# ELECTROCHEMICAL AND MECHANICAL PROPERTIES OF IRON-BASED NANOCOMPOSITES

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The analysis of the composition of electrolytic coatings for the protection of metal surfaces is considered. It is found that the use of different components for coating modification provides the possibility of obtaining surfaces with extended exploitation properties, in particular, with improved wear and corrosion resistance. A new approach to the protection of cast iron details by obtaining two types of composition coatings from binary alloys, iron-molybdenum and iron-tungsten, is proposed. It is found that the modification of iron by refractory metals up to 37 at.% leads to a noticeable change in the microstructure of the coating surface. It is found that the incorporation of refractory metals into the iron matrix is a good way to increase the microhardness of the surface by 2.5-3.5 times and to increase the wear resistance by 40%, as well as to decrease the coefficient of friction by 3-4 times in comparison with the cast iron substrate. The research results can be used for surface hardening and protection in various industries.

Keywords: binary iron alloys, molybdenum, tungsten, microhardness, friction coefficient, wear resistance

## 1. Introduction

Treatment technologies involving the application of thin-film coatings, especially electrochemical coatings, are quite common in the industry of high-tech countries [1-3]. Recently, the processes of forming electrolytic coatings based on iron triad metals alloyed with additional components have received considerable attention in the development of surface renovation, hardening, and protection [4]. The combination of the valuable properties of the alloying components makes it possible to obtain coatings with improved corrosion resistance, microhardness, and wear resistance on cast iron parts [5-7].

It was proposed to deposit Fe-W alloy with tungsten content from 30 to 60% from a citrate-ammonia electrolyte with pH 8 [8]. Electroplating was carried out at a cathode current density of 5 A/dm2 and an electrolyte temperature of 70 °C. The current efficiency (CE) was in the range of 20-28%. In [9], Fe-W alloys with a tungsten concentration of 39-69.6 wt.% were obtained at a temperature of 60 °C at a direct current density of 50 mA/cm2 from ammonia-citrate electrolytes based on Fe(III). It has been shown in [10] that ammonia-citrate baths have the necessary buffer capacity for the electrodeposition of nanocrystalline and smooth Co-W and Fe-W. A qualitative study of the mechanical behavior of electrodeposited Co-W and Fe-W alloys has been carried out using various methods.

The authors of the study [11] found that iron and molybdenum are contained in metallic form in Fe-Mo deposits obtained from ammonium citrate. Smooth and crack-free Fe-Mo coatings with a molybdenum content of 54 at.% were electrodeposited from a highly saturated ammonium acetate bath at a current density of 30 mA/cm2 [10]. The coatings were considered to be catalysts for the hydrogen evolution reaction. The composition and morphology of Fe-Mo alloys electrodeposited from a pyrophosphate bath in the AC mode were studied in [11]. However, these works did not pay attention to the study of the corrosion and mechanical properties of Fe-Mo electrolytic alloys. The stepwise mechanism of Fe-Mo alloy electrodeposition from an alkaline solution containing Fe(III) ions and sorbitol was established [12]. The incorporation of molybdenum(IV) oxide into the coatings was shown to be effective.

In [13], commercial electrolytic baths (Ni, Cr, Cu, Zn) were observed to obtain the composite coatings based on the metallic matrix incorporated with the dispersed phase - an insoluble solid with nanometric particle size. Some theoretical models for the electrodeposition of composite coatings, taking into account the adsorption and electrophoretic migration of the particles prior to incorporation, have been presented in [14]. The Fe/ZrO2 composite coatings with increased microhardness were obtained from the iron electroplating baths containing the particles of zirconia stabilized by 3 mol% of yttria [15]. Nanocrystalline Fe-W alloy and Fe-W/Al2O3 composite coatings with submicron alumina particles were obtained by electrodeposition from Fe(III)-based electrolyte with the aim of producing a novel corrosion and wear-resistant material [16]. It was found that the wear rate decreased by a factor of 10 compared to Fe-W in the presence of 12 vol% Al2O3 in the deposits, but the alumina particles slightly increased the corrosion resistance of the coatings. All of the above studies were carried out in suspension electrolytes, which require an additional stabilization procedure; therefore, the life of such electrolytes is limited.

The aim of this work is to prepare Fe-W-WO2 and Fe-Mo-MoO2 nanocomposite coatings from stable electrolytes and to study their mechanical properties and corrosion behavior.

## 2. Materials and Experimental Methods

Electrochemical nanocomposite coatings were deposited on a gray cast iron (GCI) substrate, which is widely used for the production of piston rings and other machine parts. Coatings with an iron-molybdenum or iron-tungsten alloy were deposited at a temperature of 18-40 ºC from a complex electrolyte of the composition, mol / dm3: ferrous sulfate - 0.1-0.15; sodium molybdate - 0.06-0.08 (sodium tungstate - 0.04-0.06); sodium citrate - 0.2-0.3; boric acid - 0.1; the pH was in the range of 3.0-4.5 [17, 18].

The coatings were formed in two modes: by direct current (dc) with varying current density i in the range of 2.5-6.5 A/dm2 and by unipolar pulsed current (pc) with an amplitude of 2.5-8.5 A/dm2 with a pulse duration ton of 5 ms and a pause time toff of 20 ms [19, 20]. DC polarization was performed with a stabilized DC source of the B5-49 series. The pulse electrolysis and determination of the corrosion behavior of the coatings were carried out using a PI-50-1.1 potentiostat with a PR-8 programmer.

The chemical composition of the coating surface was studied using an INCA Energy 350 energy dispersive spectrometer. The coating composition (wt%) is calculated in terms of the metallic constituents of the alloy, and the content of non-metallic adsorbed impurities (oxygen) was taken into account when assessing the surface topography. The surface morphology of the coatings was examined using a ZEISS EVO 40XVP microscope.

The corrosion rate for coated samples was determined using the method of polarization resistance [21] in environments of different compositions: 0.001 M NaOH (pH 10) against the background of 1 M Na2SO4; 0.001 M H2SO4 (pH 3) against the background of 1 M Na2SO4; 3% NaCl solution (pH 7). In order to define the corrosion resistance, polarization measurements were carried out in potentiostatic mode at the potential scanning rate of 2 mv/s. In the article, the values of the corrosion potential are given relative to a standard hydrogen electrode (SHE). The corrosion current density icor and the corrosion potential Ecor were defined by the graphical method at the intersection of the linear sections of the anode and cathode polarization dependences in the semi-logarithmic coordinates of lgi-ΔE. The corrosion depth index kh was calculated on the basis of icor as in [22].

The adhesion quality of the coatings to the substrate material was studied by polishing with chromium oxide-based pastes, bending at an angle of 90° and heating to a temperature of 150-200 °C followed by cooling in air. The microhardness of the coatings was determined using a PMT-3 microhardness tester with a load of 50-100 g. The tests were carried out after the coatings had been held for 24 hours following application. The thickness of the coatings taken for the tests was in the range of 25-30 μm.

The tribological properties of the coatings on grey cast iron were evaluated by the coefficient of friction ffr. In addition, wear resistance was also determined by tests on a 2070 SMT-1 serial friction machine with gradual loading of conjugate specimens from 0.2 kN to 0.8 kN according to the "piston ring - cylinder liner" scheme and a reciprocating friction machine.

## 3. Results and discussion

### *Composition and surface morphology of composites*

An influence of the electrolysis mode on the character of the alloy surface can be visually observed for Fe-Mo(W) coatings deposited on grey cast iron substrates. The dc mode (Fig. 1a, c) produces a very inhomogeneous surface with a large number of irregularly shaped burrs. The content of molybdenum or tungsten is higher on the coating hills compared to the whole surface. The concentration of oxygen is in the range of 18-21 wt%, which allows us to consider the coatings as composite Fe-Mo(W)-MOx, where M is Mo or W. Since incompletely reduced refractory metal oxides are formed in situ in the cathodic process, according to the alloying electrodeposition mechanisms proposed in [23], they are incorporated into the Fe-Mo(W) matrix, as also observed in [12].

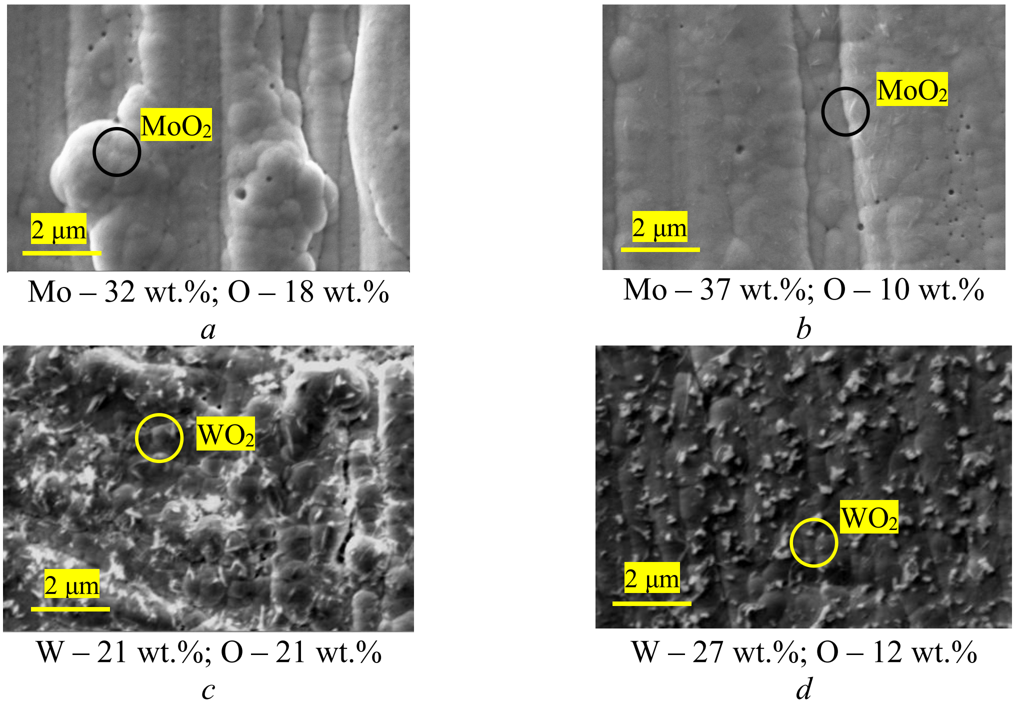



Figure 1. The surface morphology of the Fe-Mo (a, b) and Fe-W (c, d) coatings deposited on the cast iron at dc $i$ = 3.5 A/dm$^2$ (a, c); at pc $i$ = 5.5 A/dm$^2$, $t_{on}/t_{off}$ = 5/20 ms (b, d).

The use of pulsed electrolysis (Fig. 1b) helps to level the surface relief; the number of burrs is significantly reduced, and the coating becomes slightly brighter. The coatings contain 5 wt% more refractory metal and less oxygen at the level of 10-12 wt%. It should be noted that the surface of molybdenum-containing composites is globular (spheroids up to 100 nm alternate with islands of agglomerates of larger sizes up to 1-2 μm). Tungsten containing composites are finely crystalline with smaller crystallite sizes compared to Fe-Mo based coatings. Considering the data obtained, it can be concluded that more uniform and lower porosity Fe-Mo(W) based coatings with higher molybdenum (tungsten) content deposited by pc mode will have more desirable functional properties.

***Corrosion resistance***

Studies [23, 24] have shown that the corrosion of iron-based coatings with refractory metals proceeds mainly with hydrogen depolarization in acidic solutions due to the presence of iron, while in neutral and alkaline environments, it proceeds with oxygen depolarization.

It has been found that the pc deposition mode allows the formation of Fe-W-WO2 and Fe-Mo-MoO2 composite coatings with a more perfect surface morphology and a higher content of alloying components, which contributes to an increase in the corrosion resistance of the coatings obtained by pulse electrolysis. These findings are fully confirmed by the corrosion indices of the substrate material and those of the Fe-Mo(W)-based composites formed on cast iron (Table 1).

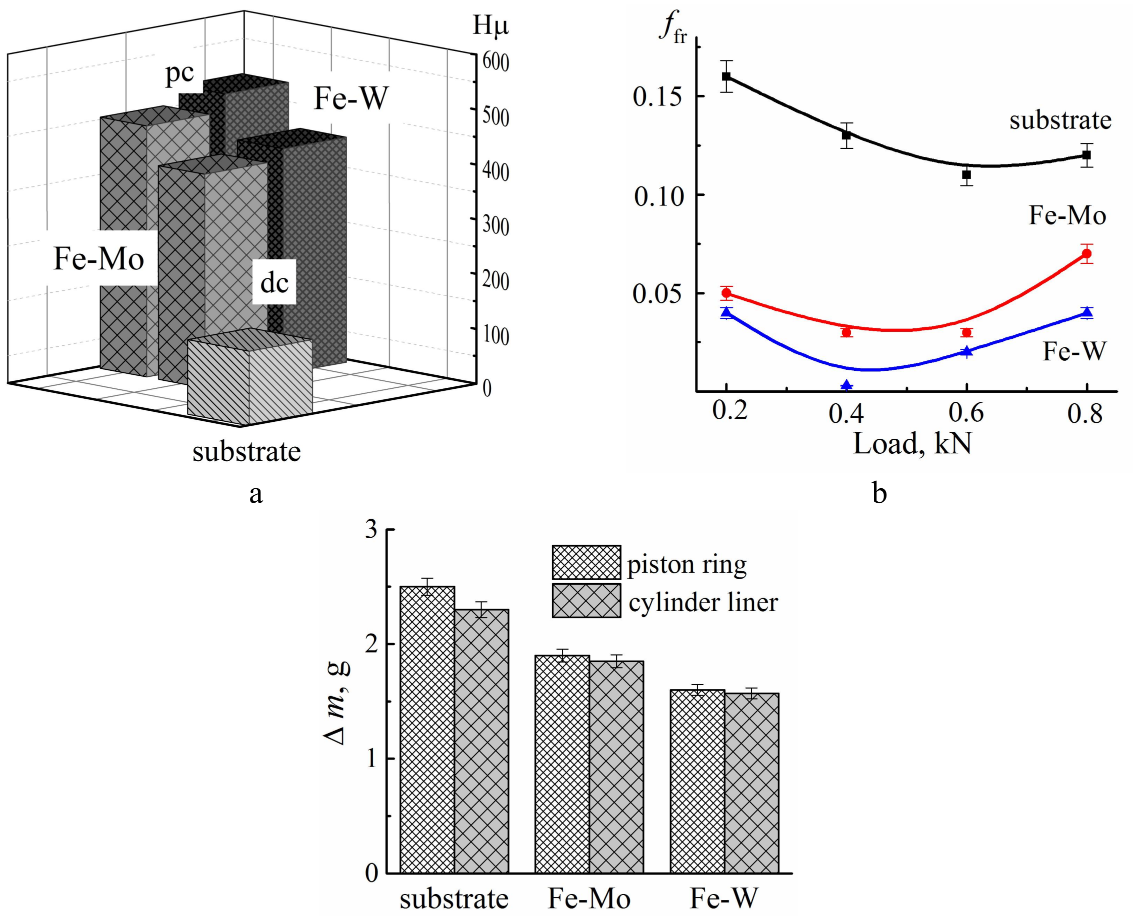
Table 1. The corrosion indices of the cast iron, and Fe-W-$WO_2$ and Fe-Mo-$MoO_2$ coatings deposited by different modes

| pH of test medium | Cast iron | | dc mode | | | | pc mode | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Fe-Mo-$MoO_2$ | | Fe-W-$WO_2$ | | Fe-Mo-$MoO_2$ | | Fe-W-$WO_2$ | |
| | $E_{cor}$, V | $K_h$, mm/year | $E_{cor}$,V | $K_h$, mm/year | $E_{cor}$,V | $K_h$, mm/year | $E_{cor}$,V | $K_h$, mm/year | $E_{cor}$,V | $K_h$, mm/year |
| 3 | –0.34 | 1.980 | –0.30 | 0.038 | –0.22 | 0.045 | –0.31 | 0.030 | –0.24 | 0.040 |
| 7 | –0.55 | 1.150 | –0.47 | 0.040 | –0.33 | 0.042 | –0.49 | 0.035 | –0.35 | 0.039 |
| 10 | –0.35 | 0.300 | –0.58 | 0.028 | –0.03 | 0.032 | –0.60 | 0.021 | –0.037 | 0.028 |

It should be noted that Fe-Mo alloy coatings have a high corrosion resistance in the corrosive environment of different acidity, regardless of the deposition conditions, compared to Fe-W. Particularly noteworthy is the increase in corrosion resistance of these alloy composites in acidic environments and in the presence of Cl-, ensured by the presence of the alloying component (Mo) in the coatings, which increases both the resistance to pitting corrosion and the tendency to passivation.

***Microhardness and tribotechnical properties of coatings.***

The use of citrate Fe(III)-based electrolytes and the electrolysis carried out at the recommended pH and current density allows the formation of uniform coatings with high adhesion to the substrate material and a minimum content of undesirable admixtures that can degrade the hardness indices of electrolytic alloys. The microhardness of Fe-Mo-MoO2 composite coatings deposited by dc mode is 4 times higher than that of the substrate material (gray cast iron) (Fig. 2 a). Such phenomena can be explained by the composition of the coating and the specific features of the morphology formed during electrodeposition. The presence of refractory components in alloys contributes to the amorphization of the coating surface, leading to an increase in microhardness. In addition, the incorporation of molybdenum and tungsten oxides into a metal matrix during electrocrystallization also has a positive effect on the microhardness indicators. It is clear that the mode of electrolysis has an effect on the microhardness of coatings.




c

Figure 2. Mechanical characteristics of Fe-Mo(W) based composites: microhardness (a), friction coefficient (b), wear resistance (c)

Thus, the iron and molybdenum alloy composites applied in the pulse electrolysis mode are characterized by higher microhardness indices (Fig. 2 a) due to a higher content of alloying components, a more perfect surface relief, and a lower number of adsorbed admixtures, as has been found for similar coatings [20, 25-29].

At the same time, Fe-W-WO2 composites are characterized by a higher microhardness compared to molybdenum-containing ones, due to the presence of tungsten, as well as a higher content of the oxide hardening phase in the coatings, as evidenced by the higher oxygen content in the tungsten-containing thin films. The results obtained for the microhardness indicators of coatings containing tungsten and molybdenum correlate with the data obtained for similar coatings by other researchers [32-33], confirming the validity of the studies carried out.

The studies of the dependence of the coefficient of friction and the disposition of suitable mundererials to scuffing at step loading showed that the ffr value of the studied coatings is 3.0 to 4.0 times lower in comparison with that of cast iron (Fig. 2 b), which is an indication of the high antifriction properties of the formed coatings. In addition, the specific features in the morphology of the cathode deposits and their porosity are the additional factors of the improvement of the antifriction properties due to the additional confinement of lubricant materials in the cavities and pores of the coatings.

It is noted that the Fe-Mo(W)-MO2 composite electrolytic coatings obtained in the proposed electrolysis modes have high adhesion to the substrate and retain it during mechanical (bending, polishing, sectioning with subsequent grinding) and thermal (heating up to 150-200°C) influences.

The wear resistance of the coated specimens was evaluated by the change in mass Δm of the test specimens of a conjugate friction pair "piston ring - cylinder liner" (Fig. 2c). A decrease in the mass of the specimens indicates wear on the surface of the parts and can be used as a quantitative measure of the wear resistance of the material. Investigations on a 2070 SMT-1 series machine with a step load of conjugated specimens from 0.2 kN to 0.8 kN according to the "piston ring - cylinder liner" scheme showed that the wear resistance of the surface of cast iron with Fe-Mo(W)-Mo(W)O2 coatings is 1.7-1.8 times higher than the wear resistance of cast iron specimens (Fig. 2, c). The research results confirm that the wear resistance of tungsten-based composites, as well as other mechanical properties, is higher than that of molybdenum-based composites (Fig. 2).

Therefore, the corrosive characteristics and the physical and mechanical properties of the Fe-Mo(W) alloy-based electroplated composite coatings allow us to consider them as promising materials for the technologies used to harden cast iron and low-carbon steel parts, and also for the maintenance services to repair and upgrade worn surfaces operating in environments of varying corrosiveness.

**Conclusions**

- The composite coatings Fe-W-WO2 and Fe-Mo-MoO2 have been deposited on cast iron substrates by different electrolysis modes from a citrate Fe(III)-based bath. The curing phase of refractory metal oxides is formed directly in the cathodic process and is incorporated into the alloy matrix, which helps to increase the uniformity of the distribution of the components throughout the thickness of the coating and its surface.

- The use of pulsed current electrolysis allows the production of more uniform coatings enriched in alloying components and with lower levels of adsorbed non-metallic impurities.

- The Fe-Mo-MoO2 composite has higher corrosion resistance due to the chemical stability of molybdenum and its oxides in environments of varying aggressiveness, including chloride-containing solutions.

- The physico-mechanical properties, such as microhardness, coefficient of friction, and wear resistance of Fe-W-WO2 composites exceed not only the base material but also molybdenum-containing coatings.

- The combination of higher strength properties and increased corrosion resistance of Fe-W-WO2 and Fe-Mo-MoO2 composite coatings in comparison with cast iron allows us to consider them as promising materials in the technology of surface hardening and restoration of worn surfaces of parts.

**Data Availability**

The data used to support the findings of this study are available from the corresponding author upon request.

**Conflicts of Interest**

The authors certify that they have no conflicts of interest.

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