ELECTRODEPOSITION OF SILVER AND ITS INFLUENCE ON THE FORMATION OF COATINGS OF MOLYBDENUM CARBIDE IN TUNGSTATE-MOLYBDATE-CARBONATE MELTS

Prof., Dr. Sc. Malyshev V. [1], Prof., Dr. Sc. Kushchevska N. [1]., Prof., Dr. Sc. Bagliuk G. D.Sc.[2], Ph.Dr. Gab A.[1], Ph. Dr. Lukashenko T.[1], Prof., Dr. Sc. Gaune-Escard M. [3]

Institute for Engineering & Technology – University "Ukraine", Ukraine [1]

I.M. Frantsevich's Institute for Problems in Materials Science of the National Academy of Sciences of Ukraine, Ukraine [2]

IUSTI, Ecole Polytechnique, Aix-Marseille University, France [3]

gbag@ukr.net

Abstract: *Electrochemical behavior of silver in tungstate-molybdate melts was studied by potentiometric and voltammetric methods. The electrode process was identified as a single-electron reversible one. The effect of silver on the electrochemical deposition of molybdenum carbide coatings and their electrochemical corrosion behavior in a sodium polysulfide melt was studied.*

Keywords: ELECTRODEPOSITION, MOLYBDENUM CARBIDE, SILVER, COATING, POWDER

1. Introduction

Electrochemical deposition of molybdenum carbide coatings from oxide and halide-oxide melts was studied earlier. Deposition of coatings with a thickness of up to 50 μm and roughness of 2-3 μm was shown to be possible. The effect of silver ions on electrochemical deposition of tungsten and tungsten carbide from chloride melts was also described [1, 2]. But the effect of silver ions on electrochemical deposition of molybdenum carbide from tungstate-molybdate-carbonate melts has not been studied yet.

In order to study cathodic reduction of silver from a tungstate melt, and apply it for electrochemical deposition of molybdenum carbide-silver coatings, we used a complex of electrochemical and physico-chemical methods such as: voltammetry, potentiometry, potentiostatic and galvanostatic electrolysis, X-ray analysis, and profilometric analysis.

2. Experimental

All the measurements were performed with an access for air. A graphite crucible (grade MPG-7) with the melt acted as an anode. The melt was prepared from pre-dried components: analytical grade Na_2WO_4 and Na_2MoO_4, chemically pure MoO_3 and $LiCO_3$. Silver molybdate was synthesized in a form of deposit by mixing aqueous solutions of $AgNO_3$ and Na_2MoO_4. A half cell $[Pt,O_2|Na_2WO_4-0.2WO_3]$ acted as a reference electrode. It was separated from the bulk melt by an alundum diaphragm [3, 4]. A face silver indicator electrode was prepared by melting the silver in an alundum tube of 1.5 mm diameter. Nickel plates (10 x 20 x 1 mm) were used as cathodes for the electrochemical deposition.

Electrochemical behavior of both molybdenum and silver should be known for elaborating the process of their electrochemical codeposition with a formation of electroplate. The electrochemical behavior of molybdenum was studied earlier [5].

3. Result and discussion

3.1 Electrochemical behavior of silver in the tungstate-molybdate melt

Two waves are observed in voltammograms for Na_2WO_4-MoO_3-Ag_2MoO_4 melts at -(0.3-0.5) V and –(1.1-1.2) V (Fig. 1). The last of them corresponds to reduction of dimolybdate ions $Mo_2O_7^{2-}$ to molybdenum metal. The major wave at the platinum electrode is preceded by the alloy-formation wave absent at the silver electrode. Potentiostatic electrolysis at the first-wave potential produces silver metal. The following changes occur in the current-potential curves with increasing Ag_2MoO_4 concentration: the silver deposition potential is shifted by about 300 mV positive; the $Mo_2O_7^{2-}$ reduction wave potential is shifted from -(1.1-1.2) V to -

(0.3-0.4) V due to electrodeposition of molybdenum on already deposited silver, the molybdenum oxidation wave is displaced from -(1.0-1.1) V to -(0.3-0.4) V.
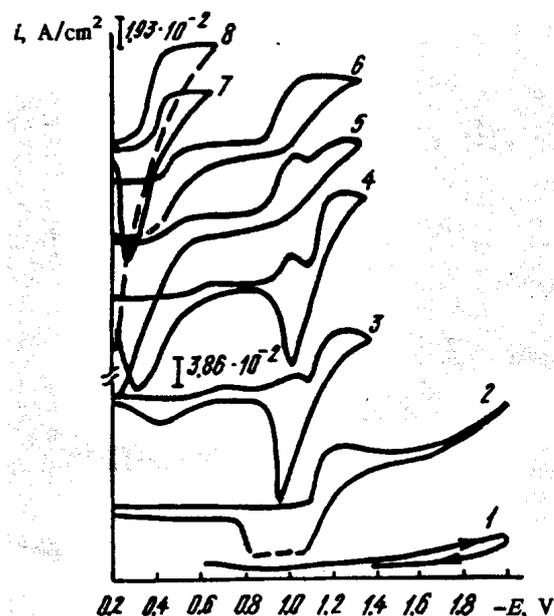

Fig. 1 *Voltammograms for Na_2WO_4 (1), Na_2WO_4 - 2mol.%MoO_3 (2), and Na_2WO_4 - 2mol.%MoO_3 - Ag_2MoO_4 melts with the following concentrations of Ag_2MoO_4: 3,4 - 2.5×10^{-5}; 5 - 5×10^{-5}; 6 - 7.5×10^{-5}; 7 - 1×10^{-4}; 8 - 1.5×10^{-4} mol/cm^3. Cathode - Pt, T = 1173 K.*

Potentiodynamic polarization curves of the silver electrode in the melt Na_2WO_4-MoO_3-Ag_2MoO_4 (Fig. 2) exhibit two waves in the potential ranges -(0.3-0.5) V and -(1.1-1.2) V, respectively. The first wave corresponds to the cathodic reduction of silver ions Ag^+ to the metallic silver. The second wave indicates the reduction of dimolybdate ions $Mo_2O_7^{2-}$ to the metallic molybdenum.

A proportionality between the limiting current i_1, and the Ag_2MoO_4 content; the wide-range independence of the $i_1/v^{1/2}$ ratio from the scanning rate of the electrode polarization (here i_1, is the limiting current, $v = dE/d\tau$ is the scanning rate), as well as the magnitude of the diffusion constant i_1/nFc (1-6 μm/s) indicate the diffusion control of the electrode process. Stationary polarization curves plotted in semilogarithmic coordinates $E - \log(i_d - i)$ confirm the single-electron reversible type of the charge transfer ($0.93 < n < 1.19$) (Fig. 3).
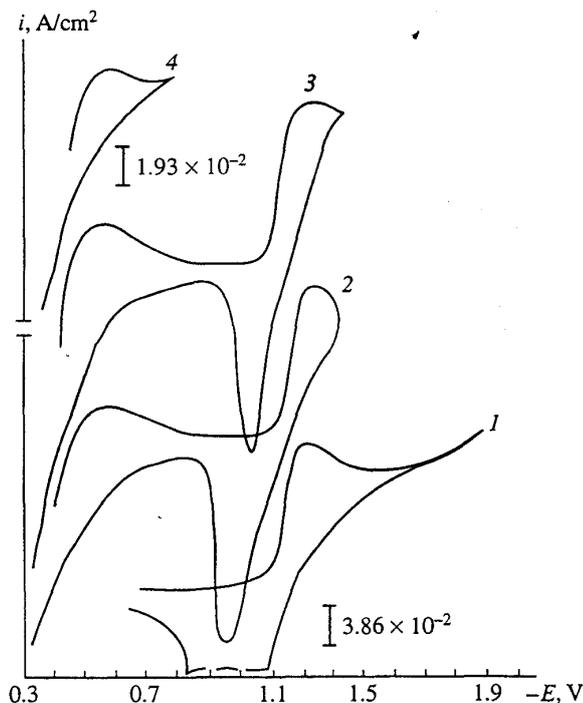
Fig. 2 *Potentiodynamic polarization curves (T = 1173 K, polarization rate 0.1 V/s) of the Ag electrode in the following melts: Na_2WO_4 - 2mol.% MoO_3 (1); Na_2WO_4 - 2mol.% MoO_3 - 75 mmol/l Ag_2MoO_4 (2); Na_2WO_4 - 2mol.% MoO_3 - 100 mmol/l Ag_2MoO_4 (3); Na_2WO_4 - 2mol.% MoO_3 - 250 mmol/l Ag_2MoO_4 (4).*
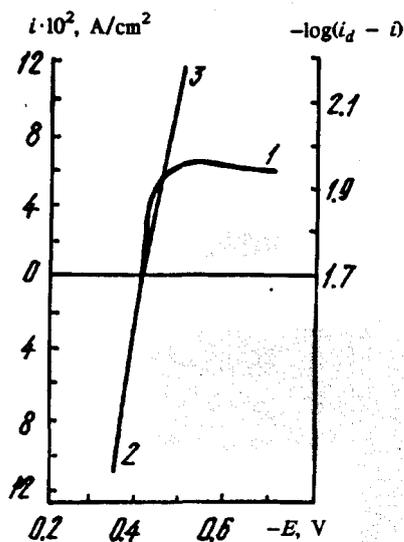
Fig. 3 *Cathodic (1) and anodic (2) polarization of silver electrode in Na_2WO_4 - 1×10^{-4} mol/cm^3 Ag_2MoO_4 melt and its semilog presentation (3). T = 1173 K.*

Potentiodynamic measurements (Fig. 4) lead to the following conclusions: (1) the silver equilibrium potential does not depend on MoO_3 content within its range from 1 to 20 mol %; (2) the dependence of silver equilibrium potential on the Ag^+ concentration corresponds to the single-electron reaction; and (3) platinum-oxygen electrode potential is almost independent of Ag_2MoO_4 content.

The abovementioned indicates that silver in the sodium tungstate solution exists in a form of single-charged cations Ag^+, that are not bonded with the O^{2-} ions.

Silver deposition potential is 0.5 - 0.6 V higher than that of molybdenum. Insofar as there are no Ag-Mo alloys in the phase diagram [6-8], silver may be supposed to somehow affect the electrochemical deposition of the molybdenum carbide and, in so doing, to affect properties of the electroplate.
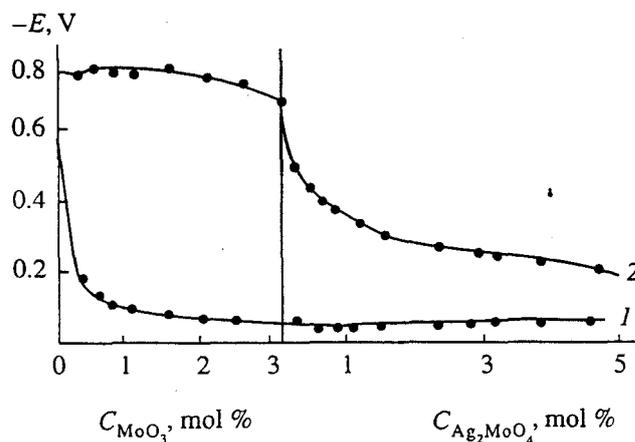

Fig. 4 *Chronopotentiometric curves of Mo (1) and Ag (2) electrodes in the Na_2WO_4 melt with the sequential addition of MoO_3 and Ag_2MoO_4. T = 1173 K.*

3.2 The effect of silver and the electrolysis conditions on electrochemical deposition of molybdenum carbide deposits

The effect of silver on the electrochemical deposition of Mo_2C coatings was studied earlier in a Na_2WO_4-Na_2MoO_4-5mol.%MoO_3-10mol.%Li_2CO_3 melt. Silver molybdate was added within the concentration range from 10^{-3} to 10^{-1} mol.%. A graphite crucible (grade MPG-7) was used as the anode. Nickel plates (10 x 20 x 1 mm) were used as the cathodes. Electrochemical deposition of Mo_2C was performed at 1073 -1223 K and cathodic current density of (2-50) x 10^2 A/m^2. The deposit was subjected to X-ray analysis (using a diffractometer DRON-2.0) and profilometric analysis (using a profilograph PR-201). The thickness of the coatings was measured by a high-speed indicator 2IGM.

Small additions of Ag_2MoO_4 (10^{-3}-10^{-2} mol.%) to the previously studied electrolyte result in significantly decreasing the roughness of the electroplate (the profile amplitude becomes lower than 1 μm instead of 2-3 μm) and increasing its maximum thickness to 150 um. However, when Ag_2MoO_4 content exceeds 10^{-2} mol %, the deposit becomes spongy and their adhesion to the substrate worsens.

At 1073 K and Ag_2MoO_4 content 10^{-3}-10^{-2} mol.% the spongy deposits Mo_2C-Ag are formed. In a temperature range of 1073 to 1123 K thin (up to 10 μm) deposits are obtained, while above 1223 K they are again non-adhered and spongy. The optimum is a range from 1123 to 1173K.

When cathodic current density is lower than 5 A/dm^2, the metallic silver is mainly deposited, within the range 5-15 A/dm^2 it is a Mo_2C-Ag coating with proper adhesion, and at a higher current density the dendrites rapidly begin to grow.

The co-deposited silver increases the free corrosion potential of Mo_2C by 0.7-0.8 V, i.e. from -1.05 ± 0.05 to -0.35 ± 0.05V.

3.3 Corrosion-electrochemical behavior of steel 45 electroplated with molybdenum carbide, in the sodium polysulfide melt

Weight loss of the samples with a Mo_2C-Ag electroplate after a 34-day test in the Na_2S_3 melt at 623 K is 3.5 ± 0.5 g/m^2, which is comparable to the losses of the diffusionally chromized Steel 45. This testifies the applicability of the electroplating for corrosion protection of containers for sodium-sulfur chemical cells.

Cyclic potentiodynamic polarization curves of the electroplated and diffusionally chromized Steel 45 recorded in the Na_2S_3 melt at 623 K are similar (Fig. 5), being analogous to the curves of the graphite electrode [9]. The cathodic peak A is attributed to a formation of the blocking layer of Na_2S_2 and the peak B is attributed to the transformation of Na_2S_2 to Na_2S. Polarization curves of samples with porous electroplate (Fig. 5) exhibit also peaks C and D, which are peculiar to steel electrodes. The peaks become more distinct with an increase in the test duration, thus

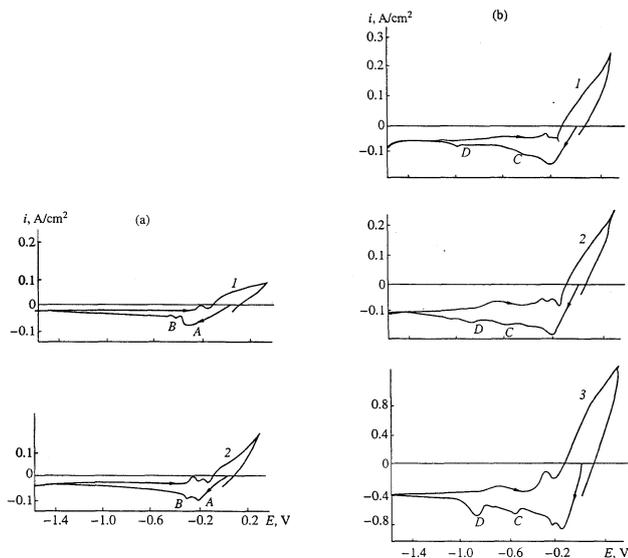indicating the accelerated etching of the defects. This fact can be used to assess the quality of plating.

Fig. 5 Cyclic potentiodynamic (0.01 V/s) polarization curves (T = 623 K) of the coated steel 45 in Na_2S_3 melt: (a) proper coatings: (1) diffusionally chromized; (2) electroplated with molybdenum carbide - silver; (b) porous with molybdenum carbide - silver coatings after exposure to the melt for 0.5 h (1) and 3 h (2); uncoated steel 45 (3).

4. Conclusion

Electrochemical behavior of silver in tungstate-molybdate melts was studied. The electrodeposition of silver proceeds according to the single-electron reversible mechanism and is diffusionally controlled. The effect of silver on the electroplating with molybdenum carbide was also studied. Conditions for proper electroplating were experimentally determined. The electroplates may be recommended for pilot corrosion protection of containers for sodium-sulfur chemical cells.

5. Literature

[1] Malyshev V.V., Kushkov H.B., Shapoval V.I., Environmentally appropriate technologies and resource saving in high-temperature electrochemical synthesis, deposition of metal coatings on superhard materials, and processing of used cutting and boring tools, in book «Green Industrial Applications of Ionic Liquids, ed. by R.D. Rogers et al., Kluwer Academic Publishers, the Netherlands, 2003.

[2] Malyshev V., Electrodeposition of different types of tungsten cathode deposits from ionic melts, Materials Science, 47, 2011, 345-354.

[3] Zoski C.G., Handbook of Electrochemistry, Elsevier, 2007.

[4] Laboratory Techniques in Electroanalytical Chemistry, ed. by Kissinger P.T., Heinemann W.R., 2nd ed., N.Y., Marcel Dekker, Inc., 1996.

[5] Malyshev V., Gab A., Gaune-Escard M., Molybdenum Electrometallurgical Processes in Ionic Melts, Materials and Manufacturing Processes, 23, 2008, 748-751.

[6] Kurlov A.S., Gusev A.I., Tungsten and Molybdenum Carbides and W(Mo)–C Diagram, Inorganic Materials, 42, 2006, 121-127.

[7] Chapter 2: Phase diagrams in alloy systems, Intermetallic Chemistry, ed. by Ferro R., Saccone A., Pergamon Materials Series, 13, 2008, 7-80.

[8] Science of Hard Materials, ed. by Viswanadham R., Springer, 2012.

[9] Dobson J.C., McLarnon F.R., Cairns E.J., Voltammetry of Sodium Polysulfides at Metal Electrodes, J. Electrochem. Soc., 133, 1986, 2069-2076.