

## INFLUENCE OF THE CONTENTS OF REFRACTORY COMPONENTS ON THE CORROSION RESISTANCE OF TERNARY ALLOYS BASED ON IRON AND COBALT

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We study the influence of the concentrations of the components of citrate electrolytes based on Fe(III) and the modes of electrolysis on the composition of the Fe–Co–Mo, Fe–Co–W, and Fe–Mo–W coatings. It is shown that the formation of ternary alloys is realized by the mechanism of competitive reduction of cobalt and tungsten (molybdenum) with iron. As the concentration of a ligand increases, the coating is enriched with a refractory component. However, the opposite trend is observed as the current density increases. The application of the pulsed electrolysis makes it possible to increase the rate of the process and to enhance the current efficiency by 70–75%. The dependence of the morphology of deposits on the nature and content of refractory components is determined by the methods of scanning electron microscopy and X-ray diffraction spectral microanalysis. The influence of the compositions of ternary coatings on their corrosion resistance in media with different acidities and on the catalytic activity in the electrochemical reaction of hydrogen release is analyzed. By the methods of polarization resistance and electrode impedance spectroscopy, it is established that the corrosion resistance of the coatings is higher than for the substrate material by 1.3–2.0 orders of magnitude. The dependence of the nature of corrosion inhibition on the composition of electrolytic alloys is investigated.

**Keywords:** electrodeposition, corrosion resistance, polarization resistance, electrode impedance spectroscopy, refractory metals, ternary alloys.

At present, it is necessary to solve numerous applied problems required for the development of new technologies and broadening of the spectrum of functional materials. Therefore, the multicomponent galvanic alloys attract especial interest of the researchers [1, 2]. By the complex realization of elevated characteristics of microhardness and wear- and corrosion resistances, as well as the high catalytic and magnetic characteristics in thin layers, it is possible to significantly extend the spheres of application of these coatings [3]. In particular, it becomes possible to avoid the toxic procedure of chromium plating [4] and create new efficient materials for the heterogeneous, electro-, and photocatalyses, etc. that are more accessible as compared with the traditional platinides.

In the case of formation of the coatings by electrochemical methods, it is possible to realize efficient control over the contents of components, deposition rates, and the state of the surface by varying the compositions of electrolytes and the modes of polarization (static, reversible, or pulsed) [5]. In each separate case, the formation of coatings depends not only on the qualitative [6] and quantitative [7] compositions of the electrolyte but also on the conditions of synthesis [8]. In turn, the structure of alloy specifies its properties and the fields of

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application of the coatings. Hence, it is necessary to study the influence of the modes of electrolysis on the compositions and morphology of the galvanic alloys.

In recent years, we observe an increase in the number of works devoted to the electrodeposition of the coatings formed by alloys of the metals from the subgroup of iron with  $d^4$ -elements [9, 10]. Special attention is given to the electrochemical deposition of alloys formed by metals of the iron triad Fe (Ni, Co) with  $d^4$ -elements Mo (W, V) because the functional characteristics of these coatings are much higher than for the alloy-forming metals. Moreover, in some cases, the researchers observed a superadditive (i.e., synergetic) improvement of the operating characteristics [11]. By introducing tungsten or molybdenum to the composition of the coatings, one can remove the internal stresses typical of the electrolytic alloys of iron and improve their adhesive properties [12] and physicochemical characteristics [13]. Note that the friction coefficient of amorphous Fe–W–P ternary alloys is lower than for the Fe–W binary alloys [14].

The elevated electrocatalytic activity of Co–W binary alloys obtained by applying impulsive currents was revealed in the model reactions of electrolytic hydrogen release and catalytic oxidation of benzene [15]. Their high corrosion resistance and catalytic activity were also recorded in [16]. By the wear- and corrosion resistances, Co–W alloys successfully compete with galvanic chromium. The hardness of the Co–W–Fe alloys with ~ 30 wt.% of tungsten is close to the hardness of chromium coatings but their corrosion resistance is much higher.

In [17, 18], it was proved that the electrodeposited Fe–Mo–W alloys with improved physicochemical and anticorrosion characteristics can be used for the strengthening and restoration of worn machine parts. Moreover, it becomes clear that the coatings formed by the Co–Mo–W alloy are most efficiently produced by electrolysis in the nonstationary mode [19]. The indicated results reveal a significant increase in the microhardness and corrosion resistance of the coatings as compared with the binary alloys and substrate materials. Since these coatings contain metals with different affinities for oxygen and hydrogen, their application for the purposes of electrocatalysis in fuel elements and flow-type batteries seems to be promising. It is worth noting that the available results mainly deal with Fe(Ni, Co)–Mo(W) binary alloys. Therefore, the introduction of an element (amorphizer) as the third alloy-forming element to the composition of the system may expectedly extend the range of functional properties of the materials. In the present work, we prove this hypothesis.

## Materials and Methods

The coatings formed by ternary alloys were deposited on substrates of St3 low-carbon steel at 25–30°C. The Fe–Co–W(Mo) and Fe–Mo–W alloys were deposited from complex Fe(III)-citrate electrolytes with variable compositions [20, 21], while the Co–Mo–W alloy was deposited from citrate-diphosphate electrolytes [19]. The solutions of electrolytes were prepared by using certified “chemically pure” and “analytically pure” reagents on distilled water. Their acidity was controlled with the help of a pH-150M device with an ESL-6307 glass electrode. The surface of the specimens was prepared according to the standard procedure [22] including the procedures of mechanical polishing, degreasing, chemical etching of low-carbon steel either in a diluted sulfate acid or in a mixture of sulfate and chloride acids in the ratio 1:1, careful washing with distilled water, and drying.

The procedure of electrolysis was carried out in a glass cell by using a two-electrode circuit with planarly located anodes made of Kh18N10T stainless steel with the ratio of the area of cathode to the area of anode equal to 1:10. The coatings were formed both in the galvanostatic mode with a variable current density of 2–7 A/dm<sup>2</sup> and under a unipolar pulsed current in the course of polarization by rectangular pulses with amplitudes of 2–5 A/dm<sup>2</sup>, the duration of pulses  $t_{\text{on}} = 2 \cdot 10^{-3} - 5 \cdot 10^{-2}$  sec, and the duration of pauses  $t_{\text{off}} = 2 \cdot 10^{-3} - 5 \cdot 10^{-2}$  sec. The volume current density was kept equal to 2 A/dm<sup>3</sup>.

The chemical composition of the coatings was found by the X-ray diffraction fluorescence method with the use of a "SPRUT" portable spectrometer. The results were checked by the method of X-ray diffraction energy-dispersion spectroscopy by using an Oxford INCA Energy-350 electron-probe microanalyzer integrated in the system of a scanning electron microscope (SEM). The surface morphology was studied in a ZEISS EVO-40XVP SEM. The images were obtained by recording the secondary electrons with the help of scanning with an electron beam. This enabled us to perform measurements with high resolving power and contrast.

The current yield was determined gravimetrically by assuming that the metals in deposited coatings are in the completely reduced state. The theoretical increment of mass of the electrolytic coating was found by the Faraday law with regard for the electrochemical equivalent of the alloy. The corrosion resistance of the coatings was determined according to the polarization dependences plotted either on the basis of the results of analysis of the cathodic and anodic voltamperograms recorded near the corrosion potential or by applying the method of electrode impedance spectroscopy [23] on specimens with an area of  $1 \text{ cm}^2$  in three model corrosive media with different acidities:  $0.001 \text{ mole/dm}^3 \text{ H}_2\text{SO}_4$  against the background of  $1 \text{ mole/dm}^3 \text{ Na}_2\text{SO}_4$  (pH 3) or 3% NaCl (pH 5) and  $0.001 \text{ mole/dm}^3 \text{ NaOH}$  against the background of  $1 \text{ mole/dm}^3 \text{ Na}_2\text{SO}_4$  (pH 9.5).

## Results and Discussion

It is known that the ternary coatings of the Fe(Ni, Co)–Mo(W, V) system can be codeposited either in the galvanostatic mode or with the use of a unipolar pulsed currents. In this case, the current density, the duration of electrolysis, and the durations of pulses and pauses affect the efficiency of the process, quality of the deposits, contents of the alloying components, and hence, the functional properties of the coatings. In choosing the quantitative compositions of solutions, we take into account the specific features of the electrochemical behavior of the components of electrolytes and the competitive reactions of hydrolysis of Fe (III) and protonation of citrate-anions specifying the ionic equilibria in the solution and the pH value of the electrolyte [24].

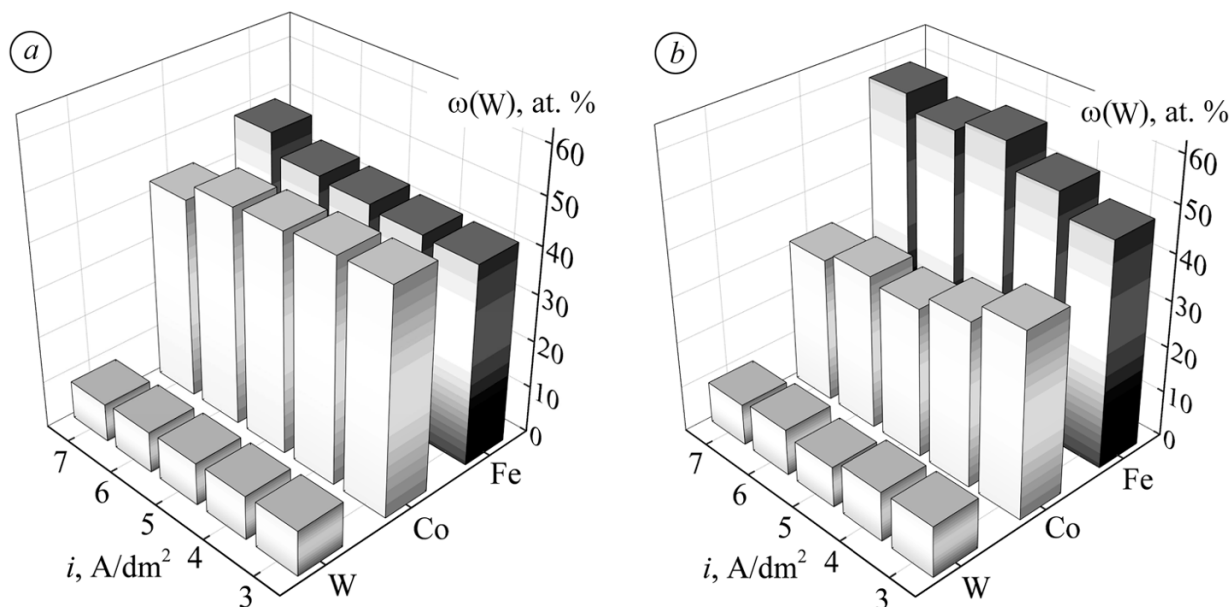
The pH value of the electrolyte increases with the concentration of citrate-ions in the solution for a fixed content of  $\text{Fe}^{3+}$  ions. As the pH value increases, the degree of protonation of citrate-anions decreases. Hence, the electrolytes differ by the ratio of the ionic forms of complex-forming substances and the ligand (and, therefore, of the electrode-active particles), which affects the composition of the coatings. The accumulated results reveal the competitive reduction of alloy-forming components; in particular, of iron, cobalt, and tungsten. The character of reduction depends on the ratio of components of the electrolyte and on the parameters of electrolysis (Fig. 1).

In the course of deposition of the Fe–Co–W alloy from an electrolyte with the ratio of the components

$$c(\text{Fe}^{3+}) : c(\text{Co}^{2+}) : c(\text{WO}_4^{2-}) : c(\text{Cit}^{3-}) = 1 : 1.3 : 0.6 : 2.7$$

for a cathodic current density of  $3\text{--}7 \text{ A/dm}^2$ , the content of cobalt in the coating exceeds the content of iron. Moreover, as the current increases, the cobalt content gradually decreases (Fig. 1a). For a current density of  $6 \text{ A/dm}^2$ , both iron and cobalt are codeposited in the alloy almost in the following ratio: 1:1.

The content of iron significantly increases with the subsequent growth of current density due to the decrease in the amounts of cobalt and tungsten. The content of refractory component of the alloy varies within the range 8–10 at.% (recalculated to the metal) with a trend to decrease as the current density increases (Fig. 1a). As the concentration of citrate in the solution increases to  $0.5 \text{ mole/dm}^3$  (Fig. 1b), the content of tungsten somewhat

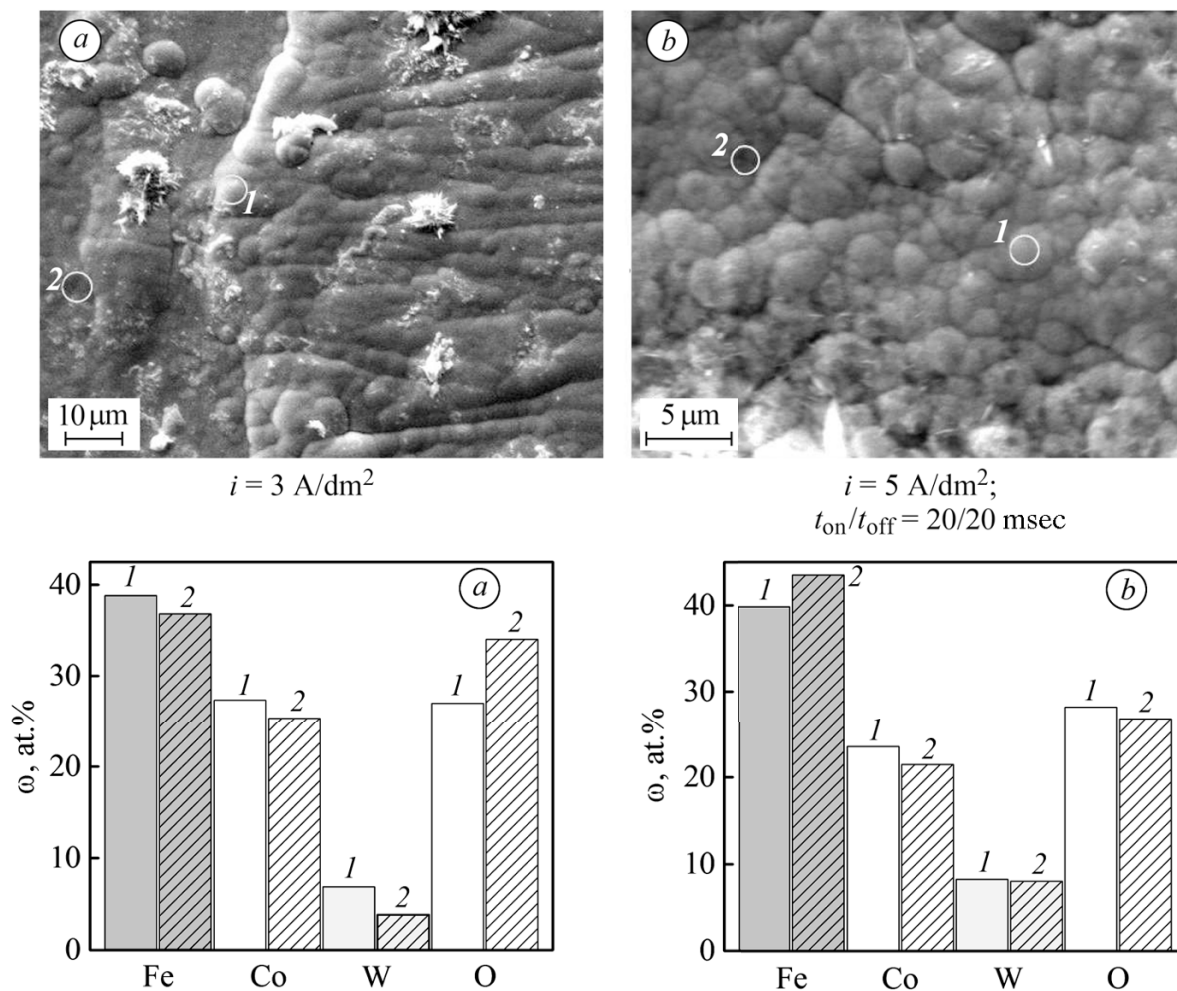


**Fig. 1.** Influence of the current density on the composition of Fe–Co–W coatings for various ratios of the electrolyte components  $c(\text{Fe}^{3+})$ :  $c(\text{Co}^{2+})$ :  $c(\text{WO}_4^{2-})$ :  $c(\text{Cit}^{3-})$ : (a) 1:1.3:0.6:2.7; (b) 1:1.3:0.6:3.3.

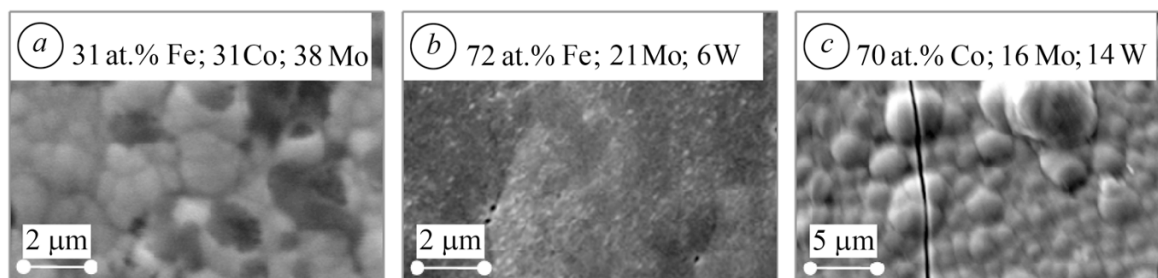
increases (to 9–11 at.%), while the other conditions remain identical. However, the trend to its decrease as the current density increases is preserved. The competitive character of the reduction of iron and cobalt becomes clearer: As the current density increases from 3 to 7 A/dm<sup>2</sup>, the iron content of the coating increases to 59 at.% with simultaneous decrease in the amount of cobalt down to ~30 at.%.

The efficiency of deposition of the Fe–Co–W alloy in the galvanostatic mode does not exceed 45% independently of the concentration of electrolyte. For current densities that do not exceed 7 A/dm<sup>2</sup>, the partial reaction of hydrogen release becomes faster. Thus, the current yield of the targeted reaction decreases down to 27%. By using the procedure of pulsed electrolysis, it is possible to get an almost twofold increase in the efficiency of the process: If the ratio  $t_{\text{on}}/t_{\text{off}}$  is fixed, then the current yields are equal to 70–75% and 63–68% for the current amplitudes equal to 3 and 5 A/dm<sup>2</sup>, respectively.

The analysis of the morphology and distribution of the components over the surfaces of the Fe–Co–W coatings reveals the formation of globular structures for both galvanostatic and nonstationary modes of electrolysis. The coatings formed by stationary currents are characterized by higher contents of oxygen whose amount increases in the cavities (Fig. 2a). Moreover, we observe a nonuniform distribution of the refractory component on the asperities and in the hollows. The nonstationary electrolysis promotes the formation of a more uniform and more ordered surfaces (Fig. 2b), as well as the increase in the content of tungsten in the coatings up to 12.5 at.% (recalculated to the metal). In this case, the contents of alloy-forming metals do not exhibit significant variations in different zones located within the scanning region. Unlike the stationary mode, the content of oxygen does not exceed 28 at.%. According to the results of the SEM analyses of the surfaces, the coatings deposited by unipolar pulsed currents have more developed surfaces in which we detect agglomerates 2–4  $\mu\text{m}$  in size formed by smaller spheroids whose sizes are smaller than 1  $\mu\text{m}$  [25]. The globular surface structure caused by the presence of the refractory amorphizing component may promote an increase in the microhardness, corrosion resistance, and catalytic activity of the coatings.

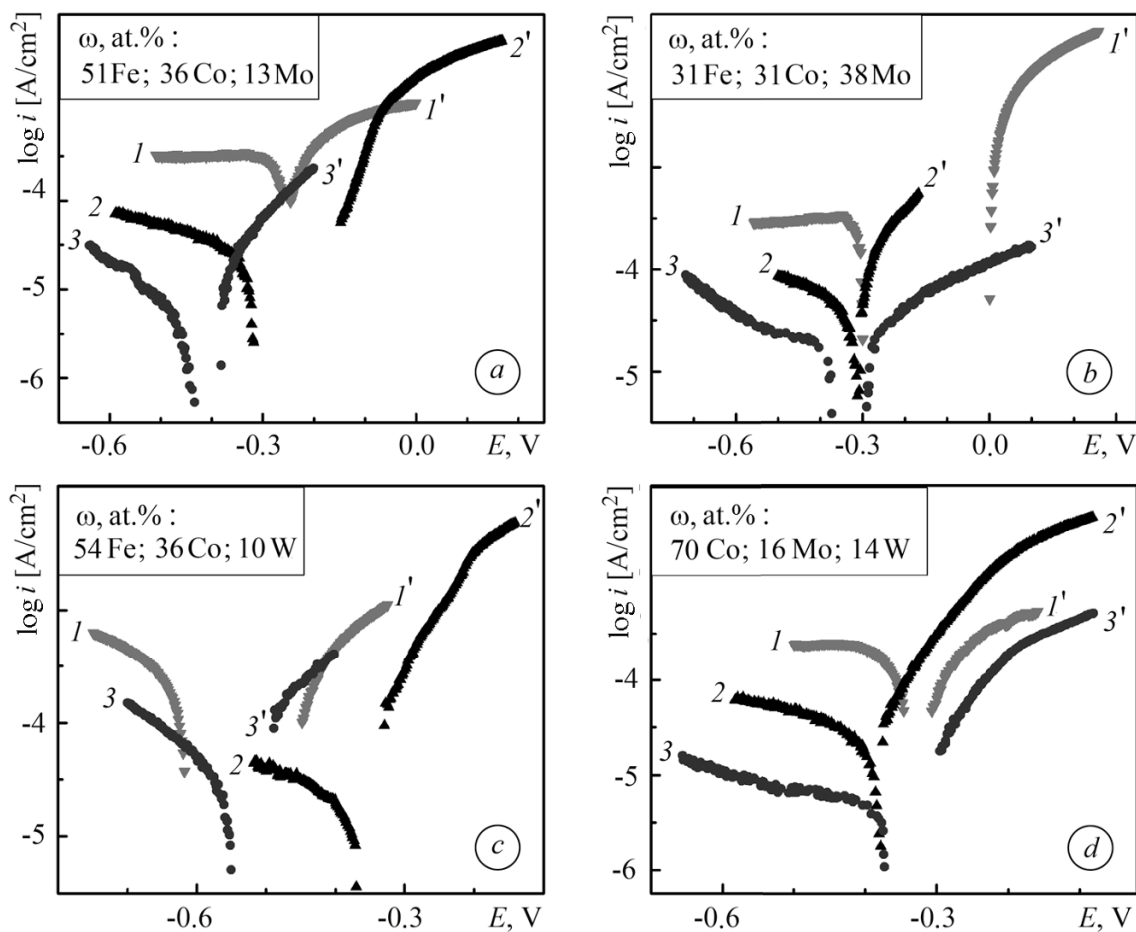


**Fig. 2.** Morphologies and compositions in the asperities (1) and cavities (2) of the Fe–Co–W coatings obtained in the galvanostatic (a) and pulsed (b, c) modes for the ratio of concentrations of the components of electrolyte  $c(\text{Fe}^{3+}) : c(\text{Co}^{2+}) : c(\text{WO}_4^{2-}) : c(\text{Cit}^{3-}) = 1 : 1.3 : 0.6 : 3.3$ .



**Fig. 3.** Surface morphologies of the coatings formed by ternary alloys from electrolytes with different compositions in the galvanostatic mode at the following current densities,  $\text{A/dm}^2$ : (a) 2.5; (b) 5; (c) 4.

The results of investigation of the surface morphology of the coatings formed by ternary alloys with various compositions (Fig. 3) also reveal a general trend to the formation of amorphous structures with different quantitative compositions and different sizes of spheroidal elements [25].



**Fig. 4.** Cathodic (1–3) and anodic (1'–3') polarization dependences for coatings in corrosive media with pH 3 (1, 1'); pH 5 (2, 2'), and pH 9.5 (3, 3').

For coatings of the Fe(Co)–Mo(W) system with different contents of alloying components deposited on the substrate of St3 steel, the results of tests for the corrosion resistance completely confirm the expected significant increase in the chemical resistance of the coatings as compared with the substrate material. In particular, the results of testing of the Fe–Co–Mo coatings (Figs. 4a, b) demonstrate that, as compared with the substrate material, the corrosion potential shifts to the positive side in acid and neutral media, whereas the corrosion rate decreases as a result of the formation of a dense film formed by acidic molybdenum oxides on the surfaces of the coatings.

On the contrary, in alkaline media, the corrosion potential shifts to the negative side due to the inhibition of the cathodic reaction as a result of passivation of the surfaces of alloys by difficultly soluble iron and cobalt hydroxides obstructing the access of depolarizers. Therefore, the highest corrosion resistance is observed for the Fe–Co–Mo coatings with 51 at.% of iron and 13 at.% of molybdenum in alkaline medium. If the coating is enriched with molybdenum, then its corrosion resistance in acid media increases due to the decrease in the amount of iron (Table 1).

The corrosion behavior of the Fe–Co–W coating (Fig. 4c) in acid media differs from the behavior of the Fe–Co–Mo alloy. In the first case, the corrosion potential is shifted to the negative side and, hence, the cathodic control over the corrosion is predominant. The inhibition of the cathodic reaction is caused by the complication

**Table 1**  
**Parameters of Corrosion of the Fe–Co–Mo, Fe–Co–W, and Co–Mo–W Coatings**

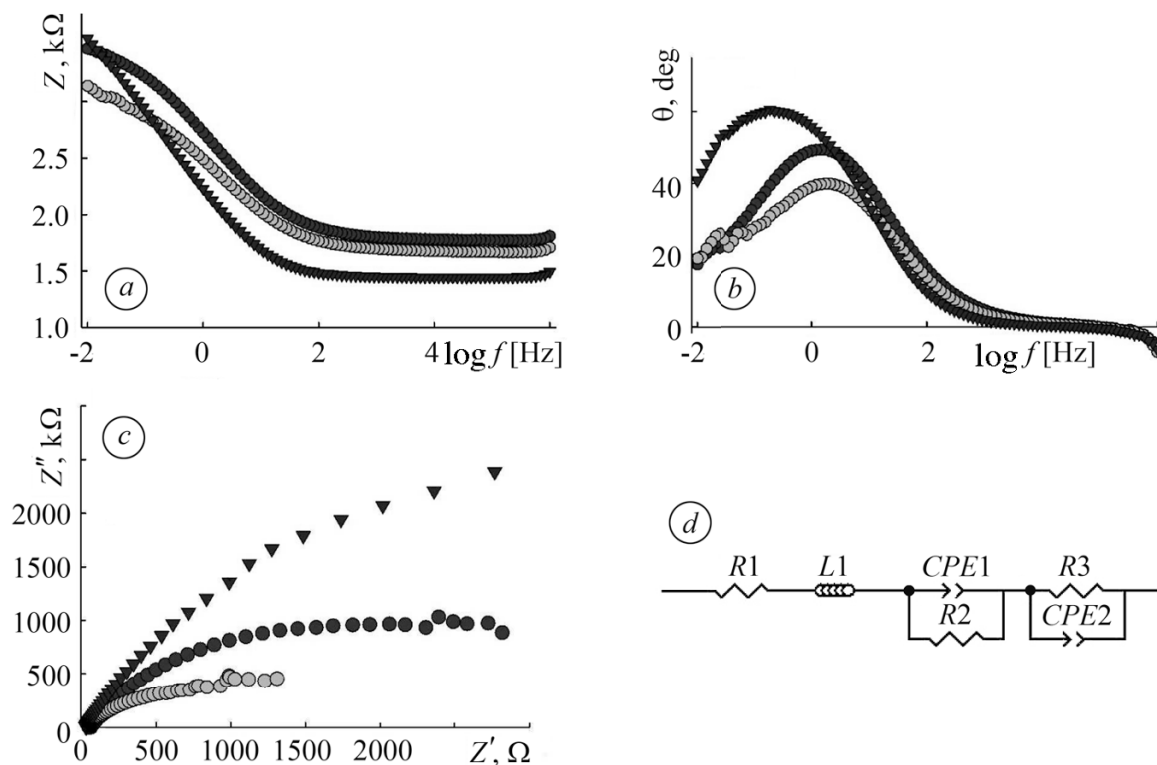
Composition of the coatings $\omega$ , at.%	pH 3		pH 5		pH 9.5	
	$E_{\text{corr}}$ , V	$\log i_{\text{corr}}$ [A/cm <sup>2</sup> ]	$E_{\text{corr}}$ , V	$\log i_{\text{corr}}$ [A/cm <sup>2</sup> ]	$E_{\text{corr}}$ , V	$\log i_{\text{corr}}$ [A/cm <sup>2</sup> ]
St3 steel	– 0.34	– 2.8	– 0.35	– 3.0	– 0.32	– 2.8
51Fe36Co13Mo	– 0.25	– 3.7	– 0.3	– 4.9	– 0.46	– 5.5
31Fe31Co38Mo	– 0.16	– 4.5	– 0.31	– 4.8	– 0.32	– 5.1
59Fe33Co8W	– 0.42	– 4.5	– 0.41	– 5.0	– 0.49	– 5.4
54Fe36Co10W	– 0.54	– 4.7	– 0.36	– 5.1	– 0.53	– 5.2
70Co16Mo14W	– 0.33	– 4.1	– 0.39	– 4.9	– 0.36	– 5.5

of the delivery of oxygen as a depolarizer explained by the formation of the films of nonstoichiometric tungsten oxides of acid nature. Note that the characteristics of corrosion resistance of the Fe–Co–W coatings with 10 at.% tungsten at pH 3 are higher than for the Fe–Co–Mo coatings with 38 at.% of the refractory component. This can be explained by the difference between the morphologies and phase compositions of these coatings and by the higher specific electric resistance of tungsten oxides.

The highest corrosion resistance in the alkaline medium is observed for the Fe–Co–W coatings with 59 at.% of iron and 8 at.% of tungsten (Table 1). As the coating is enriched with tungsten, its chemical resistance in the acid medium increases due to a decrease in the content of iron. The weakening of the corrosion current in neutral medium reveals the formation of passive films of the alloying components even in the presence of the depassivating ions ( $\text{Cl}^-$ ). Due to the ability of molybdenum and tungsten to form protective oxides with high chemical resistance in acid and neutral media, one may expect a decrease in the rate of corrosion of the Co–Mo–W coatings (Fig. 4d). In turn, cobalt oxides formed on the surface have the alkaline nature and promote an increase in the corrosion resistance of the alloy in these media (see Table 1).

The results obtained in the course of investigation of the corrosion behavior of the coatings formed by ternary alloys were checked by the method of electrode impedance spectroscopy. The electrode impedance spectra for the Fe–Co–Mo, Fe–Co–W, and Fe–Mo–W systems measured in a 3% NaCl solution reveal the presence of two phases and, hence, two interfaces (two maxima in the Nyquist–Bode curves; see Figs. 5a, c, namely, the electrolyte–oxide interface on the electrode surface and the electrolyte–metal interface). The equivalent circuit (Fig. 5d) for the analyzed systems includes the following elements:  $R_1$  is the resistance of electrolyte;  $L_1$  is the inductive component of the impedance;  $CPE_1$  is the capacitance of the electrolyte–oxide interface on the electrode surface;  $R_2$  is the resistance of the oxide layer;  $CPE_2$  is the capacitance of the electrolyte–metal interface, and  $R_3$  is a resistance equivalent to the corrosion resistance.

The substitution circuit is based on the so-called Voigt scheme for multiphase systems [23, 26]. The CPE elements specify the fractality of the phases. Moreover, their connection in the antiphase reflects the limitation on the charge transfer rate  $R_3$ . The inductance  $L_1$  is determined by the galvanomagnetic Hall effects in the region of high frequencies (Fig. 5b) related to the magnetic properties of the coatings and also to the presence of



**Fig. 5.** Plots of electrode impedance on the Bode (a, b) and Nyquist (c) coordinates in a neutral chloride-containing medium and the equivalent circuit of substitution (d) for the electrode processes in the analyzed systems: (a, b): (●)  $f$  vs.  $|Z|$  Fe–Co–Mo, (○)  $f$  vs.  $|Z|$  Fe–Co–W, (▼)  $f$  vs.  $|Z|$  Fe–Mo–W; (c): (●)  $Z'$  Fe–Co–Mo vs.  $Z''$  Fe–Co–Mo, (○)  $Z'$  Fe–Co–W vs.  $Z''$  Fe–Co–W, (▼)  $Z'$  Fe–Mo–W vs.  $Z''$  Fe–Mo–W.

**Table 2**  
**Parameters of the Circuit of Equivalent Substitution and the Parameters of Corrosion of Ternary Alloys**

Composition of the alloy $\omega$ , at.%	$E_{\text{corr}}$ , V	$R1$	$R2$	$CPE1$	$R3$	$CPE2$
		$\Omega \cdot \text{cm}^2$				
59Fe33Co8W	-0.44	46.9	503	0.7	2410	0.5
51Fe36Co13Mo	-0.42	59.5	1806	0.74	4615	0.53
64Fe24Mo12W	-0.45	27.9	7195	0.71	620	0.98

a group of metals capable of formation of hydrated oxide films with variable valence on the surfaces. These films have different specific resistances and capacitances and create several ways of conduction. The presence of galvanomagnetic effect is revealed by the transition of the phase angle to positive values in the Bode diagrams (Fig. 5b). The determined parameters of the equivalent circuit (Table 2) were used for the evaluation of the corrosion rate.



**Table 3**  
**Current Density of Hydrogen Exchange on Platinum and on the Coatings**  
**Formed by Ternary Alloys**

Composition of the coating $\omega$ , at.%	$\log i_{\text{H}}^0$ [A/cm <sup>2</sup> ]		
	pH 3	pH 5	pH 9.5
Platinum	- 3.3	- 3.2	- 3.1
51Fe36Co13Mo	- 3.1	- 2.8	- 4.0
31Fe31Co38Mo	- 3.1	- 3.6	- 3.4
54Fe36Co10W	- 3.5	- 3.4	- 3.3
59Fe33Co8W	- 3.3	- 3.1	- 3.5
87Co8Mo5W	- 3.4	- 3.6	- 3.9
78Co16Mo6W	- 3.2	- 3.3	- 3.5

As follows from Table 2, the corrosion resistance of ternary alloys depends, in particular, on the formation of a film of oxides of refractory metals whose capacitance components CPE1 are almost identical because the coatings have the same thickness. The resistance of oxide coatings  $R_2$  is maximum in the Fe–Mo–W system, which is explained by the presence of two refractory metals. However, the highest corrosion resistance  $R_3$  is observed for the Fe–Co–Mo coatings. Hence, we can state that, according to the mechanism of their protective action, the Fe–Mo–W coatings can be regarded as, to a significant extent, barrier-like, whereas the cobalt-containing alloys are barrier-protective.

The high chemical resistance of ternary alloys under the conditions of free corrosion in media with different acidities serves as a basis for their application as coatings on catalytically active electrode materials used for the purposes of the electrochemical power-generating industry. By the results of evaluation of their electrocatalytic activity determined according to the exchange current of a model electrochemical reaction of hydrogen release from solutions with different acidities  $i_{\text{H}}^0$ , it was established that the synthesized materials can be compared (by the same parameters) with metals of the platinum family (Table 3).

This fact confirms high competitiveness of the produced coatings and gives us a possibility to recommend the Fe–Co–W, Fe–Co–Mo, and Co–Mo–W ternary alloys for the systems of autonomous and reserve power supply.

## CONCLUSIONS

It is established that, in the course of formation of ternary alloys of metals from the iron subgroup with refractory d<sup>4</sup>-elements [Fe (Co)–Mo (W)], we observe the competitive reduction of cobalt and tungsten (molybdenum) with iron. This trend becomes clearer as the current density and the concentration of citrate-ions in the solution increase. It was discovered that the application of unipolar pulse currents makes it possible to increase

the content of refractory components in the coatings whose surface structures turn from fine-grained to globular as the current amplitude increases.

We analyze the influence of the compositions of Fe–Co–Mo, Fe–Co–W, and Co–Mo–W coatings on the corrosion resistance in media with different acidities. It is experimentally established that molybdenum (or tungsten) strongly increases the chemical resistance of the coatings as compared with the substrate material. At the same time, the rate of corrosion decreases if the pH value of solutions increases and if the alloy is enriched with refractory components. It is shown that the synthesized materials are comparable with platinumides by their catalytic activity in the electrochemical reactions of hydrogen release. This enables us to treat ternary alloys of the Fe(Ni, Co)–Mo(W, Mo) system as promising electrode materials for the chemical sources of autonomous and reserve power supply.

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