

Effect of elemental composition on structure and corrosion resistance of electrolytic iron-based alloys

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Abstract. The article deals with the formation of electrolytic coatings taking into account the participation of basic components and elements of nonmetallic nature by the example of iron-phosphorus and iron-molybdenum alloys. The data of X-ray photoelectron spectroscopy of surface layers are presented, which confirm the presence of nonmetallic inclusions in the coatings under study. The influence of the structure being formed on the corrosion resistance of coatings is also studied.

1. Introduction

At present, the solution of the issues of saving metal associated with corrosion processes and wear of parts of oilfield equipment is often realized by changing the properties of the surface layers of products by applying functional metal coatings. Among the various coating methods, electrolytic precipitation of alloys is the most common one. This is due to the comparative simplicity of the deposition process, the availability of control and automation, the wide variation possibilities of the properties of deposited coatings.

To strengthen and restore worn surfaces of equipment parts, electrolytic iron-based alloys can be effectively used. Recently, special interest is caused by alloys, which tend to be amorphous in the course of electrodeposition. The formation of an amorphous-crystalline and amorphous structure, associated with the influence of amorphizing elements introduced into the alloy, leads to fundamental changes in the physicomechanical and operational properties. For the practical use of such coatings, it is necessary to have a clear understanding of the structure of electrolytic alloyed amorphous alloys, which is the link between the given deposition conditions and the properties obtained.

The aim of the work was to study the influence of nonmetallic impurities on the formation of the structure and process of amorphization of the coatings obtained.

2. Material and methods

The object of the study was electrolytic alloys of iron alloyed with molybdenum and phosphorus, since these elements are effective amorphizers. The elemental composition was determined by an X-ray photoelectron magnetic spectrometer. To research the distribution of elements along the depth of the sediment, etching of the surface with an argon ion beam was used; the rate of bleeding of the surface was 5 nm/min. The change in the content of an element was judged by the relative intensity of its lines of the X-ray electron spectrum, calculated with allowance for the relative sensitivity coefficient.

A quantitative gravimetric method was used to evaluate the corrosion resistance of coatings.



3. Results and discussion

In the process of electrodeposition of iron-phosphorus and iron-molybdenum alloys, not only the basic component but also the elements of a nonmetallic nature participate, which is confirmed by the conducted studies.

The formation of iron-phosphorus coatings occurs as a result of the simultaneous discharge of ions of iron, hydrogen and hypophosphite ions. [1].

According to X-ray photoelectron spectroscopy data, the surface layers of the coatings studied are enriched with impurity elements (oxygen) (Fig. 1, Table 1).

Table 1. Composition and structure of electrolytic iron-phosphorus alloys

Phosphorus content in the sediment, %	Oxygen content in the sediment, %	Structure	Perfection of texture [111], %
0	-	BCC	100
2	-	BCC	70
4	-	BCC	55
5	0,6	BCC	30
8	-	BCC	10
9	-	BCC	5
10	0,8	BCC +AP	-
14	-	BCC +AP	-
15	-	AP	-
18	-	AP	-
22	-	AP	-
24	1,5	AP	-

AF – amorphous phase

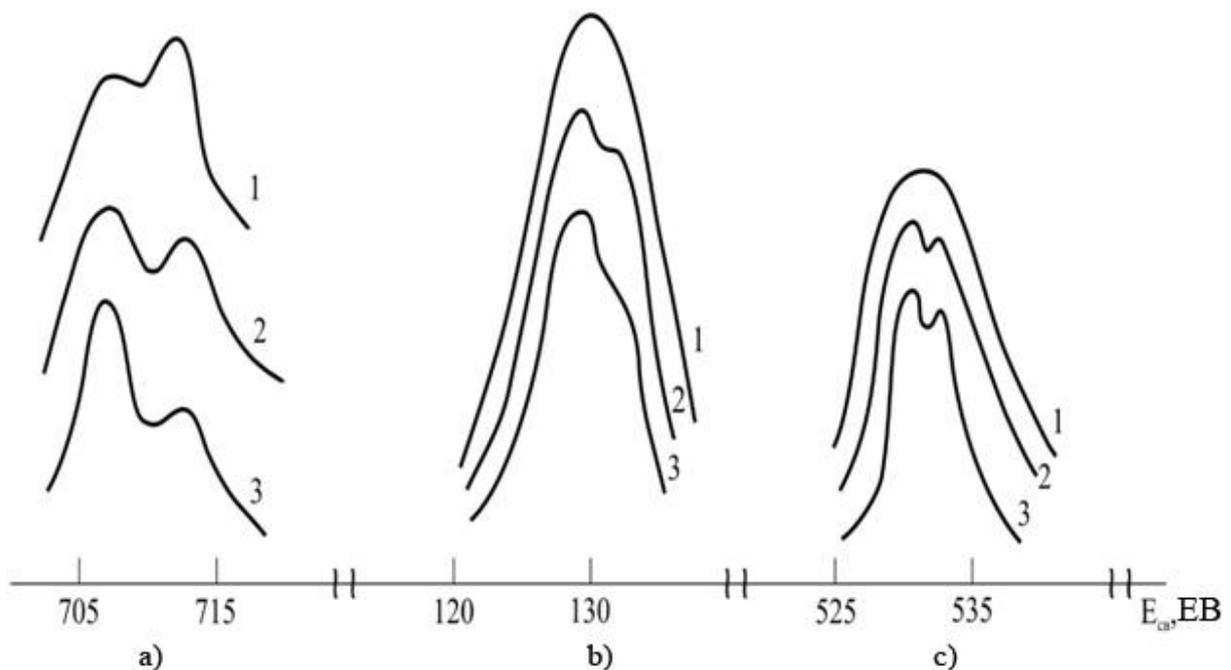


Figure 1. X-ray photoelectron spectra of Fe2p (a), P2p (b), O1s (c) amorphous (1), amorphous-crystalline (2) and crystalline (3) iron-phosphorus alloys: 1 - without ionic etching of the surface; 2, 3 - after 8 minutes of etching

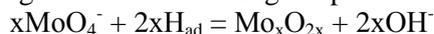
As can be seen from spectrum Fe2p (Fig. 1a), the iron in the coatings is in the metallic state (binding energy 707.8 eV) and in the form of hydroxide compounds Fe(OH)₂ and Fe(OH)₃ (710.2 - 712.3 eV). Moreover, in amorphous alloys with a high content of phosphorus, iron predominates in the oxidized state.

For the P_{2p} spectrum, two peaks with binding energies of 129.7 and 132.5 eV are observed on the surface of the coatings (Fig. 1, b). The first peak is in good agreement with the binding energy for red phosphorus (130.1 eV), and the second peak with similar values for phosphorus in hypophosphite (132.4 eV), phosphite (132.9 eV) and phosphate ions 132.1 eV [2]. Taking into account the data on the adsorption mechanism, the main reaction proceeding on the catalytically active surface of sample $\text{H}_2\text{PO}_2^- + \text{OH}^- - e \rightarrow \text{H}_2\text{PO}_3^- + \text{H}$, it can be considered that the peak of oxidized phosphorus reflects the presence of hypophosphite and phosphite ions in the coatings. The state of phosphorus in the deeper layers of the sediment, in contrast to iron, almost does not change. All spectrograms, after the ion etching of the surface, fix peaks of oxidized and reduced form (Fig. 1, curves 2, 3).

Additional information on the composition of the surface layers was obtained by studying the spectra of the O1s level. For all the samples, one peak with a binding energy of electrons in the region of 530.5-531.5 eV is fixed in the authors' experiments (Fig. 1, c). The considerable width of this peak (3.5-3.8 eV) and, in some cases, its asymmetry allow one to assume the complex structure of this signal. The peak decomposition shows that it is the result of superposition of two peaks with an electron binding energy $\sim 530,7 \pm 0,3$ and $532,6 \pm 0,2$ eV. The first peak is due to oxygen in the iron oxides, and the second one, with a higher binding energy, is due to oxygen in the oxide compounds of phosphorus (532.4 eV).

In the deposition of iron-molybdenum alloys, as in the case of iron-phosphorus alloys, three parallel processes also occur: the discharge of ions of iron, hydrogen, and molybdate ions.

However, in a number of cases, the discharge of molybdate ions occurs partially and a film is formed on the surface of the growing sediment containing the products of their incomplete reduction:



Along with the molybdenum oxides in the solid-phase film, iron hydroxides occur in the near-cathode space due to the alkalization of the electrolyte. The solid-phase film blocks the surface of the growing sediment, and thus, it should reduce the deposition rate of the alloy. Indeed, as the concentration of molybdate ions increases, the rate of deposition of coatings decreases, their quality and appearance change.

As it is known [3], in the electrodeposition of alloys of the subgroup of iron with molybdenum, a film of insoluble oxide and hydroxide compounds of lower valence is formed on the surface of the growing sediment. Moreover, the resulting film, even at a significant thickness (about 50 nm), is permeable to metal ions of a subgroup of iron, although it reduces the deposition rate of coatings. The introduction of these ions into the film leads to a change in its composition and structure: the Mo-O bonds are weakened, the bonds between molybdenum and the metal of the iron subgroup are manifested, as a result of which the molybdate ion is reduced to a metal with the formation of an alloy. Oxygen-containing compounds present in the film (Mo_xO_{2x} , $\text{Fe}(\text{OH})_x$) are also usually included in the resulting coatings, dramatically changing their structure and properties. Therefore, electrolytic alloys with molybdenum in their composition can contain a significant amount of oxygen.

The results of the experiment showed that in iron-molybdenum alloys, in addition to the base elements, there are impurity elements, oxygen and carbon with the highest concentration of nonmetallic inclusions found in the surface layer of sediments (Fig. 2, Table 2).

Table 2. Composition and structure of electrolytic iron-molybdenum alloys

Molybdenum content in the sediment, %	Oxygen content in the sediment, %	Carbon content in the sediment, %	Structure	Perfection of texture [111], %
0	-	-	BCC	100
2	-	-	BCC	80
5	-	-	BCC	70
7	0,8	0,5	BCC	60
10	-	-	BCC	30
13	-	-	BCC	10
15	-	-	BCC	5
17	-	-	BCC	2
18	2,0	1,6	BCC +AP	-
21	-	-	BCC +AP	-
22	-	-	AP	-
24	2,4	1,8	AP	-
27	-	-	AP	-
30	-	-	AP	-

AF – amorphous phase

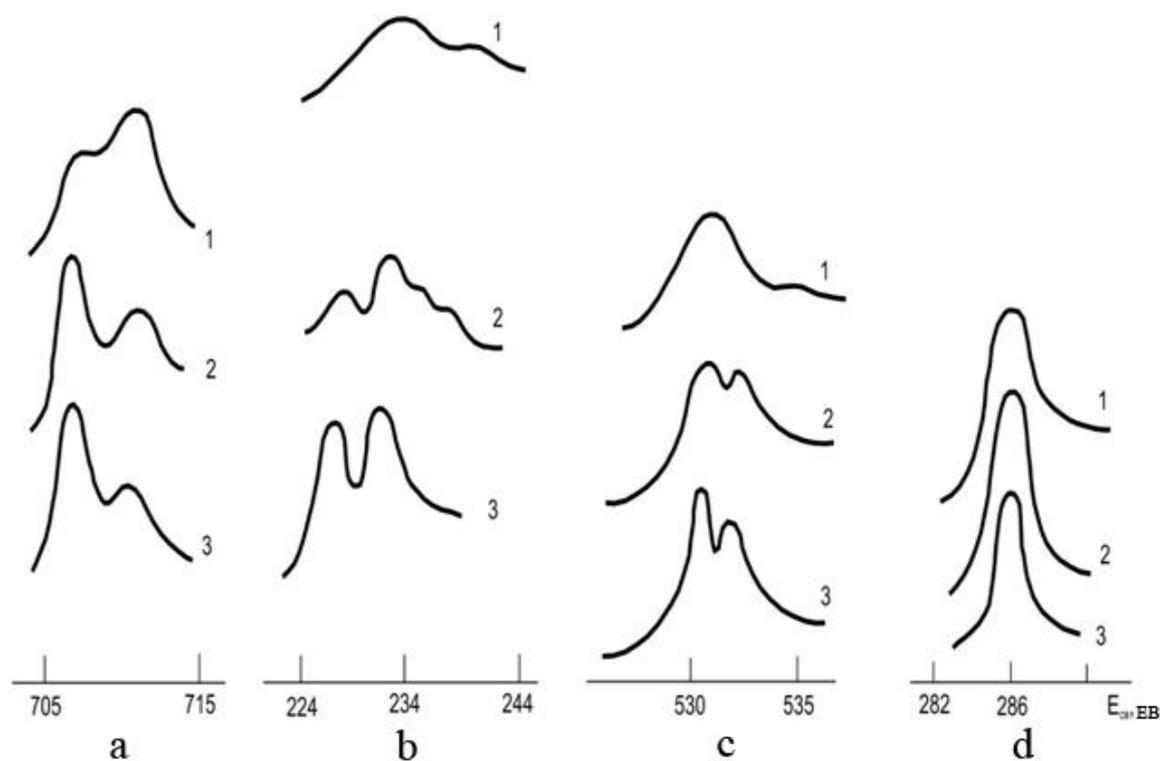


Figure 2. X-ray photoelectron spectra of Fe2p (a), Mo3d (b), O1s (c) and C1s (d) amorphous (1), amorphous-crystalline (2) and crystalline (3) iron-molybdenum alloys: 1 - without ion etching surface; 2, 3 - after 8 minutes of etching

As can be seen from the Fe2p spectrum (Fig. 2a), iron predominates in the form of Fe (II) and Fe (III) hydroxide compounds ($\sim 710.2 - 712.3$ eV). One broad peak is fixed in the Mo3d spectra in the region of 227.8 ± 234.1 eV (Fig. 2, b). The decomposition of this signal gives rise to the assertion that it is a superposition of several peaks conditioned by the presence of molybdenum in metallic (binding

energy 228.0 eV) and oxidized (oxidation state from 2+ to 6+) states.

On the O1s spectrum, the main peak is observed (Fig. 2, c) in the area of 530.5 - 531.7 eV. The considerable width of the peak and its asymmetry indicate the complex structure of this signal. Oxygen, which formed a chemical bond with metals, oxygen in solid solution, chemisorbed oxygen, as well as various forms of chemically and physically adsorbed water on the surface of the growing sediment can contribute to this peak. The bonds of O1s in hydroxide and in water bound inside the sediment are almost the same (~ 531 eV) and their identification is practically impossible.

One peak with an energy of 285.0 eV is recorded in the C1s spectrum, which indicates the presence of a C-H bond in the citrate-ion composition (Fig. 2, d).

The corrosion resistance of galvanic coatings is influenced by various factors: the nature of the deposited and base metal, the adhesion between them, the uniformity of the distribution of the coating over the surface, its porosity, nonmetallic inclusions, internal stresses in the coating. The influence of these factors is studied in detail in [4]. In addition, the structure and texture of the coatings, which can be controlled by alloying, have a significant influence on the corrosion process.

Iron-phosphorous electrolytic alloys differ significantly in their corrosion resistance from pure iron coatings having a pronounced columnar structure, so that passive films are not formed on their surfaces under the influence of corrosive media. At the same time, the corrosion resistance of alloys increases with the increase in the phosphorus content, which determines the different structural state of the coatings, in the following sequence: crystalline, amorphous-crystalline and amorphous. It is known that phosphorus in carbonaceous and stainless steels is an undesirable impurity, which worsens their corrosion resistance. However, in nonequilibrium systems, such as electrodeposited iron-phosphorus alloys, the inhibitory effect of phosphorus on the corrosion process is observed. Obviously, in the process of sedimentation, the possibility of forming groups of atoms with covalent bond of phosphide type, capable of imparting high corrosion resistance to coatings, is realized in the coating structure [5]. Moreover, with an increase in the phosphorus content in the alloys, the internal tensile stresses decrease, which contributes to the development of the corrosion process.

Amorphous coatings have the greatest protective properties, since they lack structural defects (grain boundaries, dislocations, packaging defects) that are active centers of corrosion. In addition, amorphous coatings are deposited with internal compressive stresses that impede the corrosion process [5].

The protective ability of iron-molybdenum alloys is somewhat higher than that of iron-phosphorus (Fig. 3). With increasing molybdenum content in the alloy, the corrosion resistance of coatings increases, which is explained by the greater stability of molybdenum in acid media than phosphorus [6].

As in the case of iron-phosphorus alloys, amorphous iron-molybdenum coatings have a greater protective ability than crystalline coatings. The reason for the high corrosion resistance of these alloys is associated with the formation of a protective oxide film with a high concentration of molybdenum, responsible for self-passivation [5].

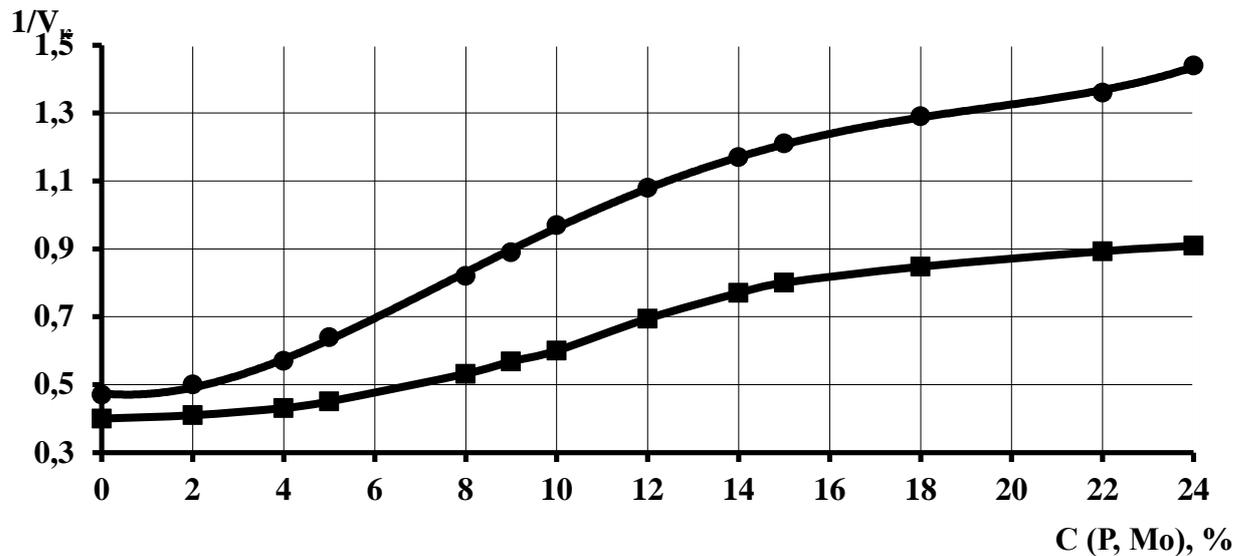


Figure 3. Dependence of the corrosion resistance of coatings with iron-phosphorus (■) and iron-molybdenum (●) alloys on the content of the alloying element

4. Conclusion

The data obtained, as well as the results of [7], show that a solid-phase oxide-hydroxide film (~ 50 nm thick) of variable composition is formed on the surface of the coatings during the electrolysis, consisting of products of an intermediate reduction of molybdate ions, citrate ions and hydroxides of the coprecipitated metals. Such film inhibits the growth of the precipitate, and the greater the concentration of molybdate ions in the electrolyte is, the more nonmetallic particles are introduced into the coatings and the more rapidly the rate of their deposition decreases.

X-ray photoelectron spectroscopic analysis shows that the surface layers of the coatings studied (thickness ~ 50 nm) are enriched with impurity elements. For iron-phosphorus alloys, it is oxygen, and for iron-molybdenum alloys it is carbon and oxygen, which in the course of electrodeposition form compounds with elements of the system that impede the diffusion mobility of metal atoms and inhibit the growth of crystals. This leads to a dispersion of the structure of the resulting coatings, the appearance of a developed surface of the boundaries between highly disoriented grains and facilitates the transition of the alloy to an amorphous state.

The increase in the corrosion resistance of the coatings studied is due to the absence of structural defects (active corrosion centers) and the appearance of internal compressive stresses that impede the corrosion process, which is a consequence of the transition of the resulting alloys to an amorphous state.

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