Influence of pulse electrolysis modes on structure and properties of coatings based on Co-Mo alloy obtained from citrate pyrophosphate electrolyte

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Abstract. The present paper has represented the results of the research of electrochemical deposition of coatings based on Co-Mo alloy obtained from the citrate pyrophosphate electrolyte. Influence of pulse electrolysis modes, in particular relative pulse duration, on current efficiency and elemental composition has been determined. Research of the obtained coating microreliefs has been performed.

1. Introduction

Intensive researches in the area of electrochemical deposition of the cobalt-molybdenum alloy have caused by a wide range of its high-performance characteristics. Due to increased hardness, melting temperature, electrical conduction, corrosion and electro-discharge stability, Co-Mo alloys are applied in vacuum and plasma electronic devices, chemical industry and etc. The present alloy also demonstrates catalytic properties and it can be used for hydrogen generation [1]. Recently, Co-Mo alloy with its magnetic properties is considered as a material for information recording and storing systems and for development of microelectromechanical system elements [2].

In spite of a high number of publications concerning electrodeposition of molybdenum alloys with metals of the Fe-group [3, 4], some aspects of the present process are still not revealed that caused by its high complexity. In particular, the pulsed mode of electrodeposition has not been studied sufficiently.

2. Experiment details

The present paper has used a citrate pyrophosphate electrolyte for the electrodeposition that is an alternative to the most researched citrate one. Tasks of the paper have been a research of parameters and modes of the Co-Mo alloy electrodeposition process and also structure and composition of the obtained coatings in order to determine conditions for deposition of high-quality coatings with the high molybdenum content and minimal number of microcracks.

Citrate pyrophosphate electrolyte of the following composition: CoSO₄ – 15.5 g/l; Na₂MoO₄ – 2.06 g/l; Na₃C₆H₅O₇ – 51.6 g/l; K₃P₂O₇ – 66 g/l; Na₂SO₄ – 7.1 g/l has been used for deposition of coatings. Deposition has been performed in modes of the steady-state and pulse electrolysis at the 9.3 pH level. Cathodic current density has been varied within the range 0.5–5 A/dm². Period of the pulse repetition within the pulse electrolysis is 100 ms, off-duty ratio has been varied from 20% to 50%. Plates of Cu-DHP oxygen-free copper with 1×2 cm² dimensions and 1 mm thickness have been
used as substrates. Substrates were mechanically polished by the felt disk without usage of the abrasive material and then they were degreased in the solution containing NaOH and Na₂CO₃ with 30 g/l concentration for each component at 70 °C temperature. Temperature of the electrolyte during the deposition was 50 °C. Electrolyte agitation was not used.

Morphology of the sample surfaces and chemical composition have been researched using the scanning electron microscope JSM-6610LV (JEOL, Japan) equipped with the X-ray fluorescence energy-dispersive detector INCA X-MAX (Oxford Instruments, England).

Current efficiency has been calculated according to ratio:

\[ \eta = \eta_{Mo} + \eta_{Co} = \frac{w_{Mo} \Delta m / E_{Mo}}{q} + \frac{w_{Co} \Delta m / E_{Co}}{q}, \]  

(1)

where \( \eta_{Mo} \) – a component of the molybdenum current efficiency; \( \eta_{Co} \) – a component of the cobalt current efficiency; \( E_{Mo} \) – an electrochemical equivalent for the molybdenum; \( E_{Co} \) – an electrochemical equivalent for the cobalt; \( \Delta m \) – a coating mass (grams); \( w_{Mo} \) – a molybdenum content in the alloy (mass); \( w_{Co} \) – a cobalt content in the alloy (mass); \( q \) – a discharge passed through the electrolyte:

\[ q = \int I(t) dt, \]  

(2)

where: \( I \) – operating current; \( t \) – deposition time.

3. Results and discussion

A set of sample coatings has been obtained under conditions of equal discharge passed through the electrolyte in order to research influence of the cathodic density of the deposition current on the current efficiency and molybdenum content in the coating. Figure 1 has represented dependencies of the current efficiency and molybdenum content during various current modes.

Figure 1. Dependence of the current efficiency (a) and molybdenum content in the alloy (b) on the cathodic current density within direct current and pulse current with various relative pulse durations – 50 % and 20 %.

In general, dependence of the current efficiency on the cathodic density for all current modes shows a falling character (figure 1(a)). Dependencies for the pulse modes of the electrochemical deposition with various relative pulse durations are similar - there is some growth in the area 1–3 A/dm². Presence of the maximum in the area 3 A/dm² can be explained by two opposed factors: on the one hand, increase of the current density leads to the growth of pH in the cathode layer that increases current efficiency, on the other hand, increase of the current density leads to depletion of the near-electrode layer and decrease of ligand metal ion concentration that followed by decrease of the current efficiency. Usage of the electrochemical deposition pulse mode for the present electrolyte leads to the decrease of the current efficiency and, at the same time, current efficiency increases with decrease of the pulse ratio. It is obviously connected with more effective recovery of the ligand metal ion concentration in the cathode space provided by the diffusion during pauses between pulses.
The highest molybdenum concentration in the coating is achieved within the current density range 2–5 A/dm² under conditions of the pulse electrochemical deposition in comparison with the direct current (figure 1(b)). Decrease of the pulse ratio leads to the concentration growth and for the present conditions of the experiment, the maximum concentration 18.3 at.% is provided at pulse ratio 20% and cathodic current density 3 A/dm².

Then the research of the structure and morphology of the coating surface have been performed for the obtained set of samples. Figure 2 shows SEM-images of typical surface parts of samples obtained during various current modes. Thickness of the coating was 8 μm in each case. As the figure shows, the pulse electrolysis stimulates an increase of the crystallization center number (figure 2(b)) that corresponds to general consideration about the pulse electrolysis described in [5]. Redistribution of the crystallization centers and growing crystal faces happens during the following cathodic pulse that leads to a periodical change of the sediment structure. Significant changes of the coating surface relief structure obtained during various pulse ratios have not been revealed. Also, it should be noted that usage of the pulse mode decreases the coating cracking.

Figure 2. SEM-images of typical parts of coating sample surfaces based on Co-Mo alloy obtained within the mode of the constant electrolysis (a) and within the mode of pulse electrolysis with pulse ratio 50% (b).

4. Conclusions
So, the performed researches have shown a possibility to control molybdenum concentration in the alloy by varying electrolysis current modes. Analysis of the alloy current efficiency within the range of the cathodic deposition current density change from 0.5 A/dm² to 5 A/dm² has been performed and peculiarities of the obtained coating microrelief have been researched.

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References
[1] Masdek N R N, Salleh Z, Koay M H and Ismail M A 2018 Materials Science and Engineering 380 012012
[2] Gomez E, Pellicer E and Duch M 2006 Electrochimica Acta 51 3214–22
[3] Kuznetsov V V, Bondarenko Z V and Pshenichkina T V 2007 Russian Journal of Electrochemistry 43 349–54
[4] Gomez E, Pellicer E and Valles E 2007 Surface & Coatings Technology 197 238–46
[5] Poventkin V V and Kovenski I M 1989 Structure of electrochemical coatings (Moscow: Metallurgy) 136