

THE ROLE OF ELECTROLYSIS REGIMES IN THE FORMATION OF METAL AND METAL OXIDE COATINGS FROM COMPLEX CITRATE ELECTROLYTES

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Recently, the development of technologies for creating high-quality alloy coatings with a specific arsenal of properties has attracted the attention of scientists. The synthesis of electrode materials based on transition metals, mainly iron, cobalt, nickel, is of particular interest [1–3]. Today, the main attention is paid not so much to the electrodeposition of individual metals as to alloys based on these metals with refractory components, in particular, tungsten and molybdenum [4–6]. These alloys are more attractive due to significantly better functional characteristics compared to the common monometallic coatings of zinc, copper, nickel, cobalt etc. Systems containing molybdenum or tungsten are more complex and require more careful study of the influence of creation conditions on the surface composition, morphology and properties.

The current trend in materials science is the creation of composite coatings [7–9]. Among the methods of such systems synthesis the electrochemical deposition from stable electrolytes occupies an important place. Alloying components or intermediate oxides are incorporated into the matrix of main metal. A promising step in this direction is the synthesis of composite materials when oxide phase is formed directly in the cathodic process. This greatly simplifies the process, because it does not require preliminary synthesis of the second phase, stabilization and adjustment of the electrolyte. From the analysis of scientific and technical literature, it became

known that such systems have an inherent higher level of functional properties. Therefore, verification of such a hypothesis regarding Fe-Co-Mo coatings and determination of the influence of electrolysis modes on the composition and functional properties of the cathode deposits was the goal of the work.

Experimental

Coatings with alloys and composites based on the Fe–Co–Mo system were deposited onto a M1 copper substrate at a temperature of 20–25 °C from complex citrate electrolytes [10]. The composition of electrolytes was monitored and adjusted as necessary. The acidity of the working solutions was determined using a pH-meter pH-150M and maintained at a level of 4,5–4,85. The surface of the samples was prepared according to the standard method, which consists of mechanical grinding, degreasing, chemical etching, thorough washing and drying. A standard electrochemical cell SEC-2 was used for studying of kinetic peculiarities of the cathodic process. The modified laboratory version was a cylindrical thermostatic cell with three inputs with sections for the working electrode, auxiliary and reference ones.

Electrodeposition of ternary alloys in the was carried out using direct (DC) and pulse current (PC) with a DC source B5-47 and a potentiostat PI-50-1.1 with a programmer PR-8.

The topography of the surface was analyzed by atomic force microscopy (AFM) using a microscope NT-206. In laboratory conditions the visual analysis of the surface of coatings using an optical microscope was carried out. The chemical composition of the coatings was determined by energy dispersive X-ray spectroscopy using an Oxford INCA Energy 350 electron probe microanalyzer integrated into system of scanning electron microscope (SEM).

To determine the free surface energy (FSE) of alloys and composites the sitting drop method was used. The angle of contact and the angle between the tangent to the droplet at the point of contact of the solid, liquid, and gaseous phases and the surface of the sample were established. According to this method, the energy of a solid surface contains the following components: the dispersion component, which is

characterized by Van-der-Waals forces, and the polar component, which is characterized by strong interactions and hydrogen bonds. [11]. The Fe-Co-Mo coatings with thickness of 25 ± 2 μm were used to determine the FSE.

The corrosion resistance of the coatings was evaluated from the results of the cathode & anode voltammograms analysis in the solutions of various mineralization [12]. The sensoric properties of the synthesized coatings were tested by the “needle-anvil” point contacts method [13]. According to this method, one electrode was mounted on a element that moved along the surface of another electrode which was fixed. The formed point contact was polarized with direct current linearly changed by the generator, and the voltage drop was recorded on the multimeter KEITHLEY 2000[14].

Results and discussion

The Fe–Co–Mo systems both deposited by DC and by PC modes have compact surface with metallic luster [15]. However, some differences in the coatings composition follow from SEM results. Depending on the electrolysis mode, the surface of the coatings is characterized by a different content of components on the hills and in the valleys [16]. An uneven distribution of the components over the surface of the coatings deposited by direct current of $i=3$ A/dm^2 was detected. On the hills of the relief, metal molybdenum dominates due to the reduction of molybdate ions through intermediate oxides to metal. On the contrary, the oxygen content is higher in valleys and reaches 33–35 at. % (Fig. 1). This is due to the incomplete reduction of molybdates and the incorporation of intermediate oxides in the coating composition. Under such electrodeposition conditions, the molybdenum content is fixed in the range of 24.5–27 at. %. Considering the content of intermediate molybdenum oxides in the composition of coatings, they can be classified as metal oxide composite materials namely Fe-Co-MoOx.

A significant decrease in the oxygen content was observed in the coatings formed by PC. This fact is due to a more complete reduction of molybdates and intermediate oxides, which occurs not only at cathodic polarization, but also during the current interruption. The first stage is the electrochemical one, and the following

chemical reaction of molybdenum oxides reduction by adsorbed hydrogen atoms occurs during a pause. On hills and in valleys, the oxygen content decreases to 21 at.% and 25 at.%, respectively [17]. So, coatings deposited by PC mode are enriched with metallic molybdenum and contain less oxygen than that obtained by DC mode. Accordingly, such systems may be classified as metal coatings.

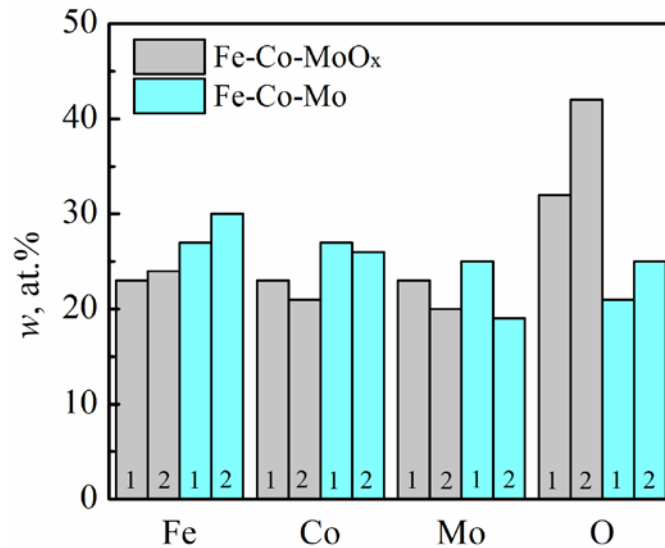


Fig. 1. Composition of coatings deposited by DC mode $i = 3 \text{ A/dm}^2$ (Fe-Co-MoO_x) and PC mode $i = 3 \text{ A/dm}^2$, $t_{on} / t_{off} = 5 \text{ ms} / 10 \text{ ms}$ (Fe-Co-Mo).

The graph shows the content of elements on the hills (1) and valleys (2).

The analysis results of the coatings with alloys and composites composition were the reason to consider the difference in the deposits nature depending the applied current mode. These differences affect the nature and surface properties of the materials, reflected by FSE parameter. The FSE value characterizes the wettability of the surface.

It is well known that adsorption on the coatings surface of oxygen ions, which displace an equivalent amount of free electrons, leads to the formation of a passive barrier film. Such a process significantly reduces the value of the surface free energy [18]. Composite and metal coatings are predictably characterized by high values of the polar component of FSE, which indicates the polarity of the surface. For example, the copper substrate parameter is of 60.07 MJ/m². Studies have shown that the FSE for Fe-Co-Mo coatings is of 127.74 MJ/m², and for Fe-Co-MoO_x composite is

slightly less (118.10 MJ/m²) but is twice higher than that of copper substrate. Such differences can be explained by the high FSE values of the alloying components of above ternary systems. Moreover, the decrease in FSE for composite coatings compared to metal ones caused by the high oxygen content also confirms our assumptions about the effect of coating composition on the state of coatings surface.

The relatively low values of the free energy of the studied surfaces are evidence of the hydrophobicity of the obtained alloys and composites, and it is one of the prerequisites for their high corrosion resistance. The protective properties of the alloys were determined by polarization resistance technique. The corrosion behavior of the ternary coatings noticeably differs from the low alloyed iron in all solutions [19].

In an acidic medium (pH 3), the corrosion potential shifts to more positive values, while the corrosion rate decreases due to the formation of film acidic molybdenum oxides on the coating surface. In slightly alkaline and neutral environments at pH 9.5 and pH 5, respectively, the corrosion potential shifts in the negative direction due to passivation of the alloy surface by sparingly soluble iron and cobalt oxides and hydroxides, which lead to inhibition of the cathodic reaction.

The analysis of corrosion resistance indices indicate that ternary alloy and composite coatings may be attributed to “stable” in an acidic environment and “very stable” in a neutral and slightly alkaline ones.

It is known that transition metals can be used as catalytic materials in various electrochemical processes or as a sensitive component in sensor devices. Therefore, it is interesting to test the sensory properties of coatings with alloys and composites of the Fe-Co-Mo system. The existence of sensory characteristics was established by creating point contacts “needle-anvil” [12], which was tested in gas media of varying composition. For study the effect of an gaseous agent, in particular hydrogen, on the behavior of a Cu|Fe-Co-Mo point hetero-contact, hydrogen was added to the cell with a short pulse to create a predetermined emitter concentration. The contact resistance R_0 in the equilibrium state before the onset of gas exposure was of 20 Ohms. The effect of a gas pulse was recorded from 25 seconds of exposure (Fig. 2). Due to

hydrogen adsorption on the surface of the conduction channel of the formed point contact, an increase in its resistance is observed, which leads to a decrease in electrical conductivity.

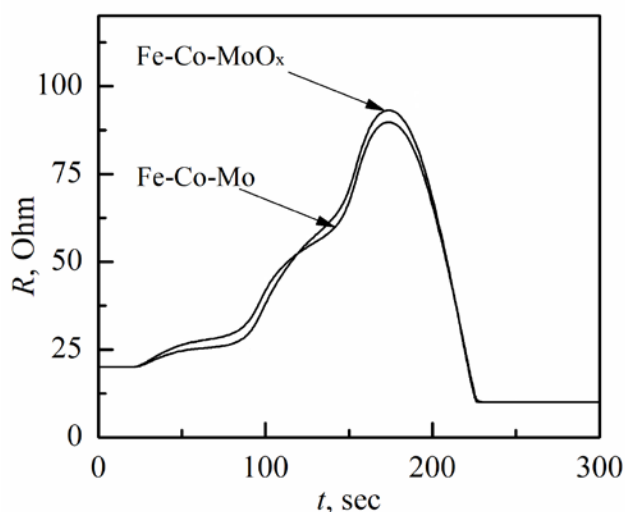


Fig. 2. The chronogram of point contacts Cu|Fe–Co–Mo and Cu|Fe–Co–MoO_x response; the effect of hydrogen with a concentration of 0.1 vol.%

The duration of the step-like decrease in electrical conductivity indicates the course of irreversible processes of interaction of hydrogen with the surface of the synthesized alloy. It was found that within 175 seconds of exposure to the emitting gas, the resistance reaches a maximum. Slightly lower values of electrical conductivity for composite metal oxide material are primarily due to the high content of refractory component oxides. Such behavior may be explained by two reasons.

Table 1. Electric-physical parameters of surface oxides

Metal	Oxide	Specific resistivity ρ ($\Omega \cdot \text{cm}$) 293 K	Chemical nature
Co	CoO	$10^6 - 10^{10}$	basic
	Co ₃ O ₄	$4 \cdot 10^3 - 10^5$	amphoteric
Fe	FeO	$10^5 - 10^8$	basic
	Fe ₃ O ₄	$4 \cdot 10^{-3}$	amphoteric
Mo	MoO ₂	$8.8 \cdot 10^{-5}$	amphoteric
	MoO ₃	$10^4 - 10^8$	acidic

In general, the increase in the electrical resistance of coatings with alloys and composites is probably due to the appearance of defects in the structure of metal sublattice as a result of the diffusion of hydrogen into the surface of coatings by ternary alloy. The other reason is the possibility of gaseous hydrogen reducing the surface layers of M_3O_4 spinel to MO oxides (M – Co, Fe), the resistance of which is much higher (Table 1). Testing of sensory properties confirmed the gradual change in electrical conductivity and high resistance of composite Fe-Co-MoO_x and metallic Fe-Co-Mo coatings.

Conclusions

1. Using a galvanostatic and pulsed modes of ternary alloy coating, Fe-Co-Mo systems with a dense surface with a metallic luster were obtained. At the same time the high content of molybdenum in the coverings synthesized by pulse electrolysis is established. Coatings that have been formed by direct current are characterized by a higher oxygen content in hills and in the valleys than coatings obtained by a non-stationary polarization regime. The differences in the composition of the coatings are explained by the chemical reaction of the reduction of intermediate oxides of molybdenum by hydrogen atoms as a result of the implementation of the Spillover effect during the pause. Coatings obtained from complex citrate electrolytes by direct and pulsed unipolar current can be classified as composite and metal coatings, respectively.

2. It was found that the value of the free energy of the surface of metal coatings and composites is 127.74 MJ/m² and 118.10 MJ/m², respectively. The FSE of the surface of Fe-Co-MoO_x composites is lower than the corresponding values for the Fe-Co-Mo metal alloy due to the higher oxygen content in its structure. Such composite coatings are chemically stable. In addition, Fe-Co-Mo(MoO_x) coatings are characterized as hydrophobic coatings.

3. Fe-Co-MoO_x composite and metal Fe-Co-Mo coatings have sensory properties for individual components of gaseous media and can be used as a sensitive element material for the sensor in determining the hydrogen concentration.

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