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Study of Ni-Mo electrodeposition in direct and pulse-reverse current

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Abstract. Process of electrochemical deposition of the coating based on a binary nickel-molybdenum alloy onto a nickel substrate under pulse mode with current reverse within the range of current density change from 2 to 9 A/dm^2 has been researched. Coating structure and its surface morphology have been studied. Method of X-ray energy dispersive spectroscopy has determined a percentage ratio of alloy components in the coating. Mode to obtain the densest and smoothest deposits has been identified under considered terms.

1. Introduction

Coatings on the basis of Ni-Mo alloy deposited by the electrochemical method have a high hardness, wear resistance, heat resistance, corrosion resistance in alkalis, chloride-containing environments and non-oxidizing acids (for example, HCl). Besides, Ni-Mo alloys are catalysts of the hydrogen electrochemical synthesis reaction that significantly decreases hydrogen evolution overpotential. At present the most available method to obtain coatings on the basis of nickel-molybdenum alloy is an electrochemical deposition from electrolytes containing nickel and molybdenum salts. This method does not require high energy and financial costs and also special complex equipment. Main issues restricting an area of galvanic Ni-Mo coating usage are coating defects in the form of cracks and also significant coating inhomogeneity and its high roughness. There are a lot of papers regarding optimization of conditions for electrochemical synthesis aimed at improvement of the surface structure and properties. Main electrolytes used for deposition of coatings based on Ni-Mo alloy are citrate and ammonia-citrate electrolytes [1–4]. Electrodeposition with direct current is traditionally used. Comparatively small number of papers dedicated to research of deposition of coatings based on Ni-Mo alloy under pulse mode is known [5–9]; very small part of them is dedicated to research of pulse mode with current reverse [10–13]. Paper [10] determined that under pulse-reverse mode of deposition surface roughness does not increase with rise of thickness in comparison with the mode of direct current, however coating surface images obtained under various modes have not been provided. Paper [11] published results of study of Ni-Mo alloy coatings under pulse-reverse mode of deposition. Obtained samples of coatings have an apparent globular structure with significant surface roughness. However, complex composition of the electrolyte complicates interpretation of obtained results. That is why, study of electrodeposition of Ni-Mo alloy under pulse-reverse current mode is important.

Purpose of the present paper is a research of influence of mode parameters of the pulse electrodeposition with reverse current on the coating structure and morphology on the basis of

electrolytic Ni-Mo alloy under its deposition from the traditional ammonia-citrate electrolyte within current densities from 2 to 9 A/dm^2.

2. Experiment method

Nickel plates of the trademark NPA1 were a substrate for experiments. Final polishing of plates was performed using diamond paste NOM 0,5/0 up to appearance of surface high luster. After polishing, substrates were processed by ultrasound in 5 M solution HCl within 20 min. Then within 30 min washing was fulfilled in acetone and after – in alcohol within the same period of time. At the conclusive stage they were washed by distilled water. Before deposition of the coating the surface was cathodically activated in the solution containing nickel chloride and hydrochloric acid at the ratio 1:1 within 3 min under current density 1 A/dm^2. Electrodeposition of the nickel-molybdenum alloy was performed under pulse-reverse current with rectangular impulse shape where the reverse pulse followed after direct pulse. Ammonia-citrate electrolyte was used with the following composition [2]: $Na_2MoO_4 \cdot 2H_2O$ – 10 g/l; $NiSO_4 \cdot 7H_2O$ – 24 g/l; $NiCl_2 \cdot 6H_2O$ – 20 g/l; potassium citrate $K_3C_6H_5O_7$ – 70 g/l; NH_4OH – 60–80 g/l up to pH – 10.5. Two-electrode cell with the insoluble platinum anode and nickel cathode was used for deposition. Potentiodynamic current-potential curves were taken in order to determine areas of electrolysis current densities under deposition of the coating by nickel-molybdenum alloy on the nickel substrate. Three-electrode cell with the silver-chlorine reference electrode and platinum anode was used for polarization of the nickel electrode. The paper used a potentiostat IPC-Pro.3A. Researches of samples were performed on a scanning election microscope JEOL JSM-6610LV equipped for the elemental analysis by an Energy-dispersive X-ray spectroscopy microanalyzer INCA X-MAX made by Oxford Instruments.

3. Results and discussion

Before execution of experiments potentiodynamic current-potential curves have been obtained with sweep rate of sample potential ±10 mV/s under room temperature in solution of the ammonia-citrate electrolyte where the following electrodeposition of the alloy was performed. Significant hysteresis reflecting changes of the sample surface state as a result of its dissolution and following reduction is observed on polarization curves of direct and reverse currents. There is a pad of limiting current (approximately in the area of 1.4–1.6 V) on a polarization curve of direct route. So, deposition of compact coating of the nickel-molybdenum alloy from the ammonia-citrate electrolyte begins under current density being corresponding to this pad registered on the polarization curve and continues under higher current densities.

However, experiments have shown that under significant increase of the current density the deposited alloy becomes more porous and quality of the coating becomes worse. It is connected with presence of diffusion limitations by nickel and molybdenum under high current densities [2]. Figure 1(a) represents a typical SEM-image of the nickel-molybdenum alloy coating surface of one of the obtained samples deposited under direct current mode onto a nickel substrate under current density 40 A/dm^2. Time of electrodeposition was 10 min.

Experiments have determined that under considered terms increase of current density above 10 A/dm^2 leads to significant changes of structure and roughness of the deposited coating surface, i.e. porosity increases, cracks and delaminations appear. Change of current within density range from 2 to 9 A/dm^2 (more acceptable range from the point of view of current efficiency and possibility to carry out a reaction of electrochemical deposition under considered experiment conditions) has shown that a current value does not influence on structure and microrelief of the coating. Typical SEM-image of the nickel-molybdenum alloy coating surface of one of the obtained samples deposited under direct current mode onto a nickel substrate under current density 5 A/dm^2 and deposition time – 10 min is shown in figure 1(b).

At the following stage a number of alloy electrodeposition experiments under mode of pulse with current reverse under duration of direct pulse 50–500 ms and duration of the reverse pulse from 10 to 200 ms was executed.

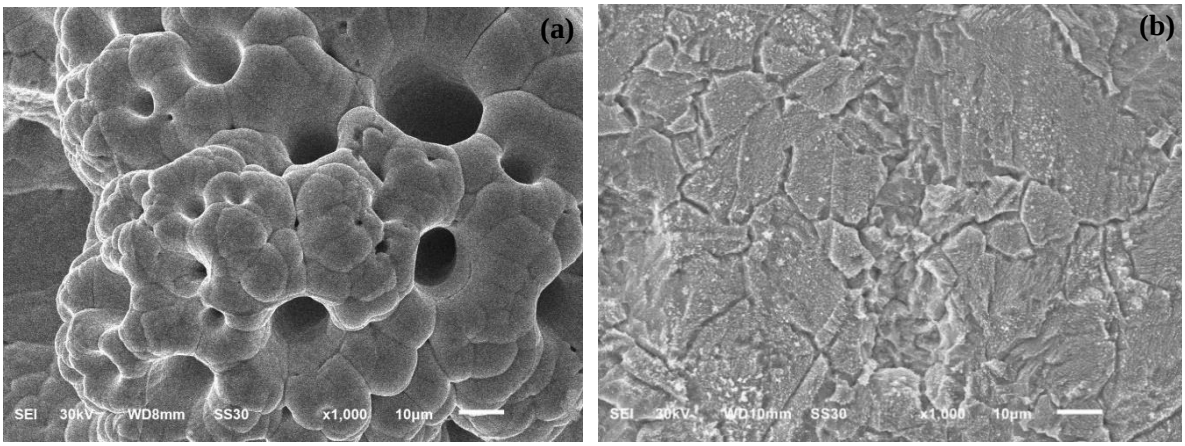

Figure 1. SEM-image of surface of the nickel-molybdenum alloy coating obtained under direct current mode onto a nickel substrate under various current densities: **(a)** – 40 A/dm^2; **(b)** – 5 A/dm^2.

Current density of the direct pulse was 5 A/dm^2, reverse one – 0.2 A/dm^2. Deposition time was 10 min in all cases. Analysis of the obtained sample surfaces has shown that within time interval of direct and reverses impulses being corresponding to tens of milliseconds (10–50 ms) a significant change of the deposited coating structure occurs: roughness and porosity decrease. "Refilling" of through cracks having a length of tens of micrometers is observed.

Figure 2 represents typical SEM-images of sample coating surfaces obtained under mode of pulse electrolysis with current reverse under various durations of reverse pulse being equal to 200 and 20 ms. Figure 3 represents SEM-images of Ni-Mo coating deposited under pulse-reverse electrolysis (5 A/dm2, 50 ms; –0.1 A/dm^2, 10 ms) at various surface magnifications. Time of electrodeposition was 10 min.

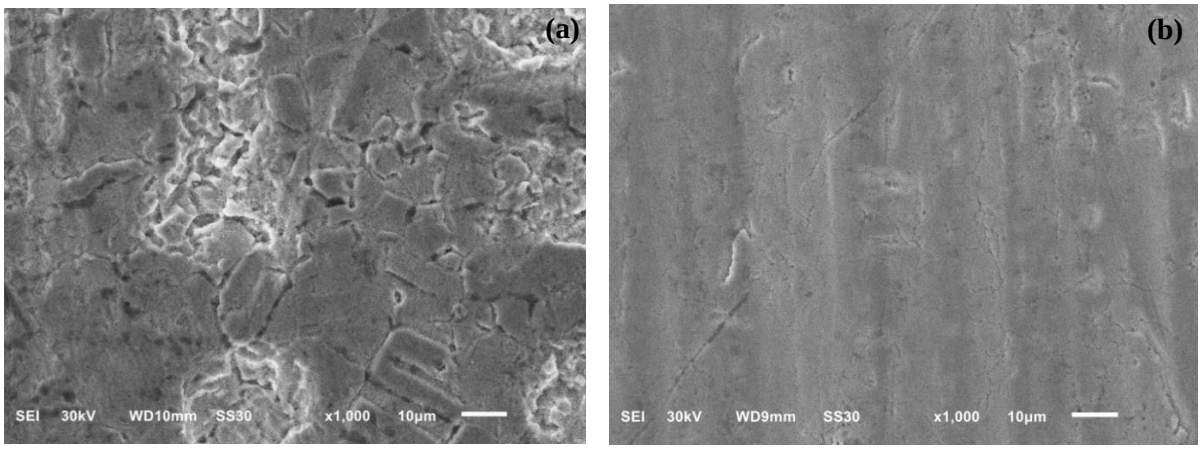

Figure 2. SEM-image of surface of the nickel-molybdenum alloy deposited under pulse electrolysis mode with current reverse onto a nickel substrate under various durations of reverse pulse: **(a)** – 5 A/dm^2, 50 ms; –0.2 A/dm^2, 200 ms; **(b)** – 5 A/dm^2, 50 ms; –0.2 A/dm^2, 20 ms.

It can be seen (figure 3) that the coating obtained within duration 10 ms of the reverse pulse has no defects (cracks), the surface of the coating is fairly smooth, characteristic dimensions of structural defects of the coating do not exceed 1 μm.

Method of X-ray energy-dispersive spectroscopy has determined a percentage ratio of nickel and molybdenum in deposits. Molybdenum content varied within 21–24 wt. %, nickel – 79–76 wt. %. Significant dependence of percentage content of alloy components on the electrolysis mode has not been detected.

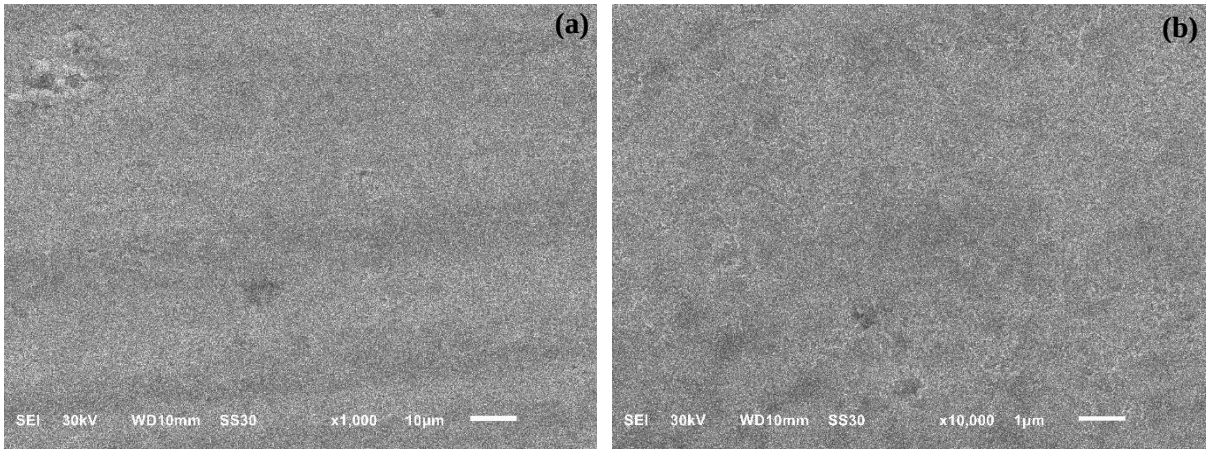

Figure 3. SEM-image of the surface of the nickel-molybdenum coating deposited under pulse-reverse current (5 A/dm^2, 50 ms; –0.1 A/dm^2, 10 ms) at various magnifications: **(a)** – ×1000; **(b)** – ×10 000.

4. Conclusions

The executed research has determined that under electrochemical deposition of the nickel-molybdenum alloy from the ammonia-citrate electrolyte, the good-quality coatings with minimum number of defects (cracks and pores) can be obtained using a non-stationary pulse mode of electrodeposition with reverse current, besides, step of reverse pulse should be within range 10–50 ms. Under such mode deposition of the alloy is possible within the whole researched range of current densities from 2 to 9 A/dm^2 without visible changes of coating structure and morphology. Besides, deposition mode does not influence on percentage content of Mo in coating.

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