

Influence of Electrolysis Parameters on Mo and W Coatings Electrodeposited from Tungstate, Molybdate and Tungstate-Molybdate Melts

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Molybdenum and tungsten coatings electrodeposition from halide-oxide and oxide melts has been realized. The influence of electrolysis conditions on physico-chemical properties of deposits has been studied. Coating structure control has been realized with the help of change of atmosphere composition above the bath and application of non-stationary current regimes during electrodeposition.

Keywords: tungsten, molybdenum, molten salt, refractory metals, CO₂ containing atmosphere

Refractory metals (including tungsten) have high heat resistance and hardness, and high plasticity if they have low contents of carbon, oxygen, and nitrogen impurities. Therefore they are important for modern science and engineering. Electrodeposition of refractory metals such as tungsten and molybdenum from ionic melts has many advantages from engineering point of view being much studied [1-8]. The application of tungsten coatings obtained electrochemically is one of the most popular methods of corrosion protection and enhancement of the wear and abrasive resistance as well as surface hardness of materials. Tungstate-molybdate oxide melts of general composition Na₂WO₄-MO₃ (M=Mo/W), were used by authors of some articles [9-11] for molybdenum (or tungsten) coatings electrodeposition. It was found earlier, that molybdenum and tungsten deposits, obtained by electrolyses of tungstate-molybdate melts, possess large-grains structure [12-15]. As a result, the deposits at the thickness of 100-200 μm become rough. One of the ways to decrease the roughness of deposit is by adding carbon dioxide into the atmosphere over electrolytic bath.

The purpose of the present work is to study the control on the structures of molybdenum and tungsten coatings by changing the atmosphere over the bath as well as using nonstationary current during electrolysis. The influence of electrolysis parameters on deposits composition and structure obtained from tungstate, molybdate and tungstate-molybdate melts (substrate material, composition of electrolyte, temperature, cathodic current density (i_k), time of deposition, and the reversing of current) is also investigated.

Experimental part

Experiments were performed in a hermetic electrolytic cell presented in a previous paper [16]. The Na₂WO₄-3 mol% Li₂WO₄, Na₂WO₄-5 mol% WO₃, Na₂WO₄-Li₂WO₄-10 mol% WO₃ molten mixtures were used as electrolytes. Steel 3, Ni, Cu, Ti and stainless steel 30XGA were used as substrate. The obtained coatings were investigated metallographically.

The grain size was measured by MIM8M and Hitachi 800 microscopes on cross-section at 40-50 mm from substrate. The microhardness was measured by PMT-3 device on a cross-section using 100 g weight ball applied to indenter. The texture of coatings was evidenced by DRON-2 and Rigaku X-ray diffractometers. The faceting of coating surfaces was determined by optical goniometer. Impulses of current were applied by using A-quad-B pulses generator.

Results and discussions

We have found that the changing of air atmosphere to the inert one (argon) did not influence practically on the grain size. In both cases, coatings were non-textured or possess very small amount of (111) texture. The only difference was the formation of more smooth grain on the surface when the electrolytic cell with argon atmosphere was used. Such similarity could arise because in the equilibrium of solid molybdenum (or tungsten) metal/melt the metal species exists in the form of oxygen-containing anions with the highest oxidation state, and oxygen solubility in such melts appears to be low. Therefore, air-on-argon replacing does not change the melt composition and, practically, does not influence the current efficiency.

On contrary, the addition of carbon dioxide in the electrolytic cell strongly influences the structure of molybdenum (or tungsten) deposited on steel 3 as substrate (table 1).

The size of grains decreases (fig. 1). for increasing the CO₂ partial pressure during the electrolyses of Na₂WO₄-Li₂WO₄-10 mol% WO₃ melt at 1023 K. Also, the CO₂ atmosphere leads into powdered tungsten deposits and to carbon powder codeposition on the cathode.

By temperature increasing the influence of CO₂ amount, diminishes and at 1173 K solid (compact) deposits of molybdenum and tungsten metals were obtained when over the electrolytic cell the atmosphere reaches CO₂ 100% vol.; however at the same temperature carbon appears at the steel 3 cathode (up to 1 mass %) from Na₂WO₄-WO₃ melt even using 25 vol.% CO₂ atmosphere. This could be

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Table 1

INFLUENCE OF ELECTROLYSIS CONDITIONS ON STRUCTURE OF MOLYBDENUM AND TUNGSTEN DEPOSITS FOR THICKNESS 100-150 μm

T/K	i_c , A/cm ²	CO ₂ , vol%	Texture	Grain size, μm	Type of sediment
Na ₂ WO ₄ -3 mol% MoO ₃					
1123	0.05	0	111	—	dendrites in edges
1123	0.05	25	amorphous	—	dendrite aggregates
1123	0.05	50	amorphous	—	powder Mo and C
1173	0.05	0	111	14.3	absence of dendrites
1173	0.05	25	111	12.6	dendrite aggregates
1173	0.05	50	amorphous	10.9	powder Mo and C
Na ₂ WO ₄ -5 mol% WO ₃					
1173	0.10	0	111	14.7	dendrite aggregates
1173	0.10	25	amorphous	12.3	knobbly dendrites
1173	0.10	50	100	10.1	uniform deposits
1173	0.10	100	amorphous	5.2	uniform deposits
Na ₂ WO ₄ -Li ₂ WO ₄ -10 mol% WO ₃					
1073	0.10	0	111	17.3	dendrite on edges
1173	0.10	25	amorphous	13.6	dendrite aggregates
1173	0.10	50	211	9.1	uniform deposits
1173	0.10	100	amorphous	2.5	uniform deposits
1173	0.05	0	amorphous	13.3	small dendrites
1173	0.05	25	100	9.6	uniform deposits
1173	0.05	50	100	7.8	uniform deposits
1173	0.05	100	100	1.5	uniform deposits

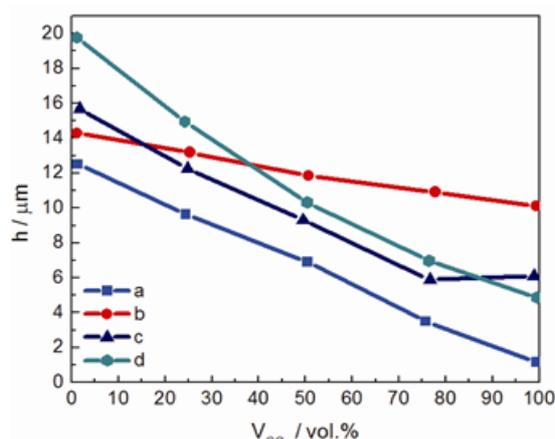
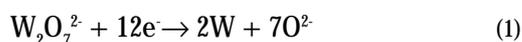


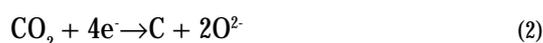
Fig. 1. Dependence of the grain size (h) in tungsten and molybdenum coatings on amount CO₂ over the melt: (a): Li, Na|WO₄-10 mol% WO₃; T=1173 K; i=0.05 Å/cm²; (b): LiNa|WO₄-10 mol% WO₃; T=1173 K; i=0.10 Å/cm²; (c): Na₂WO₄-5 mol% WO₃; T=1173 K; i=0.10 Å/cm²; (d): Na₂WO₄-3 mol% MoO₃; T=1173 K; i=0.05 Å/cm²

related with higher basicity of the melt containing sodium tungstate. In such a melt activity of oxygen ions at the same WO₃ concentration is higher than that for Na₂WO₄-Li₂WO₄ melt.

In the reaction of ditungstate-ion reduction



on the formation of each O²⁻ ion there are used up to 12/7 electrons, and in carbon dioxide reduction the process needs 2 electrons.



Thus, the activity of \tilde{F}^- ions increases in the melt, resulting in lower shift of deposition potential than that for tungsten ion reduction.

The process (2) is favourable for carbon deposition on cathode. The deposited carbon acts as a passivator blocking grains, by reducing the grains size.

Solid coatings of deposited molybdenum (or tungsten) keeping columnar structure were obtained even at 60-70 vol.% CO₂ atmosphere. The microhardness increases with

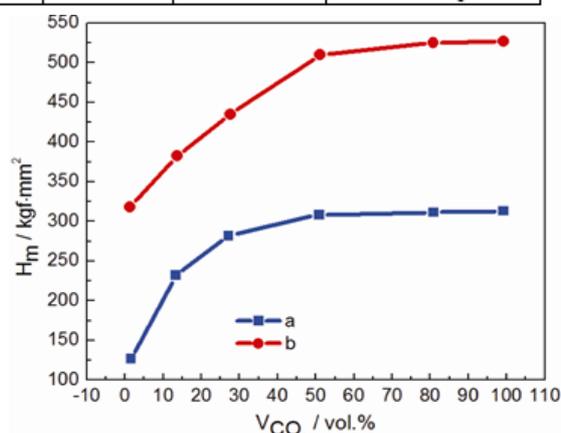


Fig. 2. Dependence of microhardness (H_m) of molybdenum and tungsten coatings on CO₂ content in atmosphere over melt: (a): Na₂WO₄-3 mol% MoO₃; T=1173 K; i=0.05 A/cm²; (b): Na₂WO₄-5 mol% WO₃; T=1173 K; i=0.05 Å/cm²

addition carbon dioxide in the atmosphere over the electrolytic cell (fig. 2). Possibly, in chloride melts not only carbon, but also oxygen-anion (being formed by CO₂ reduction) acts as a passivator by the reaction with the refractory metal ions with the formation of oxy-cations.

Such oxy-cations can be reduced on cathode to lower oxides, which appear to be included to the cathode coating together with carbon. Addition of CO₂ to the atmosphere over tungstate melts changes the morphology of surface (fig. 3a) and coatings texture. For example, at 1123 K (the process is visibly especially at 1273 K) and 10-40 vol.% CO₂, the coating grains acquire mainly the orientation with (100) direction perpendicular to substrate. Decreasing of grain size under carbon dioxide influence the process allows obtaining molybdenum and tungsten metallic coatings of 1-1.5 mm thickness (fig. 3b).

Besides the applying of CO₂ atmosphere, one of possibilities for grain size decreasing is the use of current impulses at the beginning of electrolysis or during whole time of the process [17].

Electrodeposition has been performed from Na₂WO₄-3 mol% MoO₃ and Na₂WO₄-5 mol% WO₃ melts. Nickel plates have been used as a substrate. Current impulses were applied by special A-quad-B pulses generator. The

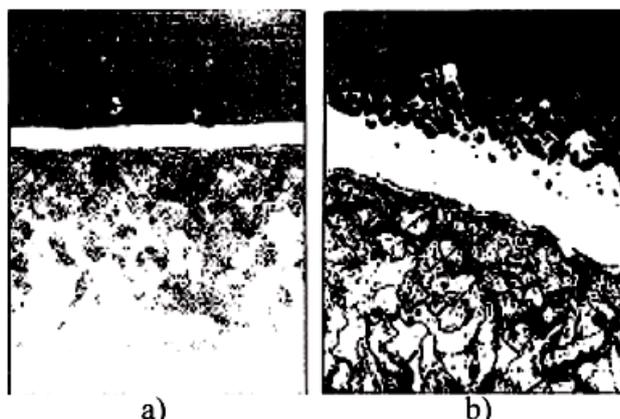


Fig. 3. Micro-photographs of cross-sections of steel 3 substrate covered by tungsten metal (x20): (a): CO₂ vol.=25%; $i_k=0.06 \text{ \AA/cm}^2$; $\tau=1.0 \text{ h}$. (b): CO₂ vol.=50%; $i_k=0.06 \text{ \AA/cm}^2$; $\tau=3.5 \text{ h}$; electrolyte-Na₂WO₄-Li₂WO₄-10 mol% WO₃ T=1173 K

cathode direct current density was $7.5 \cdot 10^{-2} \text{ \AA/cm}^2$ in all experiments.

In the case of cathode impulse applied at the beginning of electrolysis procedure a decreasing of grains size has been observed. For example, at 30 \AA/cm^2 impulse amplitude and 40-50 msec duration their size decreases from 10-14 μm to 3-5 μm . Such a grain size decreasing is, possibly, a reason for minor increasing of coating microhardness; which varies from 220 to 280 kg/mm² for molybdenum and from 380 to 440 kg/mm² for tungsten.

X-ray diffraction investigations have shown, that starting impulses up to 30 \AA/cm^2 do not influence on coating particles orientation. Independently from the starting impulses molybdenum and tungsten coatings possessed (110) preferred orientation. Applying current impulses up to 30 \AA/cm^2 increases the defects into the layers that can be explained by arising of new metal centres on each coating grain. Using impulses with amplitudes more than 50 \AA/cm^2 the coating becomes spongy with weak cohesion with the substrate. Possibly, it is typically for the conditions of practically complete disappearing of dimolybdate and ditungstate ions inside the cathode region. Coating type may depend on the secondary reduction of $M_2O_7^{2-}$ ions by sodium atoms, which form on cathode by primary reaction and percolating from cathode.

For applied electrochemistry it is convenient to use inexpensive, non-aggressive, non-hygroscopic solvent, such as equimolecular KCl-NaCl and NaCl-Na₃AlF₆ melts. Air stability, compatibility with aluminium oxide and electrolytic cell constructional materials, which allow electrolysis in opened cells with soluble tungsten (or

molybdenum) anode having relative ecological purity, are advantages of such melts. Because of refractory metals complexation the cathodic potentials for deposits on graphite, copper or nickel are less noble. In the case of steel substrate non-adherent and complicate composition coatings appear. Melts of tungstates and molybdates of alkali and alkali-earth metals appear to be typical ionic liquids. They possess relatively low melting points (for example 971 and 960 K for sodium tungstate and molybdate, the most commonly used in high-temperature electrochemistry). Also, these melts have usual viscosity (8.36 and 5.35 cP at 1000 K), but high density (3.61-3.85 and 2.57-2.81 g/cm³), electric conductivity (0.84 and 0.71 S/cm at 1073 K) and low decomposition voltage (1.53 and 1.39 V at 1000 K), respectively [18,19]. These properties of mentioned electrolytes are important for electrodeposition of refractory metals and their alloys. In [20] the possibility of tungsten electrodeposition from tungstate, boron, phosphorus and sulphur containing melts was shown. As we have found, the oxygen ions acceptors, boron oxide, sodium meta-phosphate and sodium pyrosulphate are the most technological materials. Their melts have the same advantages as halide-oxide ones. Moreover, from such melts coatings electrodeposition on different steel substrates are possible.

In [21-26] there were shown that in halide-oxide melts (KCl-NaCl-Na₂WO₄-NaPO₃, NaCl-Na₃AlF₆-Na₂WO₄-(WO₃)), or oxide melts (Na₂WO₄-B₂O₃, Na₂WO₄-NaPO₃ and Na₂WO₄-Na₂S₂O₇) is possible to perform multi-electron balances and processes, and tungsten electrodeposition may be performed. The same rules related also to molybdates melts and molybdenum electrodeposition. It is significant to note, that at a certain basicity six-electrons balance between metallic tungsten and W ion as dimmer forms exists. Our earlier obtained results [9, 10, 23, 25, 26] become the base for elaboration of technological processes for molybdenum and tungsten electrodeposition. It was interesting to compare the chosen halide-oxides and oxides melts concerning coatings deposition.

Influence of electrolysis conditions on deposits composition and structure

An important theoretical condition of strong coating-to-substrate cohesion is that the corrosion potential should be more positive than deposition potential. Therefore, for evaluation of the possibility of tungsten coatings deposition on different substrates the standard potentials of copper, nickel, steel 3, stainless steel and titanium relative to KCl-NaCl-2.5 mol% PbCl₂|Pb, NaCl-5 mol% Na₂WO₄|O₂, Pt and Na₂WO₄-20 mol% WO₃|O₂, Pt half-cells were measured (table 2).

Table 2
VALUES OF ELECTRODE POTENTIALS OF FREE CORROSION (E_c) FOR COPPER, NICKEL, STEEL 3, STAINLESS STEEL AS WELL AS THE DEPOSITION POTENTIALS FOR TUNGSTEN (E_d) IN HALIDE-OXIDES AND OXIDES MELTS

Melts composition, mol% WO ₃	E_c , V				E_d , V
	Cu	Ni	Steel 3	30 XGA stainless steel	
KCl-NaCl-Na ₂ WO ₄ - 2.5NaPO ₃ -0.35	-0.13 ÷ -0.15	-0.25÷ -0.27	-0.49÷ -0.51	-0.55÷ -0.57	-0.31÷-0.42
NaCl-Na ₃ AlF ₆ -Na ₂ WO ₄ -10.0	-0.49÷ -0.54	-0.51-0.55	-0.78-0.81	-0.75-0.79	-0.65
Na ₂ WO ₄ -B ₂ O ₃ -5.0	-1.08÷ -1.12	-1.17÷ -1.22	-1.31÷ -1.35	-1.30÷ -1.31	-1.50
K ₂ WO ₄ -Na ₂ WO ₄ -B ₂ O ₃ -5.0	-0.99÷ -1.03	-1.07÷ -1.10	-1.24÷ -1.26	-1.23÷ -1.26	-1.40÷-1.65
Na ₂ WO ₄ -NaPO ₃ -5.0	-0.85÷ -0.87	-0.89÷ -0.91	-1.07÷ -1.11	-1.02÷ -1.05	-1.20÷-1.35
Na ₂ WO ₄ -Na ₂ S ₂ O ₇ -7.5	-1.09÷ -1.11	-1.09÷ -1.17	-1.30÷ -1.34	-1.29÷ -1.33	-1.50÷-1.75

The potential of tungsten deposition is more negative than copper and nickel corrosion potential in KCl-NaCl-Na₂WO₄-NaPO₃ and NaCl-Na₃AlF₆-Na₂WO₄ melts, which causes a possibility of successful coating deposition. Under such conditions the steels become covered by in adherent powder. In Na₂WO₄-B₂O₃, Na₂WO₄-NaPO₃, and Na₂WO₄-Na₂S₂O₇ melts the standard potential of all electrodes are more positive than potential of tungsten deposition, and therefore the coatings appear to be well cohesive. These rules relate completely to the same molybdates melts and molybdenum electrodeposition. Titanium standard potentials in all melts could not be measured. Possibly, the cause of this phenomenon is the intensive oxygen dissolving in electrode surface layer. Therefore, before the tungsten deposition the titanium surface was preliminary covered by copper or nickel. Tungsten electrodeposition has been performed from halide-oxides molten electrolytes as KCl-NaCl-Na₂WO₄-NaPO₃, NaCl-Na₃AlF₆-Na₂WO₄-(WO₃) and oxide Na₂WO₄-B₂O₃, Na₂WO₄-NaPO₃ and Na₂WO₄-Na₂S₂O₇. We have investigated influence of tungstate and oxygen ions acceptor concentration, temperature, cathode current density, time of electrolysis on the coatings composition and structure. The optimal parameters for reversible deposition have been selected. The standard electrodes KCl-NaCl-2.5 mole PbCl₂|Pb at $\bar{O}=1023$ K in halide-oxides melts and Na₂WO₄-0.2WO₃|O₂, Pt at $\bar{O}=1173$ K, in oxide melts were used.

Influence of tungstate and oxygen ions acceptor concentration

Tungsten coatings in KCl-NaCl-Na₂WO₄-NaPO₃ appear at $0.02 < [PO_3^-]/[WO_4^{2-}] < 0.18$ ratio. At Na₂WO₄ concentration lower than 0.1 mol%, in the in adherent coatings the traces of phosphides were found; at concentration higher than 10 mol% Na₂WO₄, tungsten oxides peaks appeared on X-ray powder patterns. At $[PO_3^-]/[WO_4^{2-}] \geq 0.18$ ratio, tungsten and their phosphides evolve, but no coherent coating appears. Tungsten coatings in NaCl-Na₃AlF₆-Na₂WO₄ melt form only at sodium tungstate concentration of 1-15 mol%. At higher concentrations, tungsten dioxide and tungsten bronzes appear. From Na₂WO₄-B₂O₃ electrolyte the tungsten metal evolves at lower than 10 mol% boron concentration. At higher boron concentrations tungsten oxides and tungsten bronzes were found on X-ray powder patterns. Tungsten coatings from Na₂WO₄-NaPO₃ appear at phosphate concentration 0.5-15.0 mol%, whereas at higher concentration the tungsten bronzes arise simultaneously with tungsten, and coating quickly transforms to dendrites. From Na₂WO₄-Na₂S₂O₇ melt, the tungsten arises at 2.5-12.5 mol% Na₂S₂O₇ concentration, and at higher concentration coatings the deposit includes tungsten dioxide and tungsten sulphides as by-products.

Influence of electrolysis temperature

Compact tungsten coatings were obtained from halide-oxide melts at 973-1073 K and current density up to 0.25 A/cm². At higher temperatures the melt becomes unstable and more volatile. At temperatures lower than 973 K, only thin (up to 5 μm) tungsten metallic layers can be obtained, and coating quickly transforms to powder. At higher current densities the disperse tungsten powders appear. In the case of oxide melts, compact tungsten coatings were obtained at 1023-1123 K and current density up to 0.40 A/cm². At lower temperature than 1023 K thin tungsten layers up to 15-20 mm thickness can be obtained. At higher current density than 0.40 A/cm² the high-disperse tungsten powders with specific surface up to 40-50 m²/g arise.

Influence of cathode current density and electrolysis duration

The studies of influence of cathode current density and electrolysis duration, by choosing parameters of reverse covering regime, were performed for KCl-NaCl-2.5 mol% Na₂WO₄-0.35 mol% NaPO₃, NaCl-Na₃AlF₆-7.5 mol% Na₂WO₄, Na₂WO₄-5 mol% NaPO₃ and Na₂WO₄-5 mol% Na₂S₂O₇ electrolytes. Well coherent solid coatings from these melts were grown at 923-1173 K and 0.01-0.15 and 0.03-0.25 A/cm² current densities from halide-oxide and oxide electrolytes, respectively. The grain size in coating decreases with increasing of current density. But at current density higher than 0.25 A/cm² a substantial enlargement of grain size and higher roughness increasing were observed. It leads to coating-to-dendrites transformation. At current density lower than 0.025 A/cm² the corrosion rate exceeds the rate of coating formation, and coherent coating does not appear. The rate of tungsten deposition in explored interval of current densities was 5-15 μm/h for halide-oxide melts and 20-45 μm/h for oxide electrolytes, tungsten current yield in the shape of coating appears to be up to 60 and 95% respectively (fig. 4). Dependence of tungsten coating thickness on electrolysis time is shown on figure 5. Increasing of electrolysis time the current yield drops down. Mentioned above peculiarities of Na₂MO₄ and oxygen ions acceptor concentration, temperature, cathode current density and process duration are related also to the electrodeposition of molybdenum coatings.

From halide-oxide electrolyte well-coherent solid tungstate and molybdate coatings on nickel, copper, graphite, tungsten and molybdenum have been obtained. From oxide melts, the steels (Steel 3, 15X, Steel 45, 40X, 30XGA), instrumental steels (U7, U10, P6M5), hard alloys (AK6, AK20), copper-coated and nickel-coated titanium have been also used as substrates.

Therefore, changing air atmosphere on the inert one does not influence on coatings structure and grain size using tungsten-molybdenum electrolytic cells. Addition of carbon dioxide in the atmosphere over tungsten-molybdenum melts leads to transformation coating into powder and co-deposition of carbon powders together with metal. Such grain size decreasing allows increase noticeably micro-hardness and thickness of coating.

Applying cathode current impulse up to 30 A/cm² during molybdenum and tungsten electrodeposition on proper or alien substrate does not affect epitaxial deposition. The condition of such coating grow is the presence of the rest of dimmer ions in near-cathode layer. On the alien substrate the applied current impulse

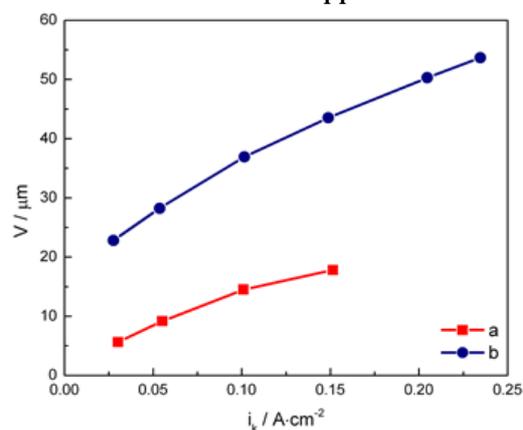


Fig. 4. Dependence of deposition rate (V) of tungstate coating (4a) from current density on copper substrates for: halide-oxide electrolyte NaCl-Na₃AlF₆-10 mol% Na₂WO₄; b: oxide electrolyte Na₂WO₄-5mol% B₂O₃

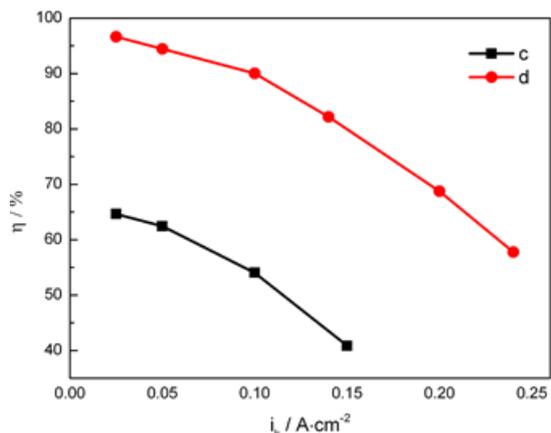


Fig. 4. Dependence of current efficiency (η) from current density on copper substrates for: c: halide-oxide electrolyte NaCl-Na₃AlF₆-10 mol% Na₂WO₄; d: oxide electrolyte Na₂WO₄-5 mol% B₂O₃;

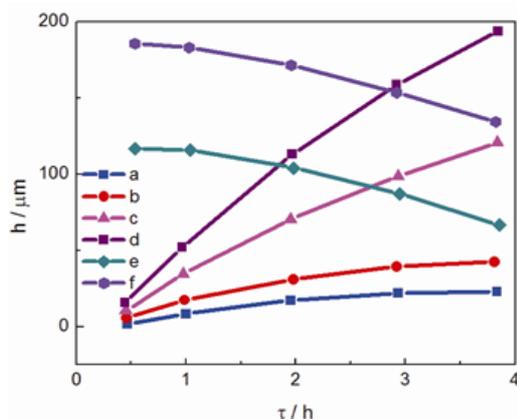


Fig. 5. Dependence on electrolysis time (t) of tungsten coating thickness (h) on nickel substrate from various melts: (curves a, b, c, e): halide-oxide electrolyte NaCl-KCl-2.5 mol% Na₂WO₄-0.35 mol% NaPO₃; (curves d, f): oxide electrolyte Na₂WO₄-7.5 mol% Na₂S₂O₇; current density: (a):0.025 A/cm²; (b):0.075 A/cm²; (c-f):0.15 A/cm²

leads to grain size decreasing and some micro-hardness increasing.

Tuning coatings structure by using reverse regime of deposition

Profile-measuring investigations show that coatings thickness increasing leads to increasing of grain size. It was tried to decrease the grain size using reverse regime of deposition. The ratio between durations of cathode and anode processes was changed from 15 to 50 s, duration of anode period 0.5-3.0 s, current density 0.2-0.5 A/cm². For example, optimal parameter for Na₂WO₄-5 mol% NaPO₃ electrolyte at 1173 K were: $i_c = 0.15$ A/cm², $i_a = 0.30$ A/cm², $\tau_c = 25$ s; $\tau_a = 1.5$ s. As a result, relatively smooth cathode coatings up to 0.5 mm have been obtained.

Conclusions

Electrodeposition of tungsten and molybdenum coatings from halide-oxide and oxide melts has been performed. An influence of electrolysis condition on physical-mechanical coatings properties has been studied.

The changing of air atmosphere on the inert one (argon) does not influence practically on the grain size. Contrary, the addition of carbon dioxide in the atmosphere over electrolytic cell strongly influences on the molybdenum (or tungsten) coating structure by decreasing the size of grains. Also, co-deposition carbon acts as a passivator

blocking grains, by reducing the growth rate and grains size. The same influence is obtained by using of current impulses.

The influence of electrolysis temperature and cathode current density as well as electrolysis time was studied extensively. Tuning coatings structure by using reverse regime of deposition was done and as a result, relatively smooth cathode coatings up to 0.5 μ m thickness have been obtained. Authors equally contributed to this work.

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