ELECTROCHEMICAL STUDY OF SODIUM TUNGSTATE-SODIUM PYROSULFATE MELTS AND TUNGSTEN COATINGS ELECTRODEPOSITED FROM THEM

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ABSTRACT

The electrochemical behavior of the dimeric complexes of tungsten in tungstate-pyrosulfate melts was studied by potentiometric and voltammetric methods. The six-electron reversible character of the electrode process was established. The effect of the electrolysis parameters on the composition, structure, and properties of deposits was studied.

INTRODUCTION

Oxygen-containing compounds of refractory metals, in particular tungsten, attract the interest of researchers due to the prospects of direct electrolysis. Tungstate melts have recently found an ever-growing application as solvents for producing refractory metals, other heavy and non-ferrous metals [1], and their compounds [2, 3]. Schibler [4] and Van Liempt [5] were among the pioneers who first implemented electrolysis of the melted tungstates of alkaline and alkali-earth metals. According to their data, either continuous layers of tungsten or tungsten-based bronzes are deposited from these melts by electrolysis.

A.N. Baraboshkin et al. [6-8] have systematically investigated the electrolysis of tungstate melts. They determined the deposition ranges of bronzes, tungsten and tungsten(VI) oxides, and found that the composition of cathode products is determined by the melt composition, temperature, and to a considerably less degree by the cathode current density. The cathode polarization of the $\text{M}_2\text{WO}_4-\text{WO}_3$ systems (M-Li, Na, K) was studied, and reversible processes of electric reduction of dimeric ions $\text{W}_2\text{O}_7^{2-}$ were proposed in works [7, 9].

The existence of these ions was confirmed by the investigated dependence of the tungsten electrode potential on the concentration of $\text{WO}_3$ [7, 10]. Various acceptors of oxygen ions – $\text{PO}_4^{3-}$ anions [11], neutral molecules $\text{MoO}_3$ [12], and $\text{CO}_2$ [13], – were applied to alter the acid-base properties of a $\text{Na}_2\text{WO}_4$ melt and thus form dimeric ions.

A goal of this work is to study the effect of sodium pyrosulfate, as a new acid additive, on the electrochemical behavior of oxy-anions of tungsten(VI), check the applicability of electroplating with tungsten from $\text{Na}_2\text{WO}_4-\text{Na}_2\text{S}_2\text{O}_7$ melt, and reveal the
physicochemical and performance properties of the plates.

EXPERIMENTAL

A complex of electrochemical and physicochemical methods was applied to study the electrochemical behavior of the oxide forms of tungsten (VI) on the background of a tungstate melt, as well as to deposit tungsten coatings from such melts. This complex includes potentiometry, voltammetry, potenti- and galvanostatic electrolysis, X-ray diffraction and microspectral analyses, profilometry, tests for wear and abrasion resistance. For identification compounds in melts IR-spectroscopy and X-ray analysis of cooled samples were used.

A $\text{Na}_2\text{WO}_4-\text{Na}_2\text{S}_2\text{O}_7$ melt was chosen as a base system for the electrochemical deposition of tungsten coatings. Extra pure sodium tungstate was dried at a temperature of 150-200°C in order to prepare the background electrolyte. Analytically pure sodium pyrosulfate was dried at a temperature 100-150°C. A platinum crucible was used as a melt container for making potentiometric and voltammetric measurements. Half-immersed platinum or silver electrodes, or tungsten leads with platinum conductor were used as the indicator electrodes. A reference half-cell $\text{Pt}, \text{O}_2|\text{Na}_2\text{WO}_4-0.2\text{WO}_3$ was separated from the basic melt by an alundum diaphragm. The cyclic voltammetry study was performed employing a Voltalab-Radiometer-Model 050 potentiostat, with the Voltamaster 4 software package. In the electrodeposition of coatings, a tungsten sheet, in the case of an alundum container, or a graphite crucible itself served as anode, while a 10 x 20 x 1 mm sheet of the metal being coated formed the cathode.

The electrode current efficiency, the thickness of coatings and their deposition rate were determined by weighing. A PMT-3 instrument was used for the determination of the microhardness of coating on a micro-section of the specimen. The quantitative data on the geometry of the surface were obtained by testing on a PR-201 profilograph. A DRON-3 type, X-ray diffractometer in the $\text{CuK}_\alpha$ irradiation of 22.8962 nm wavelength was used for carrying out the X-ray analysis of specimens, while the Cameca analyzer and the Stereoscan scanning electron microscope were employed for implementing the X-ray microspectral analysis.

A VTO-25 micrometer and 2IGM indicator were used for determining the thickness of coatings on plane-parallel plates of different materials. A potassium hexacyanoferrate solution was used for determining the porosity of the coatings applied onto a steel surface [14]. The adhesion of deposits to the base metal was assessed qualitatively [14] and the wear resistance was tested on a SMTs-2 machine with a specific load of 5 MPa in the medium of transformer oil. The abrasive resistance of coatings was tested according to the GOST (State Standard) 23208-89.

RESULTS AND DISCUSSION

Study of the Ionic Composition of the Sodium Tungstate-Sodium Pyrosulfate Melt.

For this purpose, the electromotive force of the following electrochemical circuits was investigated:
where $x$ is the mole fraction of $\text{Na}_2\text{S}_2\text{O}_7$ in the melt. The range of sodium pyrosulfate concentrations was 0-10 mol %, and the temperature of melt was 1173 K. The e.m.f. values that remained constant in the range of 5 mV during 1 h were assumed as equilibrium ones.

Figure 1. Potentials of platinum-oxygen (a) and tungsten (b) electrodes as functions of $\text{Na}_2\text{S}_2\text{O}_7$ concentration. (1) Natural coordinates; (2) semilogarithmic coordinates, $T=1173$ K.

The experimental dependence of the potential of a platinum-oxygen electrode on the
concentration of sodium pyrosulfate (Fig. la, curve 1) is explained by the formation of ditungstate ions upon adding Na$_2$S$_2$O$_7$ to the Na$_2$WO$_4$ melt:

$$2\text{WO}_4^{2-} + \text{S}_2\text{O}_7^{2-} \leftrightarrow \text{W}_2\text{O}_7^{2+} + 2\text{SO}_4^{2-}$$ [3]

The probability of this reaction taking place is confirmed by thermodynamic calculation of reaction (3) Gibbs energy. $\Delta G$ was calculated at 1173 K with the use of reference data [15, 16]. It was found that $\Delta G = -5581.46$ kJ/mol.

Thus thermodynamic calculations only suppose the possibility of reaction in tungstate melts, but these calculations can be useful to explain the model of ionic melt composition. According to calculations the most energetically profitable in most cases are reactions leading to ditungstate compositions formation. This conclusion is confirmed by structural methods (X-ray diffraction analysis and IR-spectroscopy of cold samples).

In order to identify of refractory metals compounds in sodium tungstate melts the IR-spectra and X-ray data of cooled samples were compared with IR-spectra and X-ray data of pure substances. The possibility of dimeric particles formation after adding of oxygen ions-acceptors into sodium tungstate melts was confirmed by the result of this comparison.

Using the mathematical approach [17], which we earlier applied to derive the equation of the oxygen electrode potential, we obtain, in accordance with equation (3), the final dependence:

$$E_{O_2}^*/O_2 = E_{O_2}^*/O_2 + \frac{2.3RT}{2F} \log \frac{n\text{S}_2\text{O}_7^{2-}}{[1 - 2n\text{S}_2\text{O}_7^{2-}]}$$ [4]

In conformity with equation (4), the prelogarithmic coefficient of the dependence $E_{O_2}^*/O_2 - \log \frac{n\text{S}_2\text{O}_7^{2-}}{[1 - 2n\text{S}_2\text{O}_7^{2-}]}$ should be equal to 0.016 V at 1173 K. In the considered concentration range of Na$_2$S$_2$O$_7$ the prelogarithmic coefficient of dependence (4) amounts to 0.112-0.121 V (Fig. la, curve 2). This proves that reaction (3) actually takes place in the given range of concentrations of Na$_2$S$_2$O$_7$. The consistency of the experimental and the calculated dependences confirms the correctness of the chosen model of the ionic composition of the melt.

Corrosion of a tungsten electrode in the Na$_2$WO$_4$ melt was detected at Na$_2$S$_2$O$_7$ concentration < 0.5 mol %. No corrosion of tungsten was observed at a higher concentration of sodium pyrosulfate. The equilibrium tungsten potential corresponding to the suggested model of ionic melt should result from the following possible equilibria:

$$\text{WO}_4^{2-} + 6\text{e} \leftrightarrow \text{W} + 4\text{O}_2^{2-}$$ [5]

or

$$4\text{W}_2\text{O}_7^{2-} + 6\text{e} \leftrightarrow \text{W} + 7\text{WO}_4^{2-}$$ [6]

The number of electrons per electroactive particle calculated from the prelogarithmic
coefficient of dependence \(\frac{dE}{d\log C(\text{Na}_2\text{S}_2\text{O}_7)}\) (Fig. 1b, curve 2) amounts to 1.5 for the \(\text{Na}_2\text{S}_2\text{O}_7\) concentration range of 1.0-10 mol \%. The electrode reaction (6) corresponds to this value.

Electroreduction of the Oxide Forms of Tungsten(VI) from the Na\(_2\)WO\(_4\)-Na\(_2\)S\(_2\)O\(_7\) Melt.

The limiting current \(i_{\text{lim}}\) is proportional to the concentration of sodium pyrosulfate. The term \(i_{\text{lim}}/v^{1/2}\) is constant within a wide range of \(v\) (where \(v\) is the scanning rate of polarization). Finally, the mass-transfer constant \(i_{\text{lim}}/nFC\) (where \(n\) is the number of electrons participating in the electrode process, \(F\) is the Faraday constant, and \(C\) is the concentration of the electroactive component) amounts to \((0.7-1.0)\times10^{-3} \text{ cm/s}\) for stationary waves. All these facts concordantly prove that the electrode process is controlled by the diffusion of electroactive particles toward the cathode. The rate of their formation under the given polarization conditions does not limit the electrode process.

The origin of reduction waves can be explained through studying the ionic composition of the Na\(_2\)WO\(_4\)-Na\(_2\)S\(_2\)O\(_7\) melt. In a pure sodium tungstate melt, the concentration of \(\text{W}_2\text{O}_7^{2-}\) amounts from \(10^{-4}\) to \(2\times10^{-5} \text{ mol \%}\) [17], which is considerably lower than the voltammetry sensitivity limit. Naturally there is no reduction wave in the voltammogram of this melt. Sodium pyrosulfate as an acceptor of oxygen ions shifts the equilibrium (3) to the right, thereby increasing the concentration of \(\text{W}_2\text{O}_7^{2-}\) in the melt. This anion, at a potential of \(-1.1 \pm 0.1 \text{ V}\), becomes electrochemically active in the total electrode process (6).

In the steady state voltammogram, the slope of the dependence of \(E\) vs. \(\text{lg}(i_{\text{lim}})\) at different concentrations of sodium pyrosulfate amounts to 36-42 mV, while \(n = 5.6 \pm 6.2\). Agreement of the experimental and theoretical slope values prove a reversible charge transfer in (6). The following experimental facts also confirm this reversibility: the half-wave and the peak potentials do not depend on the polarization-scanning rate up to 0.2 V/s; the concentration dependence of the equilibrium potential of the reaction (6) is well described by the Nernst equation.

Electrodeposition of Tungsten Coatings by Electrolysis of Tungstate-Pyrosulfate Melts.

In the foregoing sections, it has been shown that multielectron equilibria and the electrodeposition of tungsten with participation of its dimeric oxy-forms are possible in Na\(_2\)WO\(_4\)-Na\(_2\)S\(_2\)O\(_7\) melts. It should especially be noted that at a definite basicity of the melt, an electrode equilibrium with participation of six electrons occurs. The obtained results served as a basis for developing the processes of electrodeposition of tungsten coatings. The melts applied are stable, compatible with the available structural materials for electrolyzer, and environmentally clean.

A base metal can successfully be electroplated, if its corrosion potential \(E_{\text{cor}}\) is higher than the coating-deposition potential. Therefore, the stationary corrosion potentials of nickel, steels, and titanium (usually, tungsten is not deposited on these metals from halide and halide-oxide melts) were measured relative to a half-cell Na\(_2\)WO\(_4\)-0.2WO\(_3\)O\(_2\)Pt (see Table 1) in order to assess the possibility of their plating with tungsten. The deposition potential of tungsten proved to be lower than the corrosion potentials of nickel, St3, and stainless steel, which offers a possibility for producing good coatings. The free-corrosion potential of titanium remained unstable for a long time and varied.
jumpwise, seemingly, due to formation of lower titanium oxides. Therefore, prior to electroplating titanium with tungsten, we nitrided the former or plated it with nickel.

We investigated the effect of the sodium pyrosulfate concentration, temperature, cathodic current density, and duration of electrolysis on the composition and structure of cathodic deposits, and selected the optimum conditions of the reversal deposition of tungsten from Na₂WO₄-Na₂S₂O₇ melts. Tungsten is deposited when the concentration of sodium pyrosulfate does not exceed 15 mol %. At a higher concentration, the tungsten oxides and bronzes are detected in diffraction patterns. The coherent coatings were obtained at 1073-1323 K and a current density of up to 50 A/dm². The higher the electrolysis temperature, the more coarse-grained the deposit obtained. However, at a temperature of 1073 K we obtained tungsten layers no thicker than 10 μm, insufficiently adherent to the substrate. At 1073 K and a current density higher than 50 A/dm², the powdered, highly-disperse deposits with a specific surface of up to 30 m²/g were obtained.

Table 1. The free corrosion potentials ($E_{cor}$) of nickel, St3 steel, and 12X18H10T stainless steel, and the deposition potential ($E_{dep}$) of tungsten and tungstate-pyrosulfate melts (by two series of measurements)

| Composition of melt | $E_{cor}$, V | $E_{dep}$, V |
|---------------------|--------------|--------------|
| Component           | Concentration, mol % | Nickel | St3 steel | Stainless steel 12H18N10T | Stainless steel 12H18N10T |
| Na₂WO₄              | -92.5        | -1.18       | -1.33     | -1.34     | -1.50     |
| Na₂S₂O₇             | -7.5         | -1.24       | -1.38     | -1.35     | -1.75     |

The effect of cathode current density, duration of electrolysis, and the reversal regime conditions was investigated in an electrolyte Na₂WO₄ - 7.5 mol % Na₂S₂O₇. At a temperature of 1173 K and the current density of 1 to 10 A/dm², we obtained well-adherent, absolutely nonporous and uniform coatings. In the initial period of deposition, their grain size decreased with the increasing current density. However, at a density higher than 10 A/dm², the grains grew considerably coarser, the roughness amplitude increased from 1 to 2-3 μm, while the progressive growth of separate projections transformed into dendrite formation, interfering with a further thickening of the coating. Below the current density of 1 A/dm², the corrosion rate of a substrate for all substrates presented exceeds the deposition rate of tungsten, which causes poor adhesion of coatings. The tungsten deposition rate in the range of current densities under investigation equals 15-40 (μm/h, while its current efficiency is 85% (Fig. 2). The latter decreases with the increasing duration of electrolysis (Fig. 3).

As the coating grows thicker, a uniformly fine-crystalline structure of its surface changes to a coarse-grained one. A reversal electrolysis regime was applied in order to obtain a fine-crystalline structure. The ratio $\tau_c/\tau_a$ was varied in the range from 20 to 40, the duration of the anode phase equaled 0.5-2.0 s, and the anodic current density was in the range of 15 to 50 A/dm². For electroplating, the following electrolysis conditions are optimum: $\tau_c = 20$ s, $\tau_a = 0.5-1.0$ s, $i_c = 8-10$ A/dm², and $i_a = 20-30$ A/dm². These electrolysis conditions enable one to halve the roughness of a coating and to increase its thickness up to 200 μm.
Physicochemical and Operational Properties of the Tungsten Coatings. Continuous and well adherent tungsten coatings were obtained on graphite, nickel, copper, molybdenum, tungsten, structural (machine) steels, heat-resistant and hard alloys, as well as nitrided or nickel plated titanium.

Under laboratory conditions, we used alundum containers, tungsten plates or rods as anodes, and chemically pure initial components. In the tungsten coatings thus produced, the x-ray microspectral analysis detected admixtures (Al, Cr, Mo, and Ni) in the range...
from \(2 \times 10^{-2}\) to \(4 \times 10^{-4}\) wt %. Such a small content of admixtures affect the structure of the coatings unnoticeably. The absence of coating-peeling in the course of quality tests is an indirect criterion of its high adhesion to the substrate [14].

The porosity of the coating was tested by applying a filter paper impregnated by 10 g/l solution \(K_3[Fe(CN)_6] + 20 \ g/l \ NaCl\) on the coated steel 3 and 45 surfaces. The test duration was 5 min. The average number of pores per 100 cm² was about 5-6. According to evaluation standards [14], the pore area amounts to about 0.0 to 0.1%, which corresponds to almost nonporous coatings.

Figure 4. The distribution of iron and tungsten in the diffusion zone at the substrate-coating interface.

The microhardness of the coating was 440-460 kg/mm². The layers of the base metal adjacent to the coating are markedly strengthened, which is indicative of the mutual diffusion of the elements of coating and substrate. Figure 4 shows a 10 to 15 µm thick diffusion zone in a microsection of the tungsten-coated St3 steel, tested by X-ray microspectral analysis.

The wear resistance of a specimen was tested on a SMTs-2 instrument under a specific load of 5 MPa in a transformer oil medium with a wide range of slide velocities. The counterbody was the quenched 45 steel. The coating increased the wear resistance of steel by a factor of 4 to 6.

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The coated specimens of the 45 steel were also tested for abrasion resistance according to the GOST (State Standard) 23208-89 in a medium of 150 μm fraction of synthetic corundum under a load of 44.1 ± 0.25 N. Due to the coating, the wear resistance of the specimens increased by a factor of 3 to 5, and was only slightly inferior to that of the specimens borated from the gas phase.

CONCLUSIONS

Thus, we have investigated the electrochemical behavior of tungstate-borate melts, the electrodeposition of tungsten coatings, and studied their properties.

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