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ELECTROPLATING AND FUNCTIONAL PROPERTIES OF Fe–Mo AND Fe–Mo–W COATINGS

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Peculiarities of electrodeposition Fe–Mo and Fe–Mo–W coatings from citrate bath containing iron (III) on substrates of mild steel and cast iron are investigated. The utilization of iron (III) compounds significantly enhanced the stability and service life of electrolyte due to elimination redox reactions involving complexing and side anodic reactions. The effect of alloying components salt concentration and electrolysis mode on the quality, composition and properties of the alloys were determined. It is shown that alloys formed in nonstationary electrolysis have a uniform surface, composition and a lower content of impurities. Increased physical and mechanical properties as well as corrosion resistance of Fe–Mo and Fe–Mo–W coatings compared with the base metal are caused by the presence of propensity for passivation alloying components as well as by amorphous structure of electroplating alloys. Indicated coatings can be considered as promising in surface hardening technologies and repair of worn items.

Keywords: Fe–Mo and Fe–Mo–W alloy, citrate bath, physic-mechanical properties, electrodeposition, corrosion resistance, nonstationary electrolysis.

The development of technology and modernization of equipment in mechanical engineering and instrumentation, as well as in the chemical industry puts high requirements for physical and mechanical properties of structural metals and alloys. Intensive search for approaches to ensure high strength, wear and corrosion resistance at low cost materials must be paired with the principles of ecological compatibility and resource saving processes for their production.

The performance characteristics of materials can be effectively improved by the modification of the surface layer by electroplating. A small amount of material, the technological simplicity of the process, the possibility of formation of multi-component metal coatings which are difficult to get in metallurgical or chemical processes, as well as a wide variation of galvanic alloys properties depending on the components' nature [1] cause their promising application in industry.

To harden the working surfaces of items electrolytic chromium based coating which are characterized by high hardness and wear resistance are often utilized. However, the high aggressiveness and carcinogenicity of chromium (VI) electrolytes require additional measures to ensure the safety of personnel during the organization of process, as well as the special treatment of wastewater. Therefore,

the actual alternative chroming remains the development of the galvanic coatings with improved physical and mechanical properties, the formation of which would correspond to the criteria of resource conservation, environmental saving and cost-effectiveness.

Effectively replace of chromium coatings can be achieved by the use of electroplating iron doped with various metals [2]. Electrolytic iron hardness is significantly higher in comparison with the smelting one; however, the presence of residual stresses and electro-crystalline defects leads to cracking and poor adhesion to the base metal. Selection of components for electrolytic alloy formation is based on a wide experience in the use alloyed steels and their functional properties depending on the composition. Introduction of molybdenum and tungsten in the coating predictably allows minimizing the internal stresses inherent to the electrolytic iron and improving the physical and mechanical properties of coatings [3,4].

The aim of this work is to study the influence both of the electrolyte composition and electrolysis conditions on the quality, composition, morphology, mechanical properties and corrosion behavior of galvanic alloys Fe–Mo and Fe–Mo–W.

Experimental

Coatings were deposited on steel and the cast

iron substrates. Pretreatment of samples included grinding, degreasing, rinsing and etching.

Coatings of iron + molybdenum were formed at a temperature of 25–30°C from a complex citrate bath 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 3–4 by addition of sulfuric acid or sodium hydroxide. Iron+molybdenum+tungsten coatings were deposited from the same electrolyte containing also 0.04–0.06 M sodium tungstenate. 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 3–6 A·dm⁻² and (ii) pulsed with unipolar pulse current with amplitude i of 3.5–9.0 A·dm⁻² at a pulse duration t_{on} =5–10 ms and pause time t_{off} =10–20 ms. As anode served plates of 12Kh18N10T steel; 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 measured 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 paper are given relative to the standard hydrogen electrode (SHE).

The electrodeposition effectiveness (current efficiency C_e) was determined gravimetrically using the electrochemical equivalent of the alloy. The thickness of the coatings was calculated from the actual mass increase of the samples during the electrolysis.

The chemical composition of the coatings 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. 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 10×10×2 mm samples 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 phase

composition of the coatings was studied by X-ray structural analysis using a DRON-2.0 in the emission of iron anode.

Physic-mechanical properties of the coatings were evaluated according to metallographic studies of sections. The quality of adhesion to the substrate is set by using a polishing paste based on chromium oxide, by the bending under angle of 90° and heating to a temperature of 150–200°C, followed by cooling in air. Microhardness H_M was measured using a PMT-3 device with a diamond pyramid under a load of 50 g and 100 g; diagonal of imprint was measured by ocular micrometer MOB-1-15 (magnification of a microscope – 500).

Corrosion tests of the coatings were carried out in model media with 1 M sodium sulfate background with the addition of 3% potassium chloride (pH 7); sulfuric acid to pH 3 or potassium hydroxide to pH 11. The corrosion rate was determined by the polarization resistance technique using the analysis of anodic and cathodic polarization dependences in Tafel coordinates [5]. Depth corrosion index k_h (mm per year) was calculated using the electrochemical equivalent of the alloy [6].

Theoretic aspects

The advantages of using an iron(III)-based electrolytes for deposition of the iron alloys with high-melting metals in comparison with currently used [2,3] consist not only in the prevention of Fe(II) oxidation by air oxygen, but also by oxometalates:



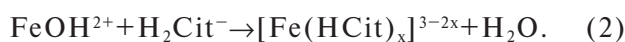
where M – Molybdenum or Tungsten.

Thus, by eliminating the side reactions, including (1), we have increased the content of molybdenum in the coating Fe–Mo and current efficiency [7] compared to the known electrolytes based on iron (II).

The competing reactions of iron cations hydrolysis and complex formation in aqueous solutions [8] as well as thermodynamic stability, the protonation and polymerization degree of oxometalates [9] significantly affect the stability and performance of electrolytes. Therefore, their account allows you to manage the processes of particle formation, which not only reduced at the cathode, but also provide a resource of the electrolyte and the reproducibility of the electrodeposition process.

It should be noted that the actual concentration of complexing agent (Fe^{3+}) and ligand (Cit^{3-}) as the composition of the resulting complex particles depend on the degree of Fe^{3+} hydrolysis and Cit^{3-} protonation, and therefore inseparably connected with a solution pH (Fig. 1). As can be seen from Fig. 1, in the range of pH 3.0–4.0 predominant ions in solution are FeOH^{2+} and H_2Cit^- which forms

complexes $[\text{Fe}(\text{HCit})_x]^{3-2x}$ by reaction:



The number of ligands x in the complex increases with the concentration ratio $c(\text{Cit}^{3-})/c(\text{Fe}^{3+})$, however, with Cit^{3-} twofold excess will dominate, in our opinion, monocitrate system $[\text{FeHCit}]^+$. The composition and polymerization degree of refractory metal oxoanions (molybdate and tungstate) depend on the concentration and the solution pH (Table 1). Naturally, the mixed heteronuclear complexes $[\text{Fe}(\text{HCit})\text{MO}_4]^-$ of which metals co-deposition in alloy occurs as for coatings Ni–Mo–W [10], can be formed with mono- and dimetalates MO_4^{2-} , HMO_4^- , HM_2O_7^- preliminary at $\text{pH} > 3$.

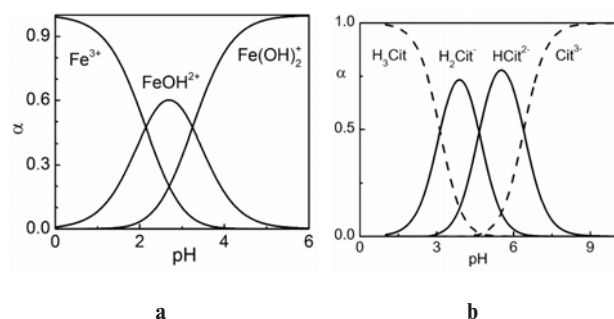


Fig. 1. Ionic equilibrium in systems $\text{Fe}^{3+}-\text{H}_2\text{O}$ (a) and $\text{Cit}^{3-}-\text{H}_2\text{O}$ (b)

Table 1

Influence of pH medium and concentration c on the composition of oxometalates in aqueous solutions

pH	c , M	The dominant form of particles
$\text{pH} > 5$	$< 10^{23}$	MO_4^{2-}
4–5	$> 10^{23}$	$\text{MO}_4^{2-}, \text{HMO}_4^-, \text{HM}_2\text{O}_7^-$
3–4		$\text{HM}_2\text{O}_7^-, \text{H}_2\text{M}_7\text{O}_{24}^{4-}, \text{HM}_7\text{O}_{24}^{5-}$
2–3		$\text{M}_8\text{O}_{26}^{4-}, \text{H}_2\text{M}_7\text{O}_{24}^{4-}, \text{HM}_2\text{O}_7^-$

Thus, we can to control the composition of double Fe–Mo and triple Fe–Mo–W plated alloys by changing the concentrations ratio of alloying metals salts, electrolyte pH and electrolysis mode. It should be taken into account the fact that the reactions of heteronuclear complexes of molybdenum and tungsten formation and subsequent their reduction in the alloy may be competing.

Results and discussion

Our study demonstrated that light shining coatings 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) at a direct current density of 3.0–3.5 $\text{A}\cdot\text{dm}^{-2}$ [8]. The coatings include 65.4 wt% iron and 34.6 wt% molybdenum (in terms of a metal) and a certain amount of nonmetallic

impurities (carbon and oxygen), which may be due both to the coating surface oxidation and adsorption of medium components on it (Fig. 1,a). An important aspect of dc deposition is uneven distribution of the alloy components at the coating surface namely a large difference between the contents of iron and molybdenum on surface projections, compared with depressions with the content of nonmetallic impurities in depressions being larger (Fig. 1,a). Also, on projections we have noticed an increased content of metals and in the depressions the higher concentration of oxygen, which can be explained by current density gradient and diffusion limitations.

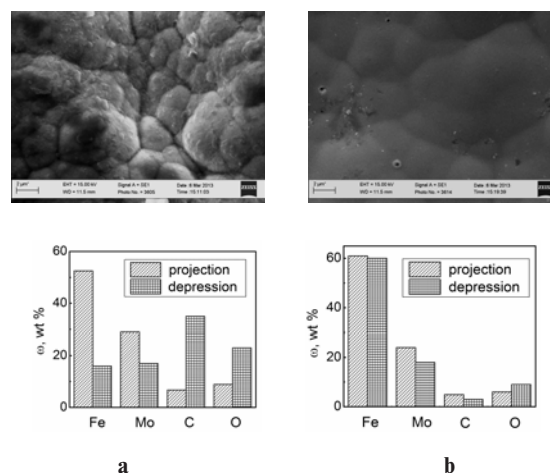


Fig. 2. Morphology and mass content (ω) of alloying elements in coatings Fe–Mo, deposited by stationary (a) and pulse (b) mode. Temperature 25°C, plated time 30 min. Magnification $\times 5000$

The pulsed electrolysis (unipolar pulsed current amplitude 4 $\text{A}\cdot\text{dm}^{-2}$, $t_{\text{on}}=10$ ms, $t_{\text{off}}=20$ ms) makes it possible to substantially reduce the amount of nonmetallic impurities and improve the coating uniformity (Fig. 1,b), 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 a fuller extent of the chemical reactions of dissociation both iron complexes and molybdenum heteropoly compounds. It is this circumstance that provides a more uniform composition at surface projections and depressions of a coating (Fig. 1,b), as it has also been observed for tungsten alloys [11].

As it was observed for a binary alloy bright and shiny bluish-gray coatings with a current efficiency of 79–83% were obtained on different substrates (steel and cast iron) from the electrolyte containing 0.1 M $\text{Fe}_2(\text{SO})_4$; 0.04 M Na_2MoO_4 and 0.06 M Na_2WO_4 (pH 3.5) at a direct current density of 3.5–4.0 $\text{A}\cdot\text{dm}^{-2}$ [12]. The results of electron microprobe analysis showed that in addition to basic components, wt%: 54.0–57.0 Fe; 25.0–26.0 Mo; 6.0–7.0 W (Fig. 3,a),

coatings include some amount of oxygen (12.0–13.0 wt%). It should be noted that while the concentration ratio of molybdenum and tungsten salts in the electrolyte of 3:2, the molar concentration of molybdenum in the coating is five times greater. This is fully consistent with the assumption of a competitive deposition in the alloy of tungsten and molybdenum as the standard step reduction potentials of the last are well known to be higher.

The coatings produced in a pulsed mode ($i = 4.0 \text{ A}\cdot\text{dm}^{-2}$; $t_{\text{on}} = 10 \text{ ms}$; $t_{\text{off}} = 20 \text{ ms}$) from the same electrolyte it was shown to be more uniform by distribution of components on the projections and in the depressions. Furthermore they are enriched by refractory components up to a total 40 wt%, also contain higher amount of tungsten and lower oxygen – 5 wt% comparing with dc deposited coatings (Fig. 3,b). Obviously, the crystallization of the alloy occurs during pulse while chemical reactions of the complexes dissociation, diffusion of the released citrate-ions in the electrolyte volume pass during the pause. Increase in the tungsten content on the projections of the relief compared with depressions and inverse relationship for molybdenum (Fig. 3,b) can be explained on the basis of the following considerations. The increased current density typical on the projections of the relief promotes the shift of the electrode potential in the negative region causing a rise in tungstate-ions reduction rate. At the same time, during the pause preferential reduction of intermediate molybdenum oxides by adsorbed hydrogen atoms in the depressions of the relief takes place.

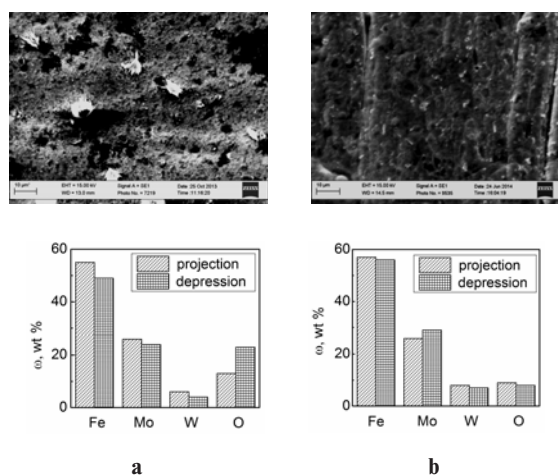


Fig. 3. Morphology and mass content (ω) of alloying elements in coatings Fe–Mo–W, deposited by stationary (a) and pulse (b) mode. Temperature 25°C, plated time 30 min. Magnification $\times 1000$

Increasing the concentration of iron sulfate (III) in electrolytes for both alloys greater than 0.15 M leads to a natural decrease in the content of molybdenum and tungsten [7,12]. This fact, as well

as the ability to hydrolyze Fe^{3+} -ions predetermine upper limit of the $\text{Fe}_2(\text{SO}_4)_3$ content in the electrolyte. Increasing the of molybdenum and tungsten salts concentration in the electrolyte up to 0.08 and 0.06 M respectively (pH 4.0) allows you to pick up their content in the alloy for about 2–3 wt%, but at a higher dopant content the quality of the coatings is deteriorated due to the growth of internal stresses.

Alkalinization to pH 5.0–6.0 to form monooxometalates in a volume of the electrolyte providing a higher content of alloying elements in the alloy (Fig. 1,b) does not result in the expected results. The concentration of molybdenum and tungsten in the coating remains almost unchanged, but the oxygen content is increased and current efficiency is significantly reduced (50.0–60.0%). This is due to an increase in the probability of formation iron (III) hydroxy-ions (Fig. 1,a) and their inclusion in the coating. In addition, the stability of the electrolyte is considerably decreased and deteriorated its performance.

Raising the current density to 5.5–6.0 $\text{A}\cdot\text{dm}^{-2}$ leads to small enrichment of a coating with alloying elements (an average of 0.5–1.0 wt%) with some decline in the electrolysis efficiency to 65.0–70.0%. Coating «is burnt» by the edges and the electrolyte pH requires adjustments after 2–3 hours of bath operation. These facts 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 accompanied by the alkalization of the cathode layer.

On this basis we can conclude the most rational ranges of solution pH 3.0–4.0 and direct current densities 3.5–4.5 $\text{A}\cdot\text{dm}^{-2}$. At the main components concentrations 0.1 M $\text{Fe}_2(\text{SO}_4)_3$; 0.04 M Na_2MoO_4 ; 0.08 M Na_2WO_4 the optimum alloying components content in the alloy with a current efficiency in the range of 65–85% as well as a stable operation of the electrolyte are achieved.

Increasing the amplitude of the pulse current amplitude in the range of 4.0 Increasing the amplitude of the pulse current amplitude in the range of 4.0–6.0 $\text{A}\cdot\text{dm}^{-2}$ at $t_{\text{on}} = 5 \text{ ms}$ and $t_{\text{off}} = 10 \text{ ms}$ promotes growth tungsten content in the alloy, although the current efficiency drops to 75%, which agrees with the previously observed data for the binary alloys of nickel and cobalt [13]. Changing the duration of pulse and pause causes little variation of tungsten and molybdenum content in the range of 1 wt% at a constant iron concentration. This confirms the assumption that molybdates and tungstates are recovered in the alloy competitively. Current efficiency varies within 5% and is in the interval 70–75% for all tested pulse modes, electrochemical deposition rate of 20–25 $\text{mm}\cdot\text{h}^{-1}$ considerably higher than known iron-based galvanic alloys with Mo and W [14].

It was established that the surface topography of galvanic alloys depends both on their composition and on the polarization mode. Firstly, the coatings deposited at a direct current irrespective of the composition are characterized by the higher roughness and larger grain size compared with coatings obtained by pulse electrolysis. Thus, coating Fe–Mo–W formed by dc are composed from the set of sharp grains with an average size of 70–100 nm, while these latter obtained by the pulsed mode have a smooth surface with the spherical grain agglomerates of 0.2–0.4 μm.

Secondly, the binary coatings Fe–Mo obtained by a pulsed mode are characterized by a greater surface roughness with the spread of grain size on the cross section (Fig. 4,a) compared with the electroplating ternary alloys Fe–Mo–W (Fig. 4,b). In addition, the coating surface topography Fe–Mo characterized by alternating sufficiently sharp projections and depressions, whereas the agglomerates Fe–Mo–W approximate to the spheroid shape at close crystallite sizes. Considering the fact that according to microprobe analysis projections of the coating surface are enriched with tungsten, we can

conclude that the latter facilitates alignment of relief. This gives grounds to expect improve corrosion resistance and microhardness of the coating compared to the substrate material.

Results of our corrosion tests demonstrate that corrosion resistance both of the coatings Fe–Mo and Fe–Mo–W produced by pulse electrolysis exceeds that of ones deposited in the steady-state mode, 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. Corrosion potentials of galvanic alloys are shifted toward the positive values by 0.25–0.35 V relative to the potential of the substrate both in acidic and chloride-containing environments, while at pH 11 the potential difference is not greater than 0.08 V (Table 2). This behavior is associated with the formation of refractory metal oxides of an acidic nature, which increase an inclination to passivity as well as pitting corrosion resistance, but is chemically unstable in the presence of alkali. Particularly noteworthy is the decrease in the corrosion rate of the binary and ternary alloys, up to five times as compared with the steel 3 substrate

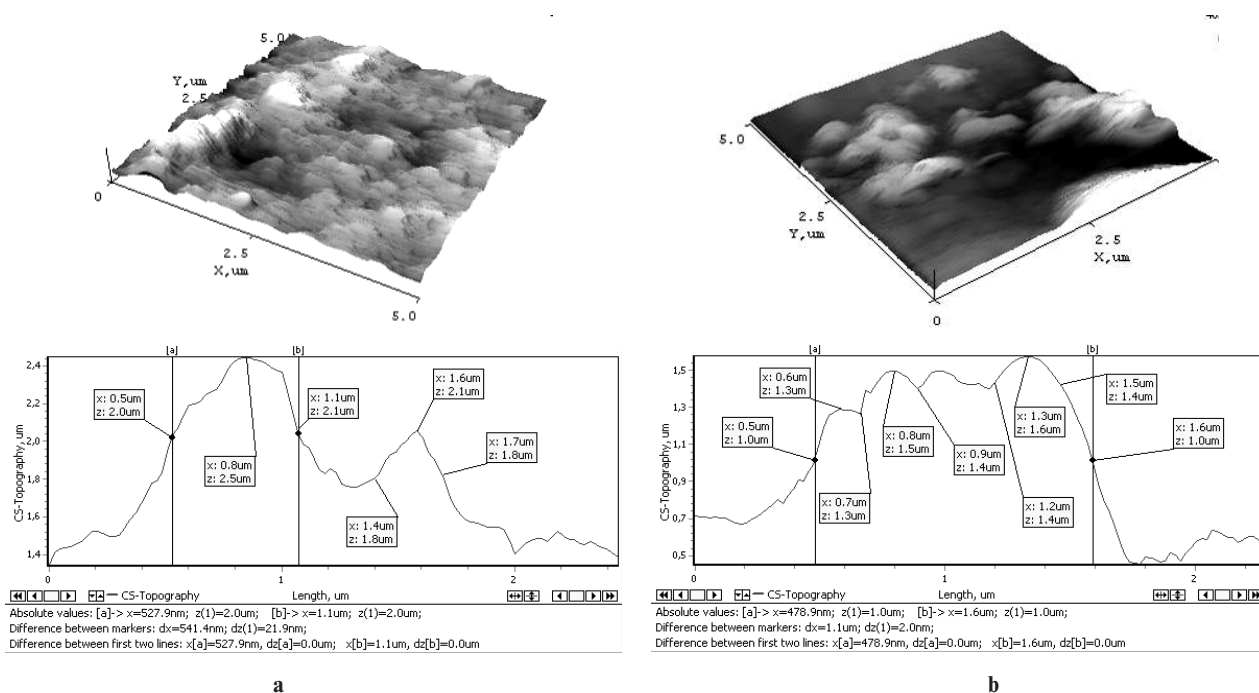


Fig. 4. 3D-map of the surface and cross sections of coatings Fe–Mo (a) and Fe–Mo–W (b) deposited in pulse mode. Scan area AFM 5×5 mm

Table 2

Corrosion indicators of testing materials in different media

pH	Corrosion indicator	Coating Fe(65)Mo(35)	Coating Fe(68)Mo(24)W(8)	Substrate
3	E_{cor} , V	–0.25	?0.26	?0.62
	k_h , mm per year	0.038	0.039	1.85
7	E_{cor} , V	–0.37	?0.32	?0.56
	k_h , mm per year	0.04	0.039	0.93
11	E_{cor} , V	–0.36	?0.34	?0.43
	k_h , mm per year	0.028	0.028	0.12

at a pH 3, and three times – in 3% sodium chloride and in an alkaline medium.

Physical-mechanical properties of the coatings were evaluated on the quality of adhesion to the substrate and on the microhardness. It was established the galvanic alloy coatings Fe–Mo and Fe–Mo–W, obtained in the different modes to have high adhesion to the substrate and maintain it in mechanical (polishing, bending, a cross-section followed by grinding) as well as thermal (heat) effects. It should be noted that the microhardness of binary Fe–Mo and ternary Fe–Mo–W alloy is about 3–4 times that of the cast iron substrate (Fig. 5,a) as well as it is also higher for pulse deposited coatings. Difference in microhardness of the coatings deposited on steel 3 in the pulse and the dc modes becomes even more (Fig. 5,b) and for steady-state electrolysis is 2.5–3.0 times that of the indicator of the substrate that is in agreement with the results of [15]. Moreover, for all electroplating modes and substrates microhardness of ternary alloys is greater than double ones due to tungsten incorporating into the coating composition.

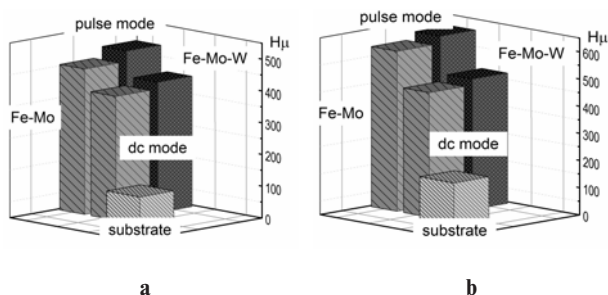


Fig. 5. Microhardness of Fe(65)Mo(35) and Fe(68)Mo(24)W(8) coatings deposited under dc and pulse modes on substrates cast iron (a) and steel 3 (b)

It was detected a series of diffraction lines for α -Fe on X-ray diffraction patterns of Fe–Mo and Fe–Mo–W coatings formed on steel substrates (Fig. 6). Furthermore, one can find quite broad halo (full width at half maximum is about 10°) at angles $2\theta \sim 57^\circ$, which indicates an amorphous structure of above mentioned materials.

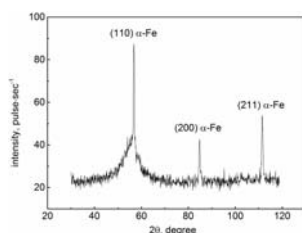


Fig. 6. X-ray diffraction for coatings Fe–Mo (a) and Fe–Mo–W (b); substrate – steel 3

Results of phase composition analysis for both Fe–Mo and Fe–Mo–W galvanic alloys are

consistent with data obtained by other researchers beside [10,14], and indicate that physical-mechanical properties of synthesized coatings increase not only at the expense of high content of refractory metal but also caused by amorphous structure of alloy.

Taking into account the high level of mechanical and anticorrosive properties of galvanic coatings Fe–Mo and Fe–Mo–W formed from citrate electrolyte we can recommend them as protective coatings for cast iron and mild and considered as promising for technology in hardening and repair when restoring worn parts.

Conclusions

(i) Uniform bright and shiny coatings by double Fe–Mo and ternary alloy Fe–Mo–W can be produced both in a dc and a pulsed mode with current efficiency of 65.0–85.0% from the complex citrate electrolyte (pH 3–4) by varying the ratio of the concentrations of iron (III) sulfate, sodium molybdate (tungstate). Raising the pH to 5–6 leads to decrease in the current efficiency of 60–50% as well as the deterioration of electrolytes stability and coating quality.

(ii) Application of unipolar pulsed current allows receiving a relatively high current efficiency and uniform coating with less nonmetallic impurities and an increased content of molybdenum and tungsten in the alloy.

(iii) Irrespective of the deposition mode electroplating alloys have an amorphous structure and the grains of coatings obtained in the pulsed mode consist of agglomerates with a diameter of 0.2–0.4 microns.

(iiii) The amorphous structure of alloys and significant content of alloying elements (Mo and W) predetermine improved physical and mechanical properties of coatings as well as high corrosion resistance. The corrosion rate of such coatings in all corrosive environments is lower and microhardness is 2–4 times that of the substrate (cast iron, mild steel).

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The features of Fe–Mo and Fe–Mo–W coatings electrodeposition from a citrate bath containing iron (III) on mild steel and cast iron substrates are investigated in the present work. The application of iron (III) compounds significantly enhanced the

stability and service life of the bath due to elimination of redox reactions involving complexes formation and collateral anodic reactions. The effect of the content of alloying components and electrolysis mode on the quality, composition and properties of the alloys are determined. It is shown that alloys formed under a non-stationary electrolysis condition have uniform surface and composition and contain fewer impurities. Improved physical and mechanical properties as well as higher corrosion resistance of Fe–Mo and Fe–Mo–W coatings compared with the basic metal are caused both by the propensity of alloying components for passivation and by an amorphous structure of electroplated alloys. The coatings under study are considered as promising in surface hardening technologies and for repairing worn items.

Keywords: Fe–Mo and Fe–Mo–W alloy; citrate bath; physical-mechanical properties; electrodeposition; corrosion resistance; non-stationary electrolysis.

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