

RESEARCH INTO INFLUENCE OF THE ELECTROLYSIS MODES ON THE COMPOSITION OF GALVANIC Fe-Co-Mo COATINGS

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Досліджено вплив енергетичних (густина струму i) і часових (тривалість імпульсу t_i і паузи t_n , співвідношення t_i/t_n) параметрів електролізу на склад та морфологію покриттів Fe-Co-Mo. Встановлено, що підвищення тривалості імпульсу сприяє збагаченню сплаву молибденом тим більше, чим вище густина струму. Показано, що зі збільшенням густини струму структура поверхні покриттів змінюється від дрібнозернистої до глобулярної

Ключові слова: амплітуда струму, імпульсний режим, покриття Fe-Co-Mo, тернарні сплави, цитратний електроліт

Исследовано влияние энергетических (плотность тока i) и временных (длительность импульса t_i и паузы t_n , соотношение t_i/t_n) параметров электролиза на состав и морфологию покрытий Fe-Co-Mo. Установлено, что увеличение длительности импульса способствует обогащению сплава молибденом тем больше, чем выше плотность тока. Показано, что с ростом плотности тока структура поверхности покрытий меняется от мелкозернистой до глобулярной

Ключевые слова: амплитуда тока, импульсный режим, покрытия Fe-Co-Mo, тернарные сплавы, цитратный электролит

1. Introduction

Solving the applied problems in the development of new technologies and extending a range of functional materials predetermines interest of researchers and technologists in the galvanic multicomponent alloys. Special attention is paid to the electrochemical synthesis of alloys by the metals of iron triad with d^4 -elements namely Fe(Ni, Co)-Mo(W) [1]. Such coatings are interesting by the possibility of combining functional properties that exceed analogous indicators for the alloy-forming metals [2]. In certain cases, researchers note the super-additive strengthening of operational charac-

teristics [3]. Comprehensive realization in the thin layers of improved microhardness, wear and corrosion resistance, catalytic, and magnetic properties makes it possible to significantly expand the scope of application of such coatings [4]. These include the replacement of toxic chromium-plating and creation of effective catalytic materials, more affordable in comparison with traditional platinoids.

The electrochemical methods of synthesis make it possible to flexibly control the content of components, rate of deposition, surface condition through the variation of the composition of electrolytes and regimes of polarization (static or pulse, reverse current or a decrease in potential) [5, 6].

It is obvious that the formation of coatings in each individual case depends first on the qualitative [7] and quantitative [8] composition of electrolyte. Second, the composition of galvanic deposits, the ratio of components and the phase composition of coatings are essentially affected by the synthesis conditions [9]. In turn, the structure of alloy pre-determines the properties and areas of application of coatings. Given this, it is a relevant task to examine influence of the electrolysis regimes on the composition and morphology of galvanic alloys.

2. Literature review and problem statement

In recent years, the international scientific literature has featured a growing number of publications that address the electrosynthesis of coatings by the alloys of metals of iron subgroup with d⁴-elements [10, 11].

An inclusion (Incorporation) into the composition of coatings of tungsten and molybdenum makes it possible to inherent internal stresses in the electrolytic alloys of iron, and to improve low adhesion [12] as well as the physical-mechanical properties of coatings [13].

Article [14] described coatings based on iron Fe-W and Fe-W-P obtained from the electrolytes of different composition, which demonstrate high wear stability and corrosion resistance. It is also noted that the friction coefficient of amorphous ternary alloys Fe-W-P is less than that of the binary coatings Fe-W.

Authors of [15] emphasize the increased wear resistance of the Fe-W, Ni-W and Co-W coatings, received from the citrate and citrate-ammonia electrolytes at low volume current densities.

The coatings Fe-Mo were obtained from the pyrophosphate electrolyte under the mode of asymmetric current in the interval of 10–100 mA/cm² [16]. As follows from the presented results, with an increase in the mean current density there is an increase in the content of iron in the alloy. Maximum current efficiency is 50 % at the content of molybdenum 47 % by mass.

Improved electrocatalytic activity of the binary alloys Co-W, obtained by pulse current, was demonstrated for the model reaction of the electrolytic hydrogen evolution and catalytic oxidation of benzene [17].

High corrosion resistance and electrocatalytic activity of the Co-W coatings was shown in [18].

The Co-W coatings synthesized by the authors of [19] under galvanostatic regime at current density of 5 A/dm² and temperature of 60 °C, demonstrate microhardness of 550 HV.

The binary Co-W and ternary Co-W-Fe coatings were obtained under galvanostatic mode at temperature 80 °C from the gluconate-chloride electrolytes [20]. It is shown that the Co-W alloys successfully compete with galvanic chromium on wear and corrosion resistance. The hardness of the Co-W-Fe alloys with the content of tungsten ≈30 % by mass is close to the hardness of chromium coatings while the corrosion resistance is considerably higher.

It is worthwhile paying attention to a number of publications on the electrodeposition of the binary and ternary alloys of cobalt and molybdenum.

The cobalt-molybdenum alloys with the content of molybdenum to 20–23 % by mass were deposited from the sulfate-citrate solutions at fixed concentration of sodium

citrate (0.2 mol/dm³) and different content of CoSO₄ and Na₂MoO₄ [21].

The inclusion of molybdenum into the deposits of cobalt leads to a considerable reduction in the coercive force and increases magnetization of the saturation [22]. It was shown [23] that the content of molybdenum in the alloy increases in proportion to the potential shift to the side of negative values. The structure of deposits changes with an increase in the current density from the close-packed hexagonal to the mixed crystalline and amorphous. In this case, the degree of crystallinity depends on the thickness of the deposit: thin films possess amorphous structure.

Compact and uniform deposits of Co-Mo with the content of Mo at 1–8 % by mass are obtained on the copper substrates [24]. The coatings were formed from different ionic liquids based on the eutectic mixtures of choline chloride (ChCl) – urea and chloroethylene glycol. Current density varied in the range of 7–25 mA/cm² at 90–100 °C.

The amorphous coatings by the Co-Mo-C alloys were obtained by electrolytic deposition in the magnetic field [25]. The content of molybdenum in the alloys varies from 27.6 to 34.2 at. %. For the alloys, deposited in the magnetic field, a decrease in the overvoltage of hydrogen evolution is observed.

The prospects of applying the electrolytic binary alloys of cobalt with molybdenum or tungsten for obtaining hydrogen by the alkaline electrolysis were demonstrated in [26]; the ternary Co-Mo-Ag in the reactions of oxidation of hydrocarbons – in [27].

Of practical interest are studies of the authors of [28, 29] on the electrosynthesis of the ternary Fe-Mo-W alloys with improved physical-mechanical and anticorrosion properties for the strengthening of parts of machines.

The expediency of using non-stationary electrolysis modes when creating the triple synergetic Co-Mo-W alloys is confirmed by research in [30]. The represented results demonstrate a considerable increase in the microhardness and corrosion resistance of coatings in comparison with the material of the substrate. The presence in such alloys of metals with different affinity for oxygen and hydrogen opens up prospects for using the ternary coatings as the catalysts and electrode materials for the fuel and flow batteries.

Furthermore, a combination of iron with cobalt and molybdenum will make it possible to substantially enlarge the range of functional properties of the materials. The combination in the thin surface layers of the increased microhardness with the soft magnetic properties will enable using the Fe-Co-Mo coatings in the systems for recording and storing information.

It should be noted that most of the published results deal with the binary Fe(Ni, Co)-Mo(W) alloys. More to the point, main attention is paid to the composition of electrolytes. Given this, a detailed study is required of the influence of parameters of the pulse electrolysis on the composition and morphology of ternary alloys.

3. The aim and objectives of the study

The aim of present work is to determine the influence of the pulse electrolysis on the composition, morphology of coatings and the effectiveness of the process of depositing the Fe-Co-Mo alloys. This will make it possible to develop

technologies of the electrochemical synthesis of new materials with the assigned combination of functional properties.

To accomplish the aim, the following tasks had to be solved:

- to determine the tendencies of changing the composition of an alloy at variation of the amplitude of pulse current and temporal parameters of the electrolysis (duration and ratio of pulse and pause);
- to examine the influence of deposition conditions on the morphology of the surface of coatings;
- to determine the influence of energy and temporal parameters of the electrolysis on the effectiveness of the process;
- to establish rational parameters of the unipolar pulse electrolysis for the synthesis of the Fe-Co-Mo coatings with a wide range of the content of components.

4. Procedure of examining the influence of the pulse electrolysis on the composition and morphology of the Fe-Co-Mo coatings

4.1. Electrolyte and the electrolysis modes for the formation of a Fe-Co-Mo coating

The coatings by the Fe-Co-Mo alloys were deposited onto the M1 copper substrate at a temperature of 20–25 °C from the complex electrolyte of the composition, mol/dm³: Na₃C₆H₅O₇·2H₂O – 0.4; Fe₂(SO₄)₃·9H₂O – 0.075; Na₂MoO₄·2H₂O – 0.06; CoSO₄·7H₂O – 0.2; Na₂SO₄ – 0.15; H₃BO₃ – 0.1. Acidity of the electrolyte was controlled by the pH-meter pH-150M (Republic of Belarus) with the glass electrode ESL-6307 (Republic of Belarus), the solution pH was maintained at the level of 4.7. Preparation of the samples' surface was carried out by a standard procedure [31], which included mechanical grinding, degreasing, chemical etching in the mixture of 50 % nitric and sulfuric acids, thorough washing by the distilled water and drying. Solutions of the electrolytes were prepared from the certified reagents of chemically pure grade (Republic of Belarus, China) on the distilled water.

The electrolysis was carried out in a glass cell according to a two-electrode scheme by the unipolar pulse current of amplitude 2–5 A/dm². Duration of the pulse and the pause was varied in the range of 2×10^{-3} – 5×10^{-2} s. We used radially arranged anodes made of stainless steel of the grade X18N10T at ratio of the area of cathode and anode 1:5. Volume current density was maintained at the level of 2 A/dm³.

4.2. Methods for examining the composition and morphology of a Fe-Co-Mo alloy

Chemical composition of the obtained coatings was determined by the X-ray fluorescent method using the portable spectrometer "SPRUT" (Republic of Belarus) with a relative standard deviation of 10^{-3} – 10^{-2} . An error in determining the content of components was ± 1 % by mass. In order to verify results, we also carried out the energy-dispersion X-ray spectroscopy using the electron-probe microanalyzer Oxford INCA Energy 350 (Great Britain), integrated into the system of a scanning electron microscope (SEM).

Morphology of the surface was studied using the SEM ZEISS EVO 40XVP (Germany). The images were obtained by the registration of secondary electrons with scanning by

the electron beam, which made it possible to perform measurement with a high resolution and contrast.

Current efficiency was determined by a gravimetric method on the assumption that metals in a deposited coating are in the completely restored state. Theoretical increase in mass as a result of electrodeposition was calculated according to the Faraday law taking into account the electrochemical equivalent of the alloy.

5. Results of the formation of a ternary Fe-Co-Mo alloy by the unipolar pulse current

Composition of the electrolyte was selected based on the results of preliminary studies into the influence of component concentration of the solution on the composition, morphology of the surface and current efficiency of the electrolytic Fe-Co-Mo alloys [32]. Nevertheless, control of the quality of coatings and over effectiveness of the electrolysis, extending of range of the content of the alloy-forming components relates to the plane of using the non-stationary current. Given this, it is necessary to establish influence of the energy (amplitude of current density) and temporal (duration of pulse and pause) parameters of the pulse electrolysis on the composition and surface morphology of the three-component alloys.

Authors have earlier examined a current density effect of the stationary electrolysis on the composition, morphology and current efficiency of the ternary Fe-Co-Mo alloys [33]. It is shown that with an increase in the current density from 2 to 4 A/dm², the content of iron in the alloy decreases from 53 at. % to 49 at. % due to the increase in cobalt concentration. The content of molybdenum in the coating does not change. An increase in the current density in the examined interval leads to a reduction in the effectiveness of the process from 65 % to 45 %. Reduction in the current efficiency is explained by the intensification of side reaction of hydrogen evolution.

The present studies demonstrate that at current amplitude of 2–3 A/dm² and the fixed ratio of the duration pulse/pause $t_{\text{on}}/t_{\text{off}}=2$ ms/20 ms, the composition of alloy is practically identical (Fig. 1, *a, b*). An increase in the current density to 5 A/dm² contributes to an increase in the content of cobalt and molybdenum in the coating due to a decrease in the content of iron (Fig. 1, *c*). The variation of current amplitude substantially influences the morphology of the deposited coatings. The deposits, obtained with at current density 2 A/dm², possess fine-grained structure. With the increase of *i* to 3 A/dm², separate spheroids form at the surface (Fig. 1, *b*), and at 5 A/dm² a developed globular structure is formed with the grain agglomerates of diameter ≈ 2 μm (Fig. 1, *c*), which agrees with results in [34].

At low current densities (2–3 A/dm²) and the fixed duration of the pause $t_{\text{off}}=10$ ms, an increase in the time of polarization ambiguously affects the composition of a coating. Fig. 2 shows that the content of cobalt and iron in the alloy changes in the range of 4–10 at. %. Maximum quantity of molybdenum ω(Mo) at 12–14 at. % corresponds to the interval t_{on} 5–20 ms (Fig. 2, *a, b*). However, at $t_{\text{on}}/t_{\text{off}}=50$ ms/10 ms, there occurs a sharp reduction in the concentration of alloying components (cobalt and molybdenum) in the coating. Simultaneously, we observe an increase in the content of iron in the alloy to 56 at. % (Fig. 2, *a, b*).

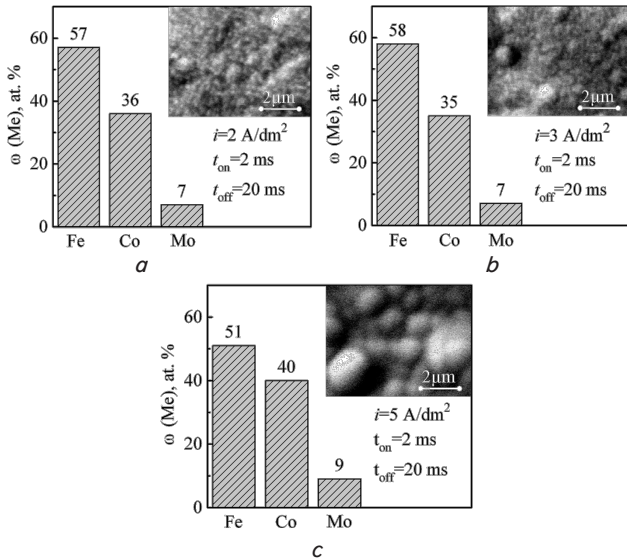


Fig. 1. Composition and morphology of a Fe-Co-Mo coating at pulse current amplitude, A/dm²: a – 2; b – 3; c – 5

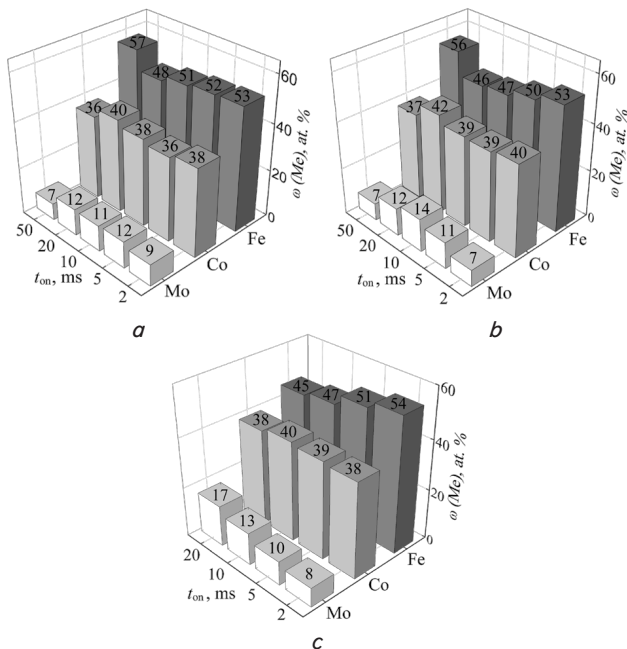


Fig. 2. Dependence of the content of components in the Fe-Co-Mo alloy on the pulse duration at $t_{off}=10$ ms and current density i , A/dm²: a – 2, b – 3, c – 5

At current density of 5 A/dm², the content of molybdenum grows proportional to the pulse duration. The maximum of the molybdenum content is registered at $t_{on}=20$ ms and is 17 at.%. The same path is followed by a reduction in the amount of iron in the coating (Fig. 2, c). Maximum summary content of the alloying components (≥ 50 at.%) is achieved at ratio $t_{on}/t_{off}=10$ ms/10 ms (20 ms/10 ms). At such composition of coatings, it is possible to expect that the obtained materials will possess improved microhardness in combination with the soft magnetic properties [35, 36].

At current density of 5 A/dm² and pulse duration of $t_{on}=2$ ms, variation of the time of pause in the limits of 2–10 ms does not exert a substantial influence on the compo-

sition and morphology of deposits (Fig. 3). An increase in the duration of pause, in full agreement with the forecast, leads to an increase in the content of molybdenum in the coating because of a decrease in the content of iron. The enrichment of coatings with molybdenum occurs at pulse duration t_{off} in the interval of 20–50 ms, which confirms the mechanism of the co-deposition of iron with cobalt by molybdenum proposed in article [37].

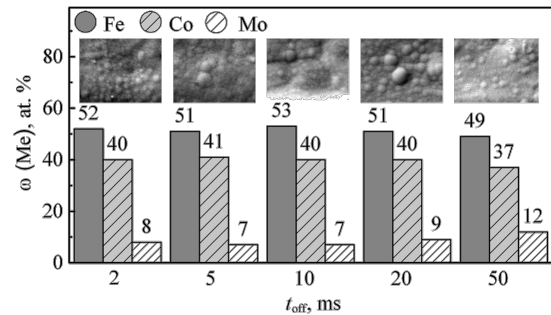


Fig. 3. Dependence of the content of components in the Fe-Co-Mo alloy on the pause duration at $t_{on}=2$ ms and current density $i=5$ A/dm². SEM images of the surface $\times 2000$

A dependence of current efficiency of the Fe-Co-Mo alloy on parameters of the pulse electrolysis has a rather complicated character (Table 1). Nevertheless, an analysis of the results of a series of experimental studies allows us to distinguish certain regularities. First, over the entire interval of current densities at fixed t_{on}/t_{off} , current efficiency grows with an increase in the pulse duration. Second, with an increase in the current density (at $t_{on}/t_{off}=\text{const}$), we observe a reduction in the effectiveness of the process. Maximum current efficiency of 80–82 % is registered at current density of 2 A/dm² and the ratio of $t_{on}/t_{off}=(5$ ms/5 ms; 10 ms/20 ms).

Table 1

Dependence of the process efficiency C_e , % on parameters of the pulse electrolysis

Ratio pulse/pause	Duration pulse/pause, ms	Current density, A/dm ²		
		2	3	5
1:1	2/2	39	27	15
1:2.5	2/5	38	40	15
1:5	2/10	59	40	23
1:1	5/5	80	27	35
1:2	5/10	39	34	31
1:4	5/20	69	51	39
1:1	10/10	57.3	52.8	44.3
1:2	10/20	81.9	65.9	54.1
1:5	10/50	65.7	63.7	68.8

Thus, an analysis of experimental data reflects the influence of parameters of the electrolysis on the composition, morphology of coatings and current efficiency. In addition, a conclusion can be drawn based on the results of experiment about a competitive recovery of molybdenum and iron. All this creates prerequisites to control the composition of an alloy not only by changing a composition of the electrolyte, but also through the variation of parameters of the pulse electrolysis.

6. Discussion of results of examining the influence of parameters of the pulse electrolysis on the composition and morphology of the Fe-Co-Mo coatings

As follows from the obtained results, an increase in the content of cobalt and molybdenum in the coating with an increase in current density is natural (Fig. 1, c). The content of iron in this case decreases, which allows us to argue about the competitive deposition of iron with cobalt and molybdenum.

According to positions [37], the mechanism of a multistage process electrosynthesis of ternary coatings by the metals of iron triad with molybdenum includes the stage of chemical reduction of the intermediate oxides of molybdenum by adsorbed atomic hydrogen. That is why the ratio of current pulse duration and the time of its interruption significantly influence the end product. An analysis of element composition of an alloy indicates the enrichment of coatings with molybdenum in the operating range of pulse 2–20 ms and pause 10–50 ms (Fig. 2, 3). Under conditions that are maximally close to the galvanostatic regime ($t_{on}/t_{off}=50$ ms/10 ms), the content of cobalt and molybdenum decreases (Fig. 2, a, b). The content of iron in this case, as noted above, grows to 56 at. %. This is explained by the reduction of iron from the particles of different nature and stability in stages: $[\text{FeHCit}]^+$ ($pK_{in}=6.3$), FeOH^{2+} ($pK_{in}=11.8$) and $[\text{FeHCitMoO}_4]^{2-}$, as shown in [38]. During current interruption (pause), the processes of reagents adsorption and reaction products desorption, dissociation of complex particles with the ligands release are fuller realized, as well as the reduction of intermediate oxides of molybdenum by the ad-atoms of hydrogen. It is obvious that under conditions close to the galvanostatic regime, the contribution of reaction of the discharge of complexes $[\text{FeHCitMoO}_4]^{2-}$ into the overall cathodic process decreases, which predictably leads to a decrease in the content of molybdenum in the alloy. Simultaneously, the cobalt reduction occurs predominantly from the complexes of $[\text{CoCit}]^-$ ($pK_{in}=5,0$) [39], which explains an insignificant change in the content of cobalt in the deposits during variation of the pulse duration.

An analysis of the coating surface morphology reveals that a larger influence on the formation of crystal lattice is exerted by current density (as energy parameter), rather than the ratio of pulse/pause. With an increase in the current amplitude, the surface morphology changes towards the formation of spheroid structures, as follows from Fig. 1. Such a change in the structure of an alloy is linked to the special features of crystallization of the alloy-forming metals. A difference in the shape and parameters of crystal lattices of iron, cobalt and molybdenum (Table 2) leads to the distortion of alloy lattice and slows the linear growth of crystals. In this case (Fig. 1, c), we observe the formation of spheroid structures. Furthermore, the atomic radii of cobalt and molybdenum exceed the atomic radius of iron by 7 and 11 %, respectively (Table 2). As a con-

sequence, during formation of a monatomic layer, the joining atoms are forced to displace from the positions of equilibrium. This results in the growing probability of realization of the transition “polycrystalline – amorphous” relative to the state of the films of the deposited alloys [40]. It is obvious that the distortion of crystal lattice is the larger, the greater the total content of iron and cobalt in the alloy. Based on data of the X-ray diffraction analysis, the globular structure of surface is characteristic for the deposits with the total content of cobalt and molybdenum >45 at. %.

Table 2

Crystal-chemical parameters of the alloy-forming components

Parameters	Fe	Co	Mo
The atomic radius, nm	0.117	0.125	0.130
Structure of the lattice	volume-centered cubic	hexagonal	volume-centered cubic
Lattice parameters, Å	2.866	a=2.505. c=4.089	3.147

The results obtained could form the basis of control over the composition and properties of multicomponent coatings with a wide range of content of the alloy-forming components, as well as development of technologies of the electrochemical synthesis of new materials.

7. Conclusions

1. It is established that an increase in the pulse duration contributes to the enrichment of an alloy with molybdenum in proportion to the increasing current density. The content of iron in the alloy increases at ratio pulse/pause $t_{on}/t_{off} > 1-2$. We revealed a tendency of the enrichment of coatings with a high-melting component and a decrease in the content of iron with an increase in current density.

2. It is shown that the character of coating surface changes from the fine-grained to the globular structure with an increase in current density due to an increase in the content of molybdenum in the alloy.

3. We established that at fixed t_{on}/t_{off} , the current efficiency rises with an increase in the pulse duration over the entire interval of current densities. With an increase in current density at stable t_{on}/t_{off} , there is a reduction in the process efficiency.

4. We determined that the most rational mode for obtaining the soft magnetic Fe-Co-Mo coatings is the regime with current amplitude of 2–3 A/dm², the duration of pulse 10–20 ms and of pause – 10–50 ms. Current with the amplitude of 5 A/dm² is recommended in order to fabricate materials with the content of a high-melting component larger than 15 at. %.

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