
**APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS**

Electrodeposition of Iron–Molybdenum Coatings from Citrate Electrolyte

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Abstract—Specific features of the electrodeposition of iron–molybdenum coatings from a citrate electrolyte based on iron(III) sulfate and sodium molybdate in dc and unipolar pulsed modes were studied. It was demonstrated that bright compact coatings with varied content of molybdenum can be produced by varying the relative concentrations of salts of the alloy-forming components and the solution pH. The current density ranges providing the high efficiency of the galvanostatic electrolysis were determined and it was shown that using the pulsed mode makes smaller the amount of nonmetallic impurities in a coating, diminishes its roughness and leads to formation of surface layers with a more uniform composition. The iron–molybdenum coatings exhibit a high corrosion resistance in corrosive media and physicochemical properties improved as compared with the base metal, which makes it possible to recommend these coatings for protection from corrosive-mechanical disintegration and restoration of the surface of worn articles.

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The reliable and stable operation of the working equipment and means of transportation and the minimization of the time of their technical maintenance at its high quality require that the already existing methods for restoration and surface reinforcement of machinery parts should be improved and new techniques should be developed. In recent years, methods for galvanochemical treatment of worn surfaces by deposition of coatings of the hard chromium, iron, nickel, copper, and zinc have been widely used. It is believed that the most promising among these is the electrolytic iron plating [1].

To indubitable advantages of coatings of this kind should be attributed their comparatively low cost, high deposition rate and substantial thickness of deposits, and widely variable microhardness. At the same time, they have such negative features as considerable hydrogen pickup resulting in the hydrogen-induced brittleness, loss of plasticity, and other dangerous aspects of hydrogen absorption, residual tensile stresses and cracked structure of deposits, especially at their high hardness, with the

result that the fatigue strength of articles decreases by 20–40% upon deposition of iron coatings [2].

To the most effective ways to restore the surface of articles and improve the wear resistance of friction pairs are commonly attributed the galvanochemical and thermochemical treatments, which appreciably improve such important consumer performance of articles as their mechanical and chemical resistance. In numerous cases, application of these technological approaches is not only an efficient, but occasionally the only way to solve problems encountered in the stage of technical maintenance of numerous kinds of machinery in various fields of the industrial complex. Attention should be given to the possibility of an appreciable improvement of the physicochemical and physicochemical characteristics of the metallic coatings being deposited via their alloying with components liable to passivity to give homogeneous alloys or composites with a metallic matrix [3]. Just this methodological aspect of applied materials science is considered to be the most promising and topical.

The corrosion resistance and the microhardness of iron coatings is raised by their joint deposition with such metals as cobalt, nickel, etc. However, there exists a purely technological problem encountered in practical use of iron-plating electrolytes, which is due to their instability [4]. Solving this problem may also make an important contribution to the resource and energy saving by galvanotechnical techniques. In our opinion, a rather promising way is to electrodeposit iron with molybdenum, tungsten, and zirconium, with the use of these metals being due to several circumstances. First, alloys of this kind have a higher chemical resistance to corrosive technological media because it is known that introduction of the above elements into alloyed steels substantially improves not only their corrosion resistance, but also the resistance to dangerous kinds of local corrosion (pitting, crevice, etc.) [5]. Second, the physicomechanical properties (microhardness, internal stress level, resistance to hydrogen embrittlement) of an alloy can be controlled by varying the relative amounts of the alloying components. Thus, the goal of our study was to determine the factors that affect the composition, morphology, and corrosion resistance of electroplated coatings of iron with molybdenum.

EXPERIMENTAL

Coatings of iron + molybdenum alloys were deposited at a temperature of 30–40°C from a complex electrolyte of composition (M): iron(III) sulfate 0.1–0.15, sodium molybdate 0.06–0.08, sodium citrate 0.3–0.4, and boric acid 0.1; the pH value was adjusted within the range 2–4 by addition of sulfuric acid or sodium hydroxide. The electrolyte solutions for electrodeposition and corrosion tests were prepared from certified reagents of chemically pure grade and distilled water. The coatings were formed in two modes: (i) galvanostatic with the current density i varied within the range 2–7 A dm⁻² and (ii) pulsed with unipolar pulse current with amplitude of 3–9 A dm⁻² at a pulse width $t_{\text{pulse}} = 5\text{--}10$ ms and pause duration $t_{\text{pause}} = 20$ ms. As anode served plates of 12Kh18N10T steel [GOST (State Standard 5949–75)]; the cathode-to-anode area ratio was 1 : 10. The galvanostatic electrolysis was performed in a B5-47 dc power source.

The pulsed electrolysis was performed and the corrosion behavior of the coatings was studied with a PI-50-1.1 potentiostat and PR-8 programming unit, equipped with a board for automated data acquisition by a specially developed program. The electrode potentials were mea-

sured relative to an EVL-1M1 silver chloride reference electrode connected to the working cell via a salt bridge filled with saturated potassium chloride solution jellied with Ceylon gelatin. The potentials presented in the communication are given relative to the standard hydrogen electrode (s.h.e.).

Coatings for analysis of the alloy composition were deposited with thicknesses of 3–20 μm on M1 copper (GOST 859–2001), and those for corrosion tests and microhardness measurements were formed on st.20 steel (GOST 1050–88). The preliminary treatment of a substrate included the standard procedure of grinding, degreasing, washing, and etching. The current efficiency of the alloys was determined gravimetrically on the assumption that the metals are incorporated into a coating in the fully reduced state. The electrochemical equivalent of an alloy, k_{al} , was found as

$$\frac{1}{k_{\text{al}}} = \sum \frac{\omega_i}{k_i},$$

where ω_i is the content of i th component of the alloy (wt %), and k_i is the electrochemical equivalent of i th component of the alloy (g A⁻¹ h⁻¹).

Based on the practical gain in mass, we calculated the thickness of the resulting coating, for which purpose the density ρ_{al} of the alloy was found from the relation

$$\frac{1}{\rho_{\text{al}}} = \sum \frac{\omega_i}{\rho_i},$$

where ρ_i is the density of i th component of the alloy (g dm⁻³).

Corrosion tests of the coatings were carried out in three media: standard 3% solution of potassium chloride (pH 7) and 1 M sodium sulfate at pH 3 and 11; the acidity of the medium was adjusted by addition of sulfuric acid or potassium hydroxide. The corrosion rate was determined by the polarization resistance method by analysis of anodic and cathodic polarization dependences plotted in semilog coordinates.

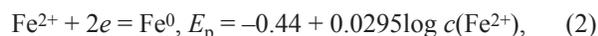
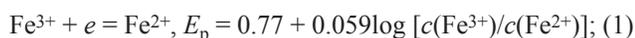
The chemical composition of the coating surface was analyzed by X-ray photoelectron spectroscopy with an INCA Energy 350 energy-dispersive spectrometer; the X-rays were excited by exposure of the samples to a beam of 15 keV electrons. In addition, an X-ray fluorescence analysis was made with a Sprut portable spectrometer

with a relative standard deviation of 10^{-3} – 10^{-2} ; the component determination error was ± 1 wt %. The surface morphology of the coatings was studied with a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were obtained by recording the backscattered electron emission (BSE) induced by the scanning electron beam, which made it possible to examine the topography with high resolving capacity and high contrast. The surface roughness was evaluated by the contact method on 14.5×15 mm samples having a thickness of 0.4 mm with an NT-206 scanning probe AFM microscope (lateral and vertical resolutions 2 and 0.2 nm, respectively; 1024×1024 scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm). The microhardness of the coatings was measured with a PMT-3 microhardness meter under a load of 20 g.

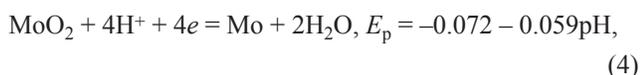
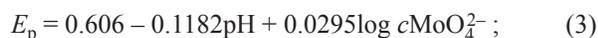
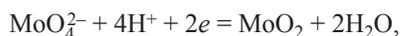
RESULTS AND DISCUSSIONS

In development of a high-throughput and stable electrolyte for coating with an alloy, it is necessary to take into account several important factors: equilibrium potentials of alloy-forming metals or electrode reactions involving these metals; competing reactions of hydrolysis and complexation in aqueous solutions; thermodynamic stability and degree of protonation and polymerization of oxo anions; and, when necessary, also the compatibility of various ligands.

The advantage of electrolytes based on iron(III) salts, especially in deposition of alloys with molybdenum, is due to at least two reasons: first, the instability of iron(II) compounds in the presence of oxidizing agents, to which undoubtedly belong oxo anions MoO_4^{2-} from which the refractory metal is reduced into the alloy. In addition, the cathodic reaction involving iron(III) includes the stages

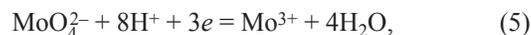


whose equilibrium potentials E_p are close to the E_p of molybdates:



and just this circumstance creates prerequisites for the alloying.

It should be noted that another way for reduction of molybdates is also possible:



In both cases, however, the thermodynamic probability of codeposition of iron with molybdenum into an alloy is rather high. Attention should be also given to the fact that molybdate(VI) ions can be reduced by atomic hydrogen at the instant of release to molybdenum(III) compounds [6] and this reaction may occur in the overall cathodic process.

The tendency of Fe^{3+} cations to be hydrolyzed and precipitate as the hydroxide $\text{Fe}(\text{OH})_3$ at pH 3.0–3.5 makes necessary use of acid iron-plating electrolytes in which condensed forms of molybdenum(VI) are predominant (Table 1), which somewhat complicates the reduction of these latter. To extend the pH range and improve the stability and working capacity of an electrolyte, it is advisable to use salts of polybasic organic acids, among which sodium citrate also exhibiting buffer properties is the most economically attractive. It is known, in addition, that molybdates tend to form heterocompounds with citrates (Cit) [7] and Cit can form stable complexes with Fe^{3+} ($\text{pK}_{[\text{FeCit}]} = 11.5$) [8], which serves as an additional electrolyte-stabilizing factor.

With consideration for the above-mentioned aspects, it can be stated that the composition of electrolytic iron–molybdenum alloys can be controlled by varying the pH value and the relative concentrations of salts of alloying metals in solution.

Our study demonstrated that light shining coatings with a bluish tint characteristic of molybdenum are formed with a current efficiency of 68.6% from the electrolyte containing 0.15 M $\text{Fe}_2(\text{SO})_4$ and 0.06 M Na_2MoO_4 (pH 3) in the galvanostatic mode at a current density of 3.0–3.5 A dm^{-2} . The coatings include 65.4 wt % iron and 34.6 wt % molybdenum (in terms of a metal); at the same time, a certain amount of nonmetallic impurities (carbon and oxygen) was found, which may be due both to the oxidation and adsorption of components of the medium on the coating surface (Fig. 1a).

Table 1. Ionic forms of molybdates(VI) in aqueous solutions of varied acidity

Electrolyte pH	Concentration, M	Predominant form of oxo metallate
5.0–8.0 and pH > 8	< 10 ⁻³	MoO ₄ ²⁻
4.0–5.0	> 10 ⁻³	MoO ₄ ²⁻ , HMoO ₄ ⁻ , HMo ₇ O ₂₄ ⁵⁻
3.0–4.0	> 10 ⁻³	HMo ₂ O ₇ ⁻ , H ₂ Mo ₇ O ₂₄ ⁴⁻ , HMo ₇ O ₂₄ ⁵⁻
2.0–3.0	> 10 ⁻³	Mo ₈ O ₂₆ ⁴⁻ , H ₂ Mo ₇ O ₂₄ ⁴⁻ , HMo ₂ O ₇ ⁻

It should be noted that the data of X-ray microanalysis point to a large difference between the contents of iron and molybdenum on surface projections, compared with depressions (Fig. 1a), with the content of nonmetallic impurities in depressions being larger. As the Fe₂(SO₄)₃ concentration is raised to above 0.15 M, the content of molybdenum in a coating decreases by 3–5 wt %. Contrary to expectations, lowering the concentration *c*[Fe₂(SO₄)₃] to 0.1 M and raising *c*(Na₂MoO₄) to 0.08 M leads, all other conditions being the same, to a decrease in the content of molybdenum in a coating to 25.3 wt % and to an increase in ω(Fe) at the same current efficiency.

Apparently, this behavior can be attributed to the formation of polymeric forms of molybdates upon an increase in their concentration in an acid medium, which complicates the process of their deposition into an alloy. Indeed, raising the pH value to 4.3, other electrolyte parameters and deposition modes remaining the same, provides a regular enrichment of a coating with molybdenum to 48.8 wt % (in terms of the metal); however,

the current efficiency of the alloy decreases in this case to 58.7% and the content of nonmetallic impurities in the surface layer becomes larger. Also noteworthy is the poorer stability of the electrolyte, in which a suspension of iron(III) hydroxide is formed upon electrodeposition at current densities exceeding 5 A dm⁻². Therefore, in view of the requirements to the stability of an electrolyte at the content of molybdenum in the alloy preserved at a level of 20–30 wt %, preference should be given to the electrolyte of composition *c*[Fe₂(SO₄)₃] = 0.1 M and *c*(Na₂MoO₄) = 0.06–0.08 M at pH 3.0–3.5.

Raising the current density to 6 A dm⁻² leads to enrichment of a coating with iron and to a decrease in its molybdenum content to 22.8 wt %; however, the current efficiency substantially decreases in this case to 48.5%. The last fact can be accounted for by a stronger polarization and a shift of the electrode potential in the negative direction, which intensifies the reaction of hydrogen evolution at the expense of the coating formation. Thus, current densities in the range 3.0–5.0 A dm⁻² should be used to deposit Fe–Mo alloy coatings in the galvanostatic mode with a current efficiency exceeding 50%.

The pulsed electrolysis (unipolar pulsed current amplitude 4 A dm⁻², pulse width 10 ms, pause duration 20 ms) makes it possible to substantially reduce the amount of nonmetallic impurities and improve the coating uniformity (Fig. 1b), with the content of iron somewhat increasing and that of molybdenum decreasing in comparison with the steady-state conditions. Apparently, the pause between the current pulses favors both a weaker hindrance to diffusion and absorption processes and a fuller extent of the chemical reactions of dissociation of iron complexes and molybdenum heteropolycompounds. It is this circumstance that provides a more uniform composition at surface projections and depressions of a coating

Table 2. Corrosion parameters of Fe–Mo coatings and substrate material

Material	Corrosion parameter					
	log <i>i</i> _{cor} , A cm ⁻²	<i>E</i> _{cor} , V	log <i>i</i> _{cor} , A cm ⁻²	<i>E</i> _{cor} , V	log <i>i</i> _{cor} , A cm ⁻²	<i>E</i> _{cor} , V
	pH 3		pH 7		pH 11	
Coating, deposition mode:						
pulsed	–2.6	–0.27	–3.75	–0.37	–4.0	–0.47
steady-state	–1.75	–0.28	–3.60	–0.31	–3.65	–0.45
St.20 substrate	–0.8	–0.62	–2.1	–0.56	–3.0	–0.32

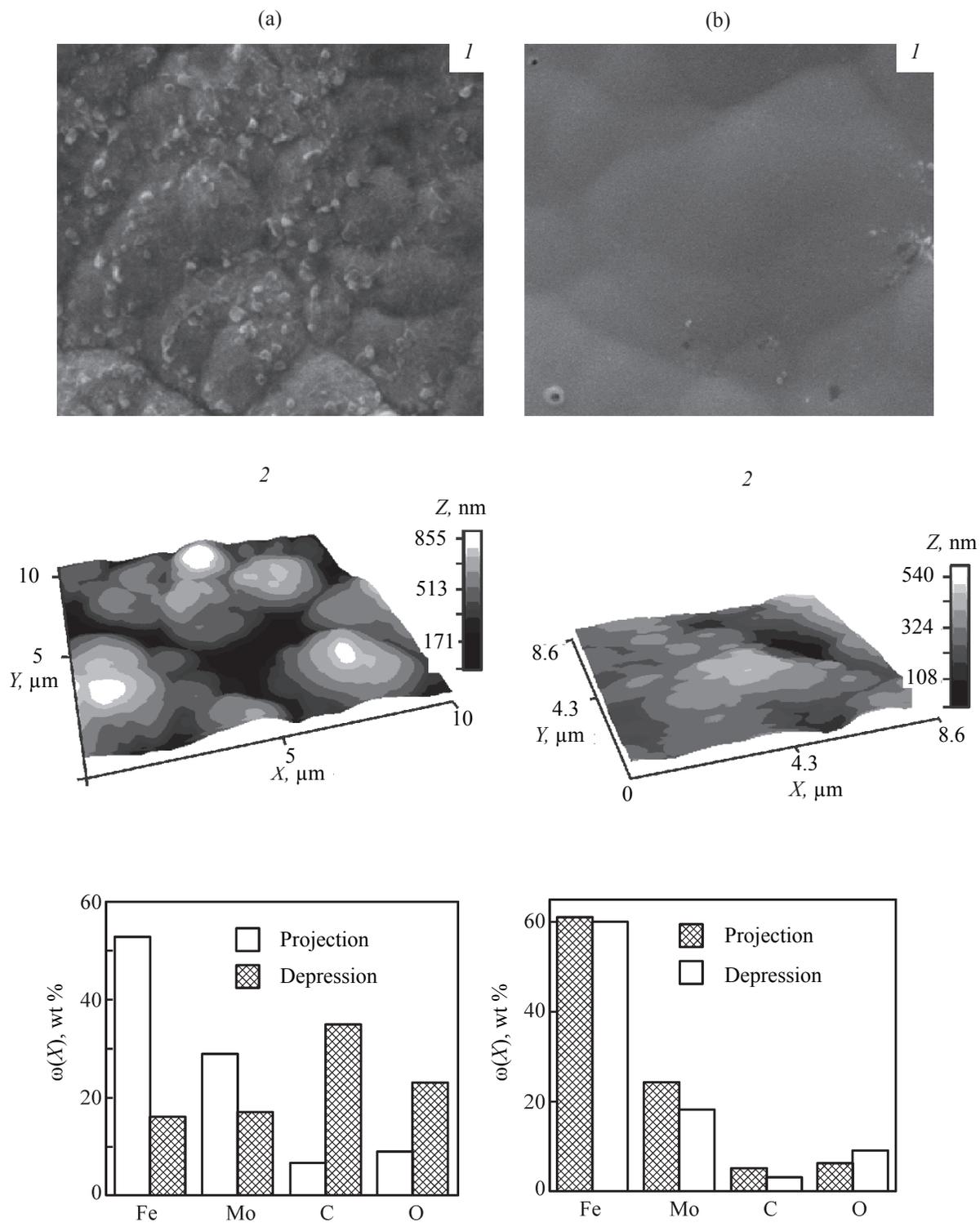


Fig. 1. (1) Morphology, (2) 3D surface map, and composition of Fe–Mo coatings deposited from an electrolyte of composition (M): $\text{Fe}_2(\text{SO}_4)_3$ 0.15, Na_2MoO_4 0.06, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ 0.3, H_3BO_3 0.1, and Na_2SO_4 0.1 (pH 3). Electrolysis: temperature 30°C, duration 30 min; SEM magnification 5000; AFM scanning region $10 \times 10 \mu\text{m}$. $[\omega(X)]$ Content of an alloy component. Electrolysis mode: (a) steady-state, $i = 3 \text{ A dm}^{-2}$ and (b) pulsed, $i = 4 \text{ A dm}^{-2}$, $t_{\text{pulse}} = 10 \text{ ms}$, $t_{\text{pause}} = 20 \text{ ms}$.

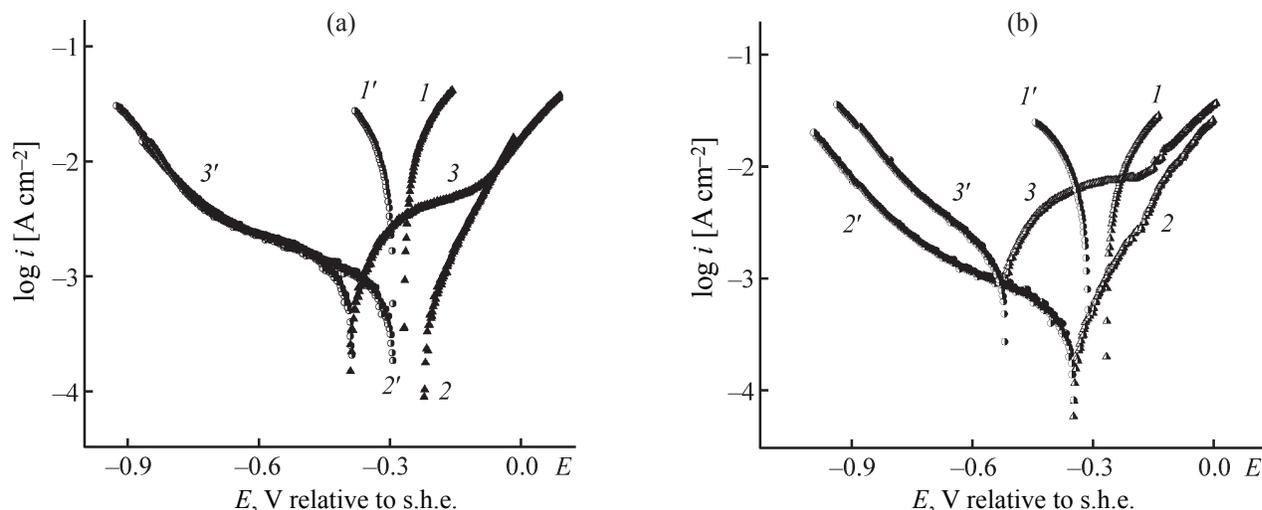


Fig. 2. (I – 3) Anodic and (I' – $3'$) cathodic polarization dependences obtained at pH values of (I , I') 3 and (3 , $3'$) 11 in 1 M Na_2SO_4 solutions and (2 , $2'$) 7 in 3% NaCl on Fe–Mo coatings deposited in (a) steady-state and (b) pulsed modes. (i) Current density and (E) potential.

and a lower roughness (Fig. 1b), as it has also been observed for tungsten alloys [9]. The experimental results demonstrate that, when current flows during a pulse, the electrode potential shifts to values corresponding to the reduction of iron by stage (2), which leads to an increase in its content in the alloy.

A positive factor is that the deposition rate of electrolytic alloys remains rather high in all modes and reaches a value of $20 \mu\text{m h}^{-1}$ with a current efficiency of 60–70%, which substantially exceeds the parameters of the conventional ways to deposit iron alloy coatings [10, 11].

Fe–Mo coatings deposited in the steady-state mode have a globular structure of agglomerated crystallites and a roughness (Fig. 1a) exceeding that of coatings obtained in the pulsed mode (Fig. 1b). Analysis of the AFM micrographs enables a more accurate estimation of the surface roughness and crystallite sizes. In the initial period of the steady-state electrolysis, large crystallites with a diameter of $1.5 \mu\text{m}$ are formed, and after that formations with a smaller diameter, 500–600 nm, start to appear in between. It can be seen in the 3D surface map that coatings deposited in the pulsed mode (Fig. 1b) are more uniform and even, with crystallites 700–800 nm in size.

Results of our corrosion tests demonstrate that the coatings deposited in the dc and pulsed modes differ in behavior. Analysis of the cathodic portions of the polarization dependences obtained on Fe–Mo coatings in media with varied aggressiveness (Fig. 2, curves I' – $3'$) shows that the corrosion occurs predominantly with hydrogen

depolarization in an acid medium (curve I') and with oxygen depolarization in neutral and alkaline media (curves $2'$, $3'$). The limiting oxygen reduction current in coatings with rough surface (Fig. 2a) exceeds the values recorded on more even deposits (Fig. 2b). The slope ratio of the linear portions of the anodic dependences $\log i$ – E grows on passing from an acid medium to those of neutral and alkaline types (Figs. 2a and 2b, curves I – 3), which indicates that the polarization resistance increases and the coating passivation becomes stronger, with the corrosion potentials regularly shifted toward negative values.

The corrosion resistance of the Fe–Mo coatings produced by nonsteady-state electrolysis exceeds that of the coatings deposited in the steady-state mode (Table 2), which can be attributed to a more homogeneous distribution of the alloy-forming components in the surface layer and to a smaller surface roughness of the former. However, the electrolytic coatings with the alloy demonstrate, irrespective of the deposition mode, a substantial increase in the chemical resistance, compared with the st.20 steel substrate, in all the corrosive media under study.

Also noteworthy is the improvement of the physico-mechanical properties of the coatings, whose microhardness (400–430 $\text{H}\mu$) is twice that of the substrate metal (200–240 $\text{H}\mu$), which makes application of these coatings advisable and promising for restoration of steel articles.

CONCLUSIONS

(1) Light compact Fe–Mo coatings with molybdenum content of 20–50 wt % are deposited in the dc mode with

a current efficiency of 60–70% from a citrate electrolyte with a varied ratio between iron(III) sulfate and sodium molybdate. Raising the solution pH favors enrichment of a coating with molybdenum.

(2) With pulsed electrolysis used, the amount of non-metallic impurities in a coating decreases and surface layers with a more uniform composition and morphology are formed.

(3) The corrosion resistance of coatings in media with varied aggressiveness becomes higher because of the passivation-prone molybdenum and exceeds that of the base metal by at least an order of magnitude. The microhardness of the coatings is twice that of st.20 steel.

These physicomechanical and corrosion-resistance properties, combined with the high deposition rate and the stability of the electrolyte, make it possible to recommend Fe–Mo coatings for use not only as means of protection, but also in techniques for restoration of worn articles.

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