

ELECTROPLATING WITH TUNGSTEN AND TUNGSTEN-MOLYBDENUM ALLOYS FROM METAPHOSPHATE-CONTAINING HALIDE-OXIDE AND OXIDE MELTS

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Abstract: The electrochemical behavior of dimeric tungsten complexes in metaphosphate-containing melts is studied potentiometrically and voltammetrically. The electrodeposition of tungsten and tungsten coatings from halide-oxide and oxide melts and the correlation between the properties of deposits and the conditions of electrolysis are investigated.

Keywords: ELECTROPLATING, TUNGSTEN, TUNGSTEN-MOLYBDENUM ALLOYS, METAPHOSPHATE, HALIDE AND HALIDE-OXIDE MELTS

1. Introduction

For the purposes of applied electrochemistry, it is convenient to use cheap, nonaggressive, and non-hygroscopic solvents, such as an equimolar KCl-NaCl composition. The concentration of stable oxygen-containing complex tungsten anions in this melt is sufficient, and the losses due to sublimation are insubstantial. The advantages of such baths are their stability in air and compatibility with aluminum oxide (alundum or corundum), which allows one to work with open electrolyzers with a soluble tungsten anode. Because of its binding in stable complexes, tungsten becomes less noble and, without contact deposition, can be cathodically applied not only to the metals of platinum family (as in purely halide solutions), but also to graphite, copper, and nickel. However, nonadherent coatings of complex composition are electroplated from these melts to steel specimens [1-3]. The melts based on tungstates and molybdates are typical ionic liquids: they are thermally stable, have comparatively low viscosity and melting point and relatively high electroconductivity and decomposition voltage [4, 5].

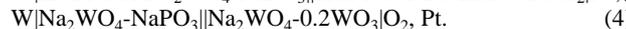
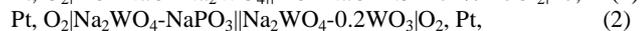
2. Experimental

The details of preparing electrolytes, the design of electrodes and cells, and the techniques of the investigation of coatings were considered in detail in [6].

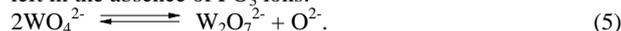
3. Result and discussion

3.1 Ionic composition of metaphosphate-containing melts

Electromotive forces (EMFs) of the following electrochemical circuits were measured:



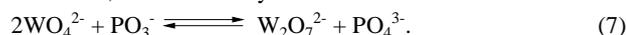
According to the conventional hypothesis on the acid-base equilibria, the equilibrium in the melts in question is shifted to the left in the absence of PO_3^- ions:



The introduction of metaphosphate leads to the binding of oxygen ions:



that is, to the summary reaction



The decrease in the activity of O^{2-} ions upon the introduction of PO_3^- ions in a chloride-tungstate melt is confirmed by the increase in the equilibrium potential of the oxygen electrode $E(\text{O}_2)$ with an increase in the concentration of PO_3^- (see Fig. 1), which, by Eq. (6), decreases the activity of the reduced oxygen form in the melt. The

derivation of an equation for $E(\text{O}_2)$ is awkward in this case because of the complex composition of the melt.

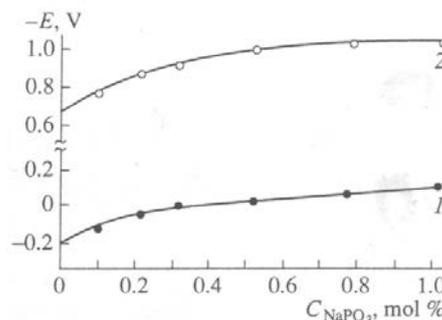
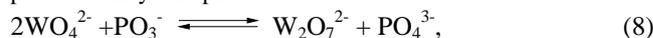


Fig. 1: The dependence of the potential of a platinum-oxygen electrode on the concentration of NaPO_3 in a $\text{NaCl-KCl-0.35 mol/dm}^3 \text{Na}_2\text{WO}_4$ melt vs. the reference electrodes (1) $\text{Pt, O}_2 / \text{KCl - NaCl - 0.3 mol/dm}^3 \text{Na}_2\text{WO}_4$ and (2) Pb/Pb^{2+} .

In the presence of PO_3^- ions in a Na_2WO_4 melt, the following processes may take place:



Using the same mathematical approach, as we applied in [7] for deriving an equation for $E(\text{O}_2)$, we come to a conclusion that in the concentration range studied, reaction (9) actually proceeds with the formation of $\text{W}_2\text{O}_7^{2-}$ and $\text{P}_2\text{O}_7^{2-}$ ions.

In $\text{KCl-NaCl-Na}_2\text{WO}_4\text{-NaPO}_3$ melts, a noticeable corrosion of tungsten is observed. At Na_2WO_4 and NaPO_3 concentrations of 0.175 and 0.06 mol/l, respectively, and a temperature of 1023 K, it is about 12.0 to 15.3 g/(m²h). The number of electrons formally calculated from the value of the pre-logarithmic factor in the $dE/d\log C$ dependence is 0.5 to 0.8, which is substantially smaller than the value of 1.5 that should correspond to the equation



The EMF of a circuit (4) was measured in a NaPO_3 concentration range from 1.0 to 10.0 mol %. At a metaphosphate concentration lower than 1.0 mol %, tungsten insubstantially corrodes (at a corrosion rate of 3 to 5×10^{-7} g/(m²h)). At a NaPO_3 concentration higher than 1.0 mol %, the corrosion is not practically observed. An equation for the attained steady-state potential of a tungsten electrode can be written in the form of Eq. (10).

Taking into account reaction (9), from the $dE/d\log 2C_{\text{NaPO}_3}$ dependence (see Fig. 2), we can estimate the number of electrons per one electrochemically active particle as 1.5. In the concentration range studied, $n = 1.44$ to 1.51. This value corresponds to electrode reaction (10).

3.2 Electroreduction of oxide tungsten (VI) forms in metaphosphate-containing melts

Tungstate ions WO_4^{2-} are not electrochemically active particles in a chloride melt. Upon the introduction of PO_3^- ions in the melt, two waves appear on the voltammograms (see Fig. 3, curve 3) at potentials of -0.1 to -0.2 V and -0.3 to 0.5 V vs. a Pb/Pb^{2+} reference electrode. At a concentration of PO_3^- in the range $0.01 < [\text{PO}_3^-]/[\text{WO}_4^{2-}] < 0.18$, the product of potentiostatic electrolysis at the above potentials is metallic tungsten. An increase in the NaPO_3 concentration to $[\text{PO}_3^-]/[\text{WO}_4^{2-}] \gg 0.18$ results in the appearance of tungsten phosphides in the products of electrolysis.

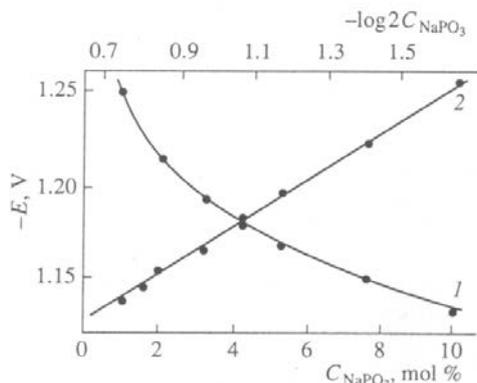


Fig. 2: (1) The dependence of the potential of a tungsten electrode on the concentration of NaPO_3 in a sodium tungstate melt and (2) its representation in logarithmic coordinates.

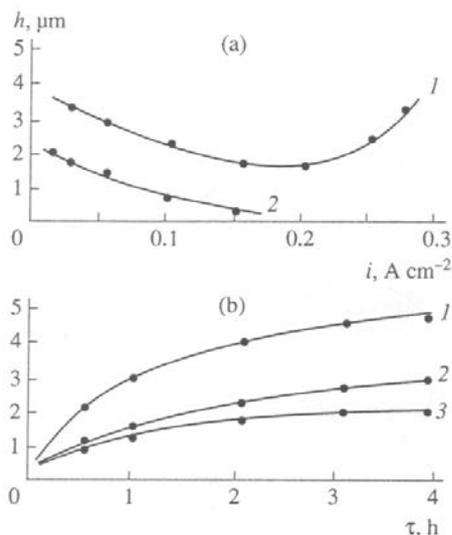
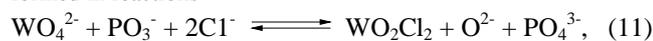


Fig. 3: The roughness amplitude of tungsten coatings on specimens of (a, curve 2; b, curves 2 and 3) St3 steel and (a, b, curves 7) copper vs. (a) the current density ($T = 1.5$ h) and (b) the duration of electrolysis (1, 2) at a direct current i_c of (7) 10 and (2) 15 A/dm^2 and (3) under reversal conditions of plating ($i_c = 15$ A/dm^2 , $t_c = 25$ s, $i_d = 30$ A/dm^2 , and $t_d = 0.5$ s): (1) $\text{KCl-NaCl} - 2.5$ mol % $\text{Na}_2\text{WO}_4 - 0.35$ mol % NaPO_3 and (2, 3) $\text{Na}_2\text{WO}_4 - 5$ mol % NaPO_3 .

Cyclic voltammograms ($E^{c-a} = (0.550 \dots 0.630) > 0.047$ V = $3.2RT/2F$) and the dependence of the half-peak potentials of the waves on the polarization rate of the electrode indicate the irreversible character of the electrode process. Modeling electrode processes [7] allows us to believe that the first wave on the voltammogram of a $\text{KCl} - \text{NaCl} - \text{Na}_2\text{WO}_4 - \text{NaPO}_3$ system corresponds to the discharge of tungsten oxychlorides, which are formed in reactions



while the second wave appears due to the discharge of ditungstate ions, which are formed in reaction (7). On the voltammograms of $\text{Na}_2\text{WO}_4 - \text{NaPO}_3$ melts, a wave corresponding to the reduction was observed at a potential of -1.1 to -1.2 V. The limiting currents were proportional to the concentration of metaphosphate added rather than to the summary concentration of tungsten in the melt. The

reduction proceeds in one stage, and the product of potentiostatic electrolysis of the melt at a potential of -1.2 V is metallic tungsten.

The proportionality of the limiting current to the concentration of sodium metaphosphate, the constancy of the $i_d V^{1/2}$ ratio (where i_d is the limiting current and V is the polarization rate), and the value of the kinetic constant i_d/nFc , which is 8.3 to 9.5×10^{-5} cm/s for the steady-state waves, indicate the fact that the electrode process is limited by the diffusion of electrochemically active particles to the electrode. Ditungstate ions, which are formed in reaction (8), become electrochemically active in the summary electrode process (10). Under the steady-state conditions, the slope of the $E - \log(i_d - i)$ dependence varies from 38 to 42 mV at different NaPO_3 concentrations, while the number n of electrons, which are transferred in the electrode process, is 5.8 ± 0.3 . This means that the charge transfer stage of Eq. (10) is reversible. The number of electrons, which is determined from the half-widths of the peaks in non-steady-state voltammograms according to Matsuda-Ayabe criterion for the NaPO_3 concentrations lower than 10 mol % and the polarization rates from 0.04 to 0.2 V/s, equals 5.9 to 6.1.

3.3 Electroplating with tungsten and tungsten-molybdenum alloys from metaphosphate-containing melts

3.3.1. The effect of the electrolysis conditions on the structure of tungsten coatings

The tungsten coatings were electroplated from $\text{KCl} - \text{NaCl} - \text{Na}_2\text{WO}_4$ or Na_2WO_4 baths with NaPO_3 admixtures. The effect of the change in Na_2WO_4 and NaPO_3 concentrations, in temperature, cathodic current density, and the duration of electrolysis on the composition and structure of the deposits was investigated, and the optimal conditions with current reversal were found for plating.

3.3.2. The effect of sodium tungstate and metaphosphate concentrations

The tungsten coatings from the $\text{KCl} - \text{NaCl} - \text{Na}_2\text{WO}_4 - \text{NaPO}_3$ melts are fit when the aforementioned concentration condition is met: $0.02 < [\text{PO}_3^-]/[\text{WO}_4^{2-}] < 0.18$. At a Na_2WO_4 concentration lower than 1 mol %, the deposit is not adherent, and no phosphide can be found in it. At a concentration higher than 10 mol %, the diffraction patterns show the presence of tungsten oxides. At a metaphosphate concentration $[\text{PO}_3^-]/[\text{WO}_4^{2-}] > 0.18$, tungsten again is deposited with phosphides, and no adherent coating is formed.

Tungsten coatings in a $\text{Na}_2\text{WO}_4 - \text{NaPO}_3$ melt form at a metaphosphate concentration from 0.5 to 15.0 mol %. Above this limit, along with tungsten, its bronzes form, and the deposit soon begins to grow as dendrites.

3.3.3. The effect of the temperature of electrolysis

Continuous tungsten coatings from a halide-oxide electrolyte were obtained at a temperature from 973 to 1073 K and a current density of up to 25 A/dm^2 . At a higher temperature, the system loses its stability, and its volatility increases. At a temperature below 973 K, only thin (up to 5 μm) tungsten layers can be obtained, and the deposit quickly transforms into a powder. At a current density higher than 25 A/dm^2 , dispersed tungsten powders are formed.

Continuous tungsten coatings from an oxide electrolyte were obtained at a temperature from 1023 to 1123 K and a current density of up to 40 A/dm^2 . At a temperature below 1023 K, only thin (up to 15 or 20 μm) tungsten layers are formed. At a current density higher than 40 A/dm^2 , highly dispersed tungsten powders with a specific surface area of 40 to 50 m^2/g form.

3.3.4. The effect of the cathodic current density and the duration of electrolysis

The effect of the cathodic current density, as well as the duration of electrolysis and the reversal conditions of plating, was

studied in KCl-NaCl — 2.5 mol % Na_2WO_4 — 0.35 mol % NaPO_3 and Na_2WO_4 — 5 mol % NaPO_3 electrolytes. Adherent, continuous, and nonporous coatings were obtained from the above electrolytes at temperatures of 923 and 1173 K and current densities of 1 to 15 and 3 to 25 A/dm^2 , respectively.

The grains size in the deposit has a minimum depending on the current density, and above 25 A/dm^2 , the crystallites become substantially larger, while the surface grows rougher. Finally, the deposit transforms into dendrites. At a current density lower than 2.5 A/dm^2 , the corrosion rate of a substrate is too large, and no adherent coating is formed.

The deposition rate of tungsten in the studied range of current densities is 5 to 15 $\mu\text{m}/\text{h}$ in a halide-oxide electrolyte and 20 to 45 $\mu\text{m}/\text{h}$ in an oxide electrolyte. The current efficiency of a tungsten coating is up to 60 and 95%, respectively. The time dependences of the thickness of a coating and its current efficiency are shown in Fig. 5. As the duration of electrolysis increases, the current efficiency drops.

From halide-oxide electrolytes, we obtained adherent continuous tungsten coatings on nickel, copper, graphite, tungsten, and molybdenum. In oxide melts, the coatings were obtained also on different instrumental steels, hard alloys and nitric-, copper-, or nickel-plated titanium.

3.3.5. The controlling of the structure of coatings by reversal conditions of plating

Profilometric investigation shows that, as the deposit thickens, its single-phase fine-crystalline structure transforms into a coarser one. We tried to prevent the formation of a coarse-grain structure by applying reversal conditions of electrolysis. The duration ratio of the cathodic to anodic period was varied from 15 to 50 at a duration of the anodic period from 0.5 to 3.0 s, and the anodic current density was changed from 20 to 50 A/dm^2 . The following conditions are optimal for a Na_2WO_4 - 5 mol % NaPO_3 electrolyte at 1173 K: ($i_c = 15 \text{ A}/\text{dm}^2$, $i_a = 30 \text{ A}/\text{dm}^2$, $\tau_c = 25 \text{ s}$, and $\tau_a = 1.5 \text{ s}$). In this case, relatively smooth coatings of a thickness of up to 0.5 mm were obtained at the cathode.

3.4. Physicochemical properties and performance of tungsten coatings

The coatings are light-gray microgranular continuous deposits. By the data of x-ray spectral microanalysis, alien metallic admixtures are contained in an amount of up to 0.02 wt % and do not noticeably affect the structure of coatings. According to standard estimates [8], the pores area in coatings is 0.0 to 0.2%, which is considered as an indication of a practically nonporous coating.

The microhardness does not change across the coating and equals 460 to 485 kgf/mm^2 . The diffusional area of 5 to 20 μm , revealed with the x-ray spectral microanalysis of the cross sections of a specimen, indicates that there is a mutual diffusion of the elements of the coating and the substrate, which provides the proper adherence of the coating. The continuity of the transition from the coating to the substrate was confirmed by stereoscanograms of spallings of the specimens, which concurrently showed a pronounced columnar structure of the deposit.

The specimens of steel 45 with a tungsten coating were thoroughly tested in a friction pair with a quenched steel 45 counterbody. As a result of the plating, the wear resistance increased by a factor of 4.5 to 5.7.

The specimens of steel 45 with tungsten coatings were tested for abrasive resistance in an electrocorundum 100- μm fraction at a load of $52 \pm 0.25 \text{ N}$. Due to the coating, the abrasive resistance increased 2.5 to 4.3 times.

4. Conclusion

Thus, we studied the electrochemical behavior of tungsten-metaphosphate melts, the electroplating with tungsten from them, and the properties of the coatings.

5. Literature

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