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INFLUENCE OF ALLOYING ELEMENTS ON CORROSION-MECHANIC PROPERTIES OF MULTI-COMPONENT ELECTROLYTIC ALLOYS

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ВПЛИВ ЛЕГУВАЛЬНИХ ЕЛЕМЕНТІВ НА КОРОЗІЙНО-МЕХАНІЧНІ ВЛАСТИВОСТІ БАГАТОКОМПОНЕНТНИХ ЕЛЕКТРОЛІТИЧНИХ СПЛАВІВ

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АНОТАЦІЯ

Досліджено кількісний і фазовий склад покривів тернарними сплавами Fe-Co-Mo(W) та Co-Mo-W(Zr), осаджених з моно і білігандних електролітів постійним та імпульсним струмом. Результати рентгеноструктурного аналізу свідчать про аморфно-кристалічну структуру сплавів, наявність фаз інтерметалідів Fe₇Mo, Fe₇Co, FeCo, Co₇W₆, Fe₇W₆, разом із α-Fe та Fe₃C, причому розміри кристалітів аморфної частини знаходяться в інтервалі 7–8 нм. Методом сканівної електронної спектроскопії, атомно-силової мікроскопії і рентгеноспектрального мікроаналізу встановлено вплив природи та вмісту тугоплавких і рідкісних металів на морфологію, шорсткість поверхні покривів, а також розміри кристалітів і агломератів. Методом поляризаційного опору встановлено, що корозійна стійкість покривів на 1,3–2,0 порядки величини вища за параметри матеріалу підкладки. Визначено залежність швидкості корозійного процесу у хлоридвмісному середовищі від складу електролітичних сплавів. За даними спектроскопії електродного імпедансу встановлено еквівалентні схеми заміщення, їх параметри і доведено тотожність показників корозійного опору, одержаних різними методами. Проаналізовано вплив складу і морфології поверхні на мікротвердість електролітичних сплавів. Показано, що за фізико-механічними характеристиками тернарні покриття Fe-Co-Mo(W), Co-Mo-W(Zr) не поступаються електролітичним покриттям твердим хромом.

KEY WORDS: *electrochemical deposition, corrosion resistance, polarization resistance, impedance spectroscopy, refractory metals, ternary alloys, microhardness.*

A settlement application of new technology and expanding the range of functional materials leads to an increased interest of researchers and technologists to galvanic multicomponent alloys. Particular attention is paid to the electrochemical deposition of iron and cobalt alloys with Molybdenum and Tungsten, as the functional properties of the coatings exceed those for alloying metals [1, 2]. Complex realization in thin layers of increased microhardness, wear and corrosion resistance, catalytic, magnetic properties can significantly expand the scope of such coatings [3, 4]. The electrochemical deposition the coatings provide flexible control of the components content, the rate of deposition and the surface morphology due to variation in the electrolytes composition and polarization modes [5, 6]. The coatings composition essentially depends on the electrolyte concentration [7], but the electrodeposition conditions significantly affect the galvanic alloys composition, morphology, and, accordingly, properties [8, 9]. In view of this, the study of the influence of electrolysis modes on the alloying components content, surface morphology, and corrosion-mechanical properties of ternary coatings is relevant.

EXPERIMENTAL

Coatings Fe-Co-Mo (W) were formed on the substrates of copper M1 and steel at a temperature of 25 – 30 °C from complex Fe(III) based electrolytes [10]. Electrolysis was carried out in a glass cell for a two-electrode scheme using planar positioned anodes of stainless steel X18H10T at

the ratio of cathode to anode area 1 : 5. The deposition of the coatings was carried out at a constant current density of 2 – 5 A/dm² and unipolar pulse current amplitude of 2 – 7 A/dm² in the on / off time range of 2– 20 msec. Volumetric current density maintained at the level 2 A/dm³. Coatings Co-Mo-W (Zr) were deposited from biligand electrolytes using pulse current [11].

The elemental composition and morphology of the samples were analyzed using a scanning electron microscope ZEISS EVO 40XVP. Images of the samples surface were obtained by recording the secondary electrons (BSE), which allows investigate the topography with high resolution and good contrast. Image processing was done using software SmartSEM. The chemical composition of the coatings surface was determined by the X-ray fluorescence method and by analysis of the characteristic X-ray spectrum, which was recorded by an energy-dispersive spectrometer INCA Energy and portable spectrometer "Sprut". The analysis was carried out at a minimum of 3 points with the subsequent averaging of the obtained values in the absence of significant deviations.

Microanalysis phase composition was performed on X-ray diffractometer DRON-3M radiation cobalt anode Cu-K α 1 ($\lambda=1.5405$ Å). The registration of diffractograms was carried out at a sliding angle of 2.5°, and the recording of reflections was carried out on fixed samples. X-ray diffractograms (XRD) were recorded in discrete mode with a step $2\theta=0.1^\circ$ and exposure at each point for 20 sec at an operating voltage of 35 kV and a current of 20 mA.

Coatings surface relief was determined by contact method using atomic force microscope probe (AFM) NT-206 (probe CSC-37, cantilever B) with a lateral resolution of 3 nm. The analysis of AFM images was performed using Explorer software.

Corrosion tests of coatings were carried out by the method of polarization resistance in 3 % NaCl. Corrosion current density i_{cor} was determined as in [12]. of corrosion test results were verified by electrode impedance spectroscopy (EIS) technique in 3% NaCl. Electrode impedance spectra were registered on planar electrodes of an area of 1 cm² using electrochemical module Autolab-30 (PGSTAT301N Metrohm Autolab), equipped with FRA-2 in a frequency range of 10⁻² – 10⁶ Hz. Module management was performed using Autolab 4.9 standard procedure followed by data set processing in the package Zview 2.0. The modeling of the interfacial boundary structure and state was performed by equivalent substitution circuit method. Parameters of equivalent circuit with an error less than 10 % were accepted for consideration.

Microhardness of alloy coatings and substrate determined by the diamond pyramid indentation on PMT-3 device under load of $P = 0.02-0.2$ kg and the time of endurance of 10 sec. The experiment was carried out after coats aging during 24 hours at room temperature at a minimum of 3 points with subsequent averaging of data; the confidence interval was ± 10 . The thickness of the coatings for all analysis was not less than 30 μ m.

RESULTS AND DISCUSSION

The substrate of mild steel is characterized by evenly surface (Fig. 1a), while the Fe-Co-Mo coatings surface is more developed and globular comparing with the substrate (Fig. 1b). Cross section profile between markers 1 and 2 indicates the grain sizes to be in the range of 2–3 μ m, wherein larger spheroids are formed with a smaller grains of sizes of 0.2–0.5 μ m (Fig. 1d). Moreover one can observe the parts of different morphology (Fig. 1c). AFM data analysis demonstrates the globular surface of Fe-Co-W coatings with conglomerates size of 2.5–3.5 μ m (Fig. 1d) which is more developed comparing with substrate and Fe-Co-Mo deposits.

The X-ray analysis points to an amorphous-crystalline nature of Co-Mo-W(Zr) coatings, and intermetallic phases Co₇W₆, Co₃Mo and Co₇Mo₃ were found. Wide halo detected at angles 2θ of 40–59° indicates the coherent-scattering region size of the amorphous part to be 2–8 nm. Inter-metallic phases Co₇W₆ and Fe₇W₆, as well as α -Fe and cementite Fe₃C and a low halo with width about 10° at angles 2θ 50–55° are detected at diffraction patterns of Fe-Co-W deposits [10]. Diffraction patterns for Fe-Co-Mo alloys exhibit broad halo at angles 2θ 45–58°, and phases Fe₇Mo, Fe₇Co, FeCo. The coherent-scattering region size of the amorphous part for Fe-Co-Mo(W) coatings is of 3–7 nm. Above intermetallides as well as globular surface predetermine high microhardness and corrosion resistance.

Corrosion of cobalt based coatings as it follows from the nature of alloying components proceeds predominantly with oxygen depolarization in 3 % NaCl. The open circuit potential of Fe-Co-

W coatings shifts to the negative side compared with the steel substrate indicating cathodic control of the corrosion (Table 1).

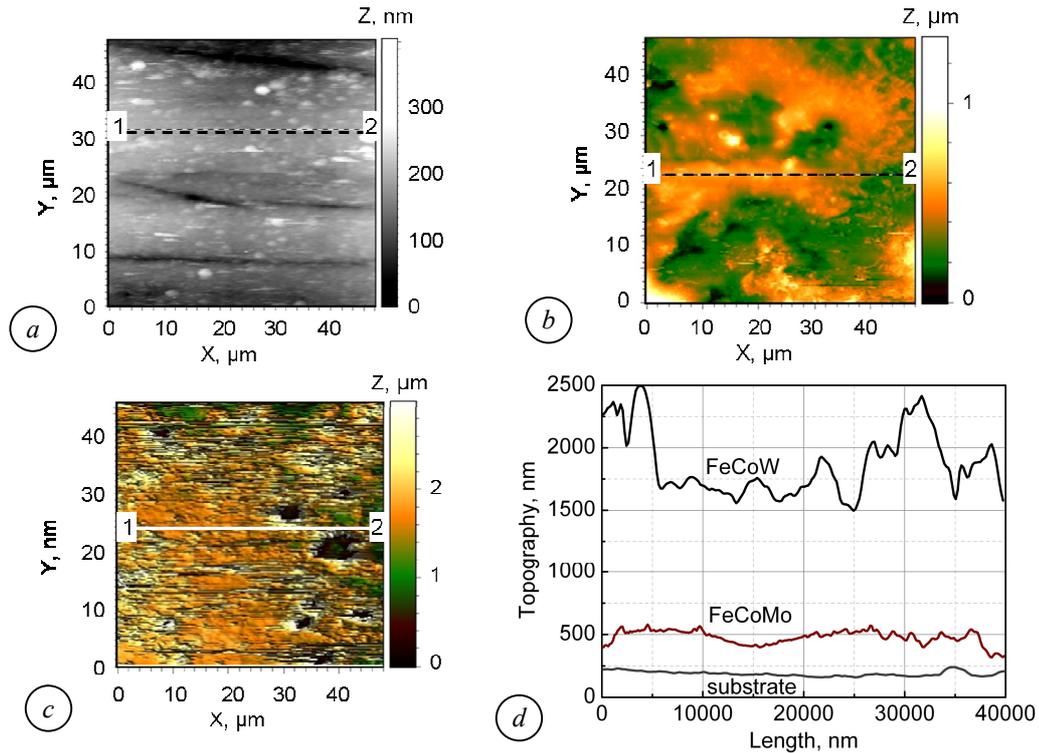


Fig. 1. 2D-maps of surface steel substrate (a), and deposits FeCoMo (b), FeCoW (c) and cross section profile between markers 1–2 at scanning area 40 x 40 μm (d).

Corrosion current decreasing indicates the formation and stability of alloying components passive oxide film, even in the presence of activating Cl^- ions. The Fe-Co-Mo alloy open circuit potential shift to a positive side compared with substrate material (Table 1). The corrosion rate decreases due to the formation of acidic molybdenum oxide film on the surface. The corrosion index of ternary alloys Co-Mo-W(Zr) in chloride-containing media is almost halved compared with binary systems (Table 2). First, it is associated with a decrease in roughness and smoothing out the relief of ternary coatings (Fig. 1). Secondly, it is known that Mo, W, and Zr enhance corrosion resistance to pitting, and their joint presence, obviously, increases the effect. Moreover, with increasing total content of alloying metals, corrosion resistance increases.

Table 1. Corrosion indexes of binary and ternary coatings

Composition (at.%)	E_{oc} , V	$\lg i_{cor}$, A/cm ²	$k_h \cdot 10^3$, mm/year	R_f , Ohm·cm ²
Steel substrate	-0.50	-2.0	300	50
Co76-Mo24	-0.20	-3.7	2.9	390
Co84-W16	-0.35	-3.7	1.0	400
Fe51Co36Mo13	-0.30	-4.8	0.44	1800
Fe31Co31Mo38	-0.31	-4.9	0.42	2000
Fe54Co36W10	-0.36	-5.1	0.23	2100
Fe59Co33W8	-0.39	-4.8	0.44	1700
Co83-Mo12-W5	-0.37	-4.2	0.82	500
Co79-Mo16-W5	-0.38	-4.4	0.68	890
Co72-Mo24-Zr4	-0.50	-5.2	0.14	2500

Verification of polarization method results was carried out using electrode impedance spectroscopy (EIS) technique. The equivalent scheme for Fe-Co-Mo(W) systems contains the elements: R1 is the electrolyte resistance, L1 is the inductive component, CPE1 is the capacity of interface electrolyte / oxide on the electrode surface, R2 is the resistance of the oxide layer, CPE2 is the capacity of interface electrolyte / metal, and R3 is corrosion resistance. The basis of the scheme is

the so-called Wojte scheme for multiphase systems, and the elements of the CPE determine the fractal nature of the phases, and their inclusion in the antiphase indicates the charge transfer limitation of R3. The inductance resistance L1 is due to the appearance of galvanomagnetic Hall effects at high frequencies (Fig. 2a) related to the magnetic properties of the coatings. The other reason is alloying metals capability forming hydrated oxide films of varying valence, which differ in specific resistance and capacity and cause several conduction paths. The appearance of the galvanomagnetic effect is confirmed by the transition of the phase angle towards the positive values (Fig. 2b). SEI plots for Co-Mo-W(Zr) deposits (Fig. 3, 4) are less complicated; and equivalent circuit differs by one R-CPE chain.

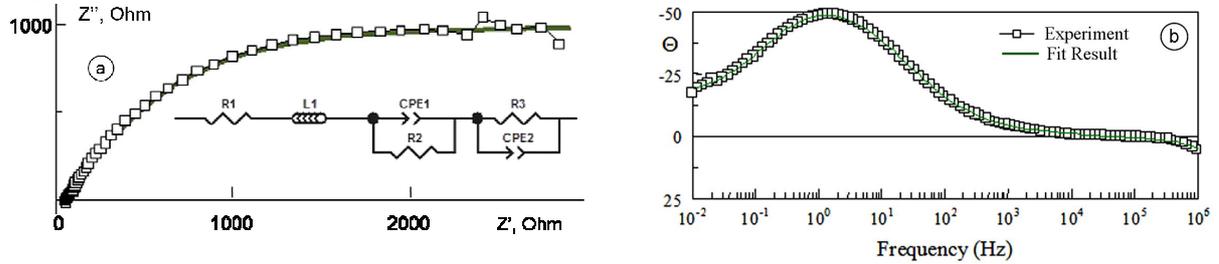


Fig. 2. Nyquist plots (a) and frequency dependence of phase angle (b) for Fe-Co-Mo coated samples in 3 % NaCl.

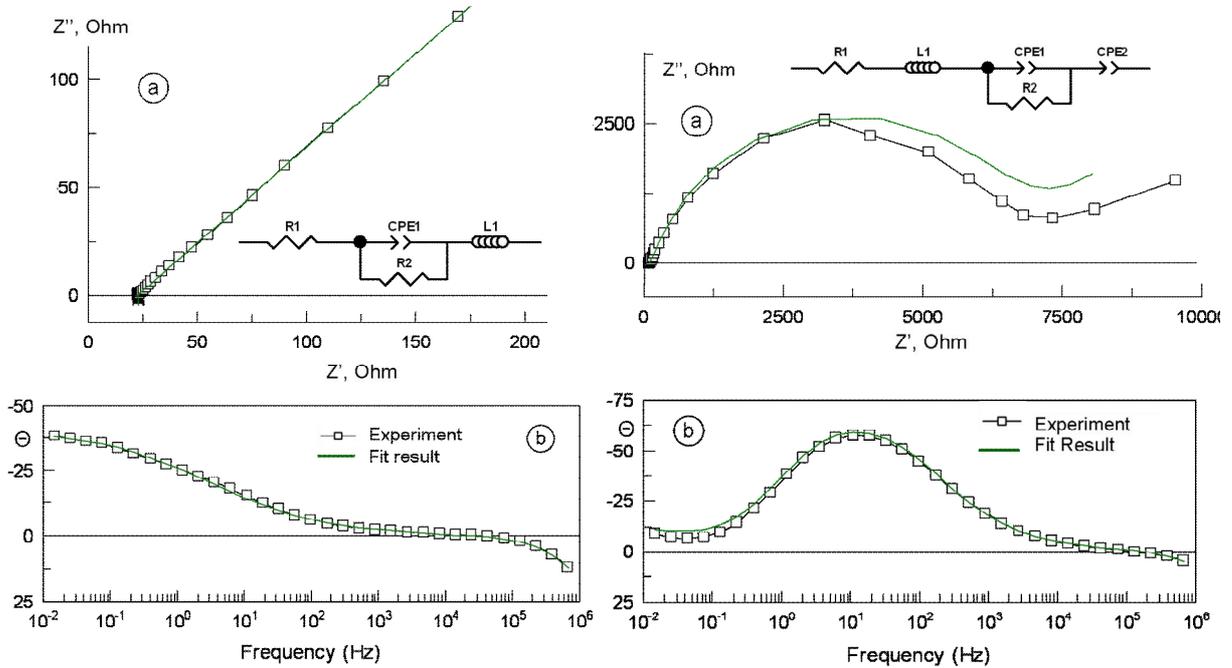


Fig. 3. Nyquist plots (a) and frequency dependence of phase angle (b) for Co-Mo-W coated samples in 3 % NaCl.

Fig. 4. Nyquist plots (a) and frequency dependence of phase angle (b) for Co-Mo-Zr coated samples in 3 % NaCl.

The relatively near values of the corrosion current density, calculated from data of polarization resistance technique and R_f data from EIS analysis, are also evidence of correctness both the parameters of the corrosion process determination, and the validity of the electrochemical systems equivalent circuit. Parameter R_f for tested materials decreases in the range:

$$R_f(\text{Co-Mo-Zr}) > R_f(\text{Fe-Co-W}) \approx R_f(\text{Fe-Co-Mo}) > R_f(\text{Co-Mo-W}) \gg R_f(\text{steel substrate}).$$

Microhardness of ternary Fe-Co-Mo(W) and Co-MoW(Zr) alloys is about 4–5 times that of the mild steel substrate (H_V 200) and was shown to increase with tungsten content. Moreover, H_{μ} of ternary alloys is greater than that of binary [13] due to super-additive contribution of refractory metals, more perfect surface relief and intermetallic phases. The maximum microhardness H_V of 1100 is exhibited by ternary deposits of composition Co83-Mo11-W6 with W/Mo ratio as 1/3. Since microhardness of the ternary alloy is close to that of chrome deposits (H_V 700–800) it allows us to recommend Co-Mo-W electrolytic alloys to replace chromium plating.

The corrosion and microhardness parameters of coatings obtained by pulsed electrolysis are higher in comparison with ones deposited at direct current.

CONCLUSIONS

1. The quantitative and phase composition of galvanic ternary alloys Fe-Co-Mo (W) and Co-Mo-W (Zr) deposited from mono- and biligand electrolytes at direct and pulsed current is determined. The results of X-ray diffraction analysis indicate an amorphous-crystalline structure of alloys, and the presence of intermetallic phases Fe₇Mo, Fe₇Co, FeCo, Co₇W₆, Fe₇W₆ та α -Fe i Fe₃C.

2. The effect of the nature and content of refractory metals on coatings surface morphology, roughness, as well as the size of crystallites and agglomerates has been determined by scanning electron spectroscopy, and atomic force microscopy.

3. The dependence of the corrosion process rate in the chloride-containing medium on the composition of the electrolytic alloys was determined using polarization resistance technique. It is proved that the corrosion resistance of the coatings is 1.3–2.0 orders of magnitude higher than the parameters of the substrate material. According to the spectroscopy of the electrode impedance, equivalent substitution schemes have been established and their parameters have been calculated, according to which the identity of the corrosion coefficients obtained by different methods has been proved.

4. The influence of composition and surface morphology on the physical and mechanical characteristics of the coatings is analyzed. It was established that ternary alloys Fe-Co-Mo (W), Co-Mo-W (Zr) by microhardness are not inferior to the electrolytic chromium coatings.

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