI), molybdate, tungstate and lithium or sodium carbonates are molybdenum, tungsten, their bronzes and carbides, carbon.

It is established that the phase composition of electrolysis products is determined by the concentration of carbonate in the melt.

Particular conditions of plating coating of molybdenum and tungsten carbides on carbon, nickel and copper materials are determined.

Molybdenum carbide coatings of electrolyte $\text{Na}_2\text{WO}_4\text{-Li}_2\text{MoO}_4\text{-Li}_2\text{CO}_3$ are deposited at equality (within 2.5 mol%) of concentrations molybdate and lithium carbonate. However, their concentrations should not exceed 10 mol%. At lower concentrations of molybdate in the precipitate are detected carbon, molybdenum, molybdenum carbide, and at high concentrations – molybdenum oxides. At lower concentrations of carbonate in the sediment dominates molybdenum and at large concentrations mainly free carbon is released. More affordable industrial reagent-source of molybdenum is its oxide.

Keywords: high-temperature electrochemical synthesis / cathode products / oxides of molybdenum (VI) / oxides of tungsten (VI) / diagram of compositions of cathode products

Schlüsselwörter: Hochtemperatur – Elektrolyse / kathodische Produkte / Molybdänoxid / Wolframoxid / Chemische Zusammensetzung der kathodischen Produkte

1 Introduction

Increased interest in the development of new and effective methods for obtaining refractory compounds

– carbides, borides, silicides, alloys and intermetallic compounds of metals of IV–VI B groups is dictated by their use for the needs of modern technology [1–4]. Comparative analysis of existing methods for the synthesis of metal-like refractory compounds showed that one of the most promising,

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but so far little studied is the method of high-temperature electrochemical synthesis [5–7].

It is based on many electron processes electrowinning of metals and non-metals from ionic melts. Lack of information about the theoretical foundations and management principles of the multi-electron processes and high-temperature electrochemical synthesis processes preclude implementation of the electrometallurgical synthesis in practice. However, accumulated at the turn of the century, systematic data on many-electron processes of electrowinning of refractory metals and non-metals, served as the scientific basis and impetus to a rising tide of interest in the problems of high-temperature electrochemical synthesis.

In this regard, the study of cathode products of halide and oxide as well as carbonaceous melts and implementation of high-temperature electrometallurgical synthesis of molybdenum and tungsten carbides based on its results are the actual problem of modern materials science.

2 Aim of the investigations

For practical use of halide and oxide carbonate melts are necessary systematic studies to identify areas of electrowinning of various electrolysis products. For coating of molybdenum and tungsten carbides, we have proposed electrolytes based on a eutectic mixture of sodium chloride and lithium fluoride or on the basis of sodium tungstate, in which are dissolved the oxides of molybdenum or tungsten (VI), molybdate, tungstate, and lithium or sodium carbonate [8–13].

The purpose of this study was to investigate the cathode products composition of the carbonaceous melts based on a eutectic mixture of sodium chloride and lithium fluoride and the melts based on a sodium tungstate depending on the conditions of the electrolysis and implementation of high-temperature electrochemical synthesis of the electroplating of molybdenum and tungsten carbides.

3 Materials and experimental details

As in the case studying the composition of the cathode products of tungstate-molybdate oxide melts, the research results can be conveniently represented

as diagrams of the cathode products composition [9–13]. Electrolyses of melts $\text{NaCl-LiF-Na}_2\text{MoO}_4$ (Na_2WO_4)– Na_2CO_3 were carried out in graphite containers of MPG-7 grade. Electrolyses of melts $\text{NaCl-LiF-Na}_2\text{MoO}_4$ (Na_2WO_4)– Na_2CO_3 were carried out in graphite containers of MPG-7 grade. The melt was prepared from pre-dried reagents NaCl and LiF of KhCh grade, Na_2MoO_4 , Na_2WO_4 and Na_2CO_3 of AR grade. The electrolyte was purified from impurities by electrolysis at a cathode current density of $10 \dots 15 \text{ A/dm}^2$ to obtain sustainable solid precipitate. Cathodes are nickel, copper; steel plates $1 \times 2 \text{ cm}$ on the nickel current lead.

Precipitations were investigated by X-ray and metallographic. Microhardness on the cross-sections was measured by the PMT-3 device under load of 100 gauss; lattice parameters – by the DRON-3 diffractometer in $\text{Cu-K}\alpha$ – radiation; coatings thickness – by the 2IGM multirev indicator, in some cases – metallographically.

4 Results

4.1 Halide and oxide melts

Diagrams of cathode products composition of the studied systems are shown in Fig. 1 and 2. Reduction wave of molybdenum from a molybdate-ion on the background of the eutectic melt NaCl-LiF on

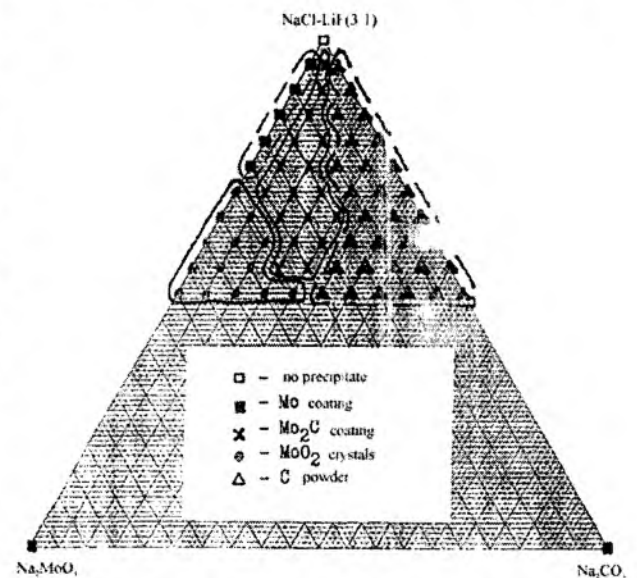


Figure 1. Diagram of compositions of cathode products of a system $\text{NaCl-LiF (3:1)-Na}_2\text{MoO}_4\text{-Na}_2\text{CO}_3$. $T = 1173 \text{ K}$; cathode – C, Ni, Cu ; anode – graphite; $i_k = (5.0 \dots 7.5) \cdot 10^{-2} \text{ A/cm}^2$

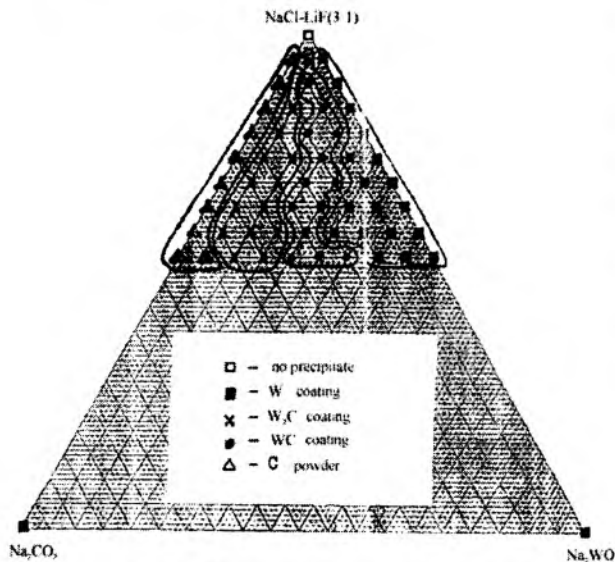


Figure 2. Diagram of compositions of cathode products of a system NaCl–LiF (3:1)– Na_2WO_4 – Na_2CO_3 . $T = 1173 \text{ K}$; cathode – C, Ni, Cu; anode – graphite; $i_k = (5.0 \dots 7.5) \cdot 10^{-2} \text{ A/cm}^2$

0.2 V more positive than the reduction wave of tungsten from a tungstate-ion, and is almost at the same potentials as the reduction wave of carbon from carbonate-ion [8]. This fact as well as the existence of molybdenum carbide only of Mo_2C composition, makes it easier to create the conditions of crystallization of molybdenum carbide as a solid precipitate. Tungsten and carbon form two carbides – WC and W_2C . Achievement of the WC crystallization as a solid precipitate is almost impossible, since WC is formed at a certain excess of free carbon. Carbon is the passivating agent of the growth front of electrolytic precipitation. Therefore, for crystallization of tungsten carbide as a solid precipitate is needed more fine process monitoring of electrosynthesis and conduct it in a mode of obtaining of W_2C [14].

Experiments at 1173 K, and a cathode current density of 8 A/dm^2 show that at the concentration of Na_2MoO_4 in the melt of not more than 15 wt%, solid precipitation of molybdenum is evolved at the cathode. At great concentration of molybdate along with molybdenum are deposited its oxides. Solid tungsten precipitations were obtained at the concentration of Na_2WO_4 in the melt of not more than 20 wt%, tungsten oxides are also coprecipitated at the larger concentration. From melts containing only carbonate, amorphous carbon powder is released.

For the deposition of MO_2C coatings was used melt containing 5 wt% Na_2MoO_4 . At the concentra-

tion of Na_2CO_3 up to 2 wt% solid precipitations of Mo– Mo_2C alloys are released at the cathode, which composition depends on the concentration of carbonate; at 2–4 wt% – continuous Mo_2C precipitations; and at higher concentrations coating is loosened by an excess release carbon.

For deposition of tungsten carbide coating was used a melt containing 5 wt% of Na_2WO_4 , when the content of Na_2CO_3 up to 0.2 wt% at the cathode are released solid precipitations of W– W_2C alloys, which composition also depends on the carbonate concentration; at concentration of 0.2 ... 0.5 wt% appear solid precipitations of W_2C , at 0.5 ... 1.0 wt% – solid precipitations of W_2C –WC; and at higher concentrations – inadherent precipitation WC–C.

To study the influence of other parameters of electrolyte on the properties and coatings structure of Mo, W, Mo_2C , W_2C are selected following optimum melts: NaCl–LiF – 5 wt% Na_2MoO_4 . (Na_2WO_4), NaCl–NaF – 5 wt%. Na_2MoO_4 – 2 wt%. Na_2CO_3 and NaCl–LiF – 5 wt% Na_2WO_4 – 0.4 wt% Na_2CO_3 . Solid precipitations are obtained at 1073–1323 K. oxides are precipitated along with metal or carbides at lower temperatures. Good adherent uniform non-porous coatings are obtained at a current density of $2 \dots 15 \text{ A/dm}^2$ and a deposition rate of $2 \dots 20 \text{ m/h}$. Current output of carbide coatings is up to $40 \dots 50\%$, their thickness – 30 micrometres. Low current output in the case of carbide coatings is caused the deposit growth front violation as a result of its passivation by the lithium oxide formed during the electrode reaction [15]. Subsequently carbides are deposited in powder form. The total current output of carbides in the form of coating and powder is close to 100%.

A coarse-crystalline structure of the resulting coatings was ground using the reverse mode of electrolysis conduction. Ratio of duration of the cathode and anode period τ_k/τ_a was changed within $30 \dots 60 \text{ s}$, duration of the anode period was $0.5 \dots 1.5 \text{ s}$, its current density was equal to $15 \dots 50 \text{ A/dm}^2$. This has resulted in increasing the thickness of metal coating up to 200 microns, and carbide up to 100 microns. Optimal parameters of the reverse mode: $\tau_k = 45 \text{ s}$, $\tau_a = 1.5 \text{ s}$, $i_k = 8 \dots 10 \text{ A/dm}^2$, $i_a = 20 \dots 30 \text{ A/dm}^2$.

4.2 Oxide melts

Besides, the halide and oxide carbonate melts for electrodeposition of molybdenum, tungsten and their carbides, tungstate-molybdate-carbonate oxide melts

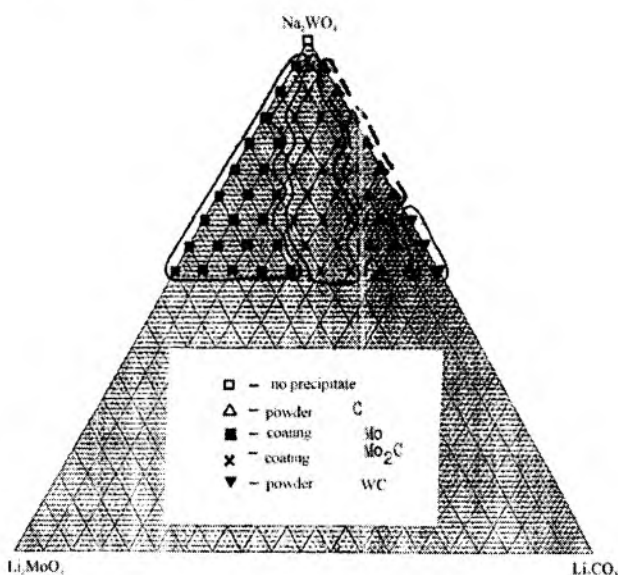


Figure 3. Diagram of compositions of cathode products of a system $\text{Na}_2\text{WO}_4\text{-Li}_2\text{MoO}_4\text{-Li}_2\text{CO}_3$. $T = 1173 \text{ K}$; cathode – C, Ni, Cu; anode – graphite; $i_k = (5.0 \dots 7.5) \cdot 10^{-2} \text{ A/cm}^2$

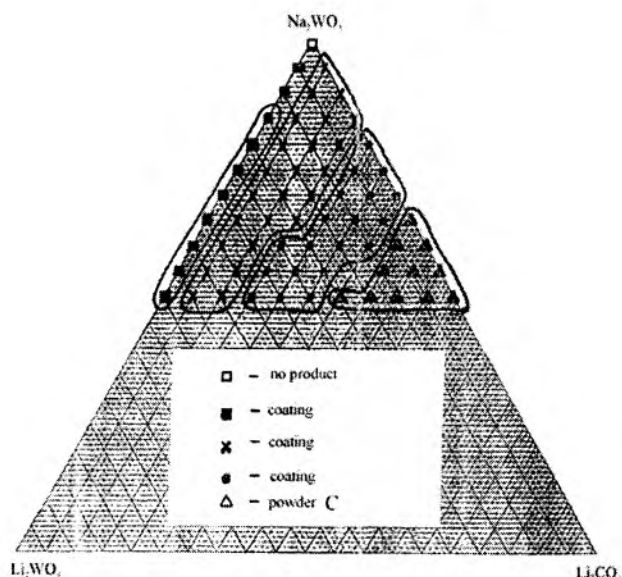


Figure 5. Diagram of compositions of cathode products of a system $\text{Na}_2\text{WO}_4\text{-Li}_2\text{WO}_4\text{-Li}_2\text{CO}_3$. $T = 1173 \text{ K}$; cathode – C, Ni, Cu; anode – graphite; $i_k = (5.0 \dots 7.5) \cdot 10^{-2} \text{ A/cm}^2$

were also used. Diagrams of cathode products composition of the studied systems depending on the electrolysis conditions are shown in Figs. 3–6.

Molybdenum carbide coatings of electrolyte $\text{Na}_2\text{WO}_4\text{-Li}_2\text{MoO}_4\text{-Li}_2\text{CO}_3$ are deposited at equality (within 2.5 mol%) of concentrations molybdate and lithium carbonate. However, their concentrations should not exceed 10 mol%. At lower concentrations of molybdate in the precipitate are de-

tected carbon, molybdenum, molybdenum carbide, and at high concentrations – molybdenum oxides. At lower concentrations of carbonate in the sediment dominates molybdenum and at large concentrations mainly free carbon is released. More affordable industrial reagent-source of molybdenum is its oxide. When used is necessary approximately twice as much carbonate than when using lithium molybdate, Fig. 4.

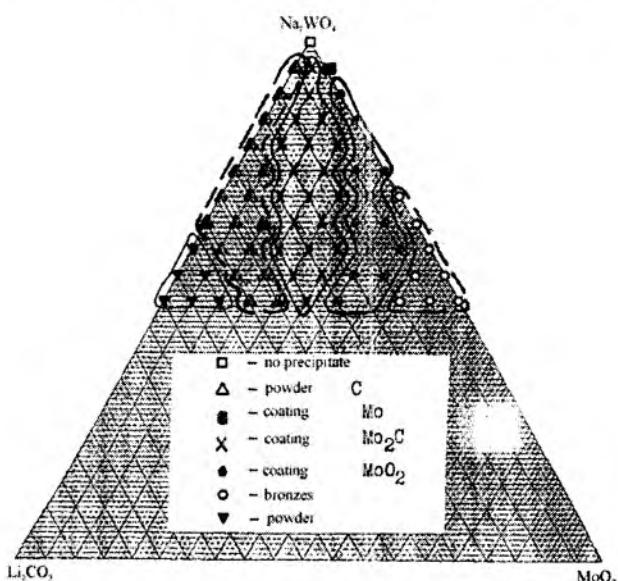


Figure 4. Diagram of compositions of cathode products of a system $\text{Na}_2\text{WO}_4\text{-MoO}_3\text{-Li}_2\text{CO}_3$. $T = 1173 \text{ K}$; cathode – C, Ni, Cu; anode – graphite; $k = (5.0 \dots 7.5) \cdot 10^{-2} \text{ A/cm}^2$

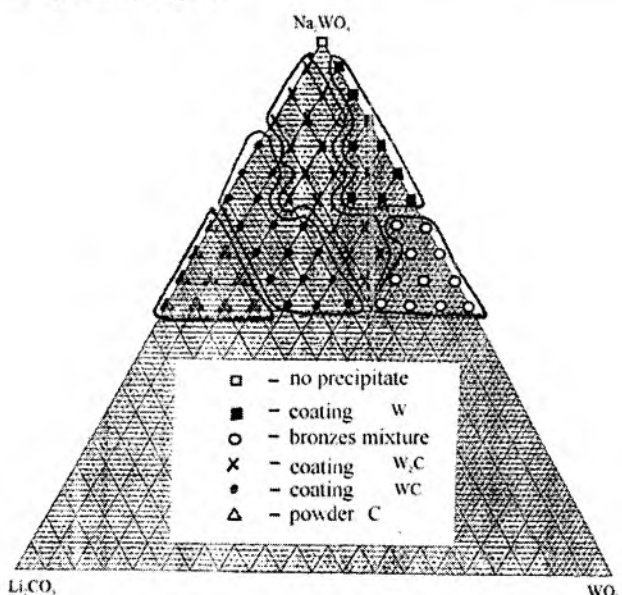


Figure 6. Diagram of compositions of cathode products of a system $\text{Na}_2\text{WO}_4\text{-WO}_3\text{-Li}_2\text{CO}_3$. $T = 1173 \text{ K}$; cathode – C, Ni, Cu; anode – graphite; $i_k = (5.0 \dots 7.5) \cdot 10^{-2} \text{ A/cm}^2$

Solid carbide coatings of molybdenum are obtained at 1073–1223 K and current densities above 0.5 A/cm². At temperatures below 1073 K and current density above 0.5 A/cm² are obtained high-dispersive powders of molybdenum carbide with a specific surface of 30 m²/h. Good coupled uniform solid nonporous coatings of electrolyte Na₂WO₄ – 5 mol% MoO₃ – 10 mol% Li₂CO₃ at 1173 K are obtained at current densities from 0.01 to 0.10 A/cm². Coating deposition speed in the studied range of current density is 5 ... 25 m/h, current output of molybdenum carbide in the form of a coating is up to 80%. Maximum coating thickness up to 100 μm.

Application of the reverse mode of electrolysis conduction allowed grinding of a coarse structure and increase coatings thickness up to 200 μm. Optimal parameters are as follows: ratio $\tau_k/\tau_a = 20 \dots 40$, duration of the anode period – 0.5–2.0 s, current density – 0.15–0.50 A/cm².

Tungsten carbide coatings W₂C from the electrolyte Na₂WO₄–Li₂CO₃ are deposited at concentrations of Li₂CO₃ up to 15 mol%. Tungsten carbide coatings WC are deposited at large values of the concentration of Li₂CO₃. Tungsten coatings are deposited at concentrations of Li₂WO₄ more than 10 mol% in the absence of lithium carbide, Fig. 5.

Observed behaviour is approximately similar during using of tungsten oxide as a source of tungsten. Separating area of sodium tungsten bronzes is observed only at concentrations of WO₃ more than 30 mol%, Fig. 6.

5 Summary

Research results of the cathode products composition molten in a systems NaCl–LiF–Na₂MoO₄ (Na₂WO₄)–Na₂CO₃ and Na₂WO₄–Li₂MoO₄ (Li₂WO₄, MoO₃, WO₃)–Li₂CO₃ have shown that for plating coating by the high-temperature electrochemical synthesis method may be offered above mentioned electrolytes. Areas of electrowinning of molybdenum, tungsten, their bronzes and carbides, carbon are identified. Data in Figs. 1–6 show that the phase composition of the electrolysis products and cathode deposits characteristics is determined by the concentration of the carbon source in the melt of the lithium and sodium carbonates.

It is shown that the cathode products of electrolysis of melts based on a eutectic mixture of sodium chloride and lithium fluoride as well as melts based on

sodium tungstate in which dissolved oxides of molybdenum (VI) or tungsten (VI), molybdate, tungstate and lithium or sodium carbonates are molybdenum, tungsten, their bronzes and carbides, carbon.

It is established that the phase composition of electrolysis products is determined by the concentration of carbonate in the melt.

Particular conditions of plating coating of molybdenum and tungsten carbides on carbon, nickel and copper materials are determined.

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Received in final form: September 1st 2014 T 331