MATHEMATICAL MODEL OF EXPERIMENTAL METHODS FOR OBTAINING THE STRUCTURE FACTOR WHEN STUDYING THE INFLUENCE OF CATHODIC OVERVOLTAGE ON THE STRUCTURE OF ELECTRODEPOSITED ALLOYS Ni-P, Fe-P AND Co-P

MATHEMATICHNA MODEЛЬ ЕКСПЕРИМЕНТАЛЬНИХ МЕТОДІВ ОТРИМАННЯ СТРУКТУРНОГО ФАКТОРУ ПРИ ДОСЛІДЖЕННІ ВПЛИВУ КАТОДНОЇ ПЕРЕНАПРУГИ НА СТРУКТУРУ ЕЛЕКТРООСАДЖЕНИХ СПЛАВІВ Ni-P, Fe-P І Co-P

The paper considers the diffractograms obtained during X-ray studies that have relative units, and for the study of close order, the structural factor that has electronic units is used. It is emphasized that the nonlinearity of the mathematical model necessitates the use of numerical methods and means of their computer implementation. The structure factor is obtained from experimental data by introducing various corrections that depend on the wavelength of the radiation, the geometry of the survey, the shape of the samples and their composition. Electrolyte solutions with a minimum concentration of Na₂HPO₄ were used to determine the effect of pulsed current regimes on the close order of Ni-P,
Co-P and Fe-P alloys. To clarify the phase state of the alloys, the micro electronograms of the alloys with the maximum phosphorus content were considered. The described approach is implemented for the case of research of cathodes overvoltage on the structure of electrodeposited alloys.

Keywords: mathematical model, structure factor, diffractogram, scattering intensity, normalizing factor, structure modeling.

When studying diffractograms obtained during X-ray studies, they have relative units, and for the study of close order, the structure factor is used, which has electronic units. The structure factor is obtained from experimental data by introducing various corrections that depend on the wavelength of the radiation, the geometry of the survey, the shape of the samples and their composition. Monochromatization methods are based on the selective reflection of radiation with a wavelength \( \lambda \) from a number of atomic planes of a single crystal with an interplane distance \( d \) and use the Wolff-Bragg condition. When studying diffractograms obtained during X-ray studies, they have relative units, and for the study of close order, the structure factor is used, which has electronic units. The structure factor is obtained from experimental data by introducing various corrections that depend on the wavelength of the radiation, the geometry of the survey, the shape of the samples and their composition.

For this purpose, the property of scattering intensity is used: when the modulus of the scattering vector increases \( S \) structure factor \( i(S) \) goes to unity \( (s \to \infty, i(x) = 1) \). It was also established that during pulsed electrodeposition to achieve an amorphous state in alloys Ni-P, Co-P, Fe-P a 1—2% lower phosphorus content is required, compared to alloys deposited using direct current.
Analysis of recent research and publications

Diffractograms obtained during X-ray studies have relative units, and for the study of close order, the structure factor is used, which has electronic units. The structure factor is obtained from experimental data by introducing various corrections that depend on the wavelength of the radiation, the geometry of the survey, the shape of the samples, and their composition [1—3]. Monochromatization methods are based on the selective reflection of radiation with a wavelength of \( \lambda \) from a number of atomic planes of a single crystal with an interplane distance of \( d \) and use the Wolf-Bragg condition [4]:

\[
2d \sin \theta = n \lambda ,
\]

where \( \theta \) — half the scattering angle, \( n =1,2,... \) — reflection order.

The peculiarity of this method is that it is at an angle \( 2\theta \) there is a reflection of higher orders of radiation with wavelengths \( \lambda/2, \lambda/3 \) etc. To get rid of harmonics in the registered radiation, modern methods of radio electronics allow using a discriminator to limit the energy of pulses from the upper and lower limits and select the maximum amplification factor [1—3].

For a flat sample, the absorption coefficient has the following expression [5]:

\[
A(2\theta, E, E') = \frac{A_0 \sin \beta}{\mu(E) \sin \beta + \mu(E') \sin \gamma} \left(1 - \exp \left[-t \left(\frac{\mu(E) + \mu(E')}{\sin \gamma + \sin \beta}\right)\right]\right),
\]

reflected rays and the surface of the sample, respectively; \( \mu(E) \) — absorption coefficient with energy \( E \), \( t \) — sample thickness, where \( A_0 \) — cross section of the primary beam; \( \gamma \) and \( \beta \) — angles between incident and reflected rays.

In addition, the reflection of X-ray radiation from a single crystal is accompanied by a partial polarization of the radiation. The same polarization occurs during the scattering of radiation by the sample, therefore, a polarization correction is introduced into the experimental intensity associated with the difference in polarization conditions during scattering at different angles:

\[
P(2\theta) = \frac{(1 + k \cos^2(2\theta))}{1 + k'},
\]

(for the focus system used \( k'=1 \)).

To obtain the structure factor, it is necessary to convert the experimental scattering intensity, which is obtained in an arbitrary scale of units, with the help of normalizing factors to electronic scattering units. For this purpose, the property of scattering intensity is used: when the modulus of the scattering vector increases \( S \) structure factor \( i(s) \) strive to one \( (S \to \infty, i(\infty) = 1) \), but the value \( i(s) \) should be transformed in such a way that for the case when Compton scattering is registered, it would be included in the expression of the structure factor [3]:

\[
i(s) = \frac{\left[I(s) + I_k(s)\right] - I_k(s)}{f^2(s)},
\]

where \( I_k(s) \) — intensity of compton scattering of an atom.

The first term in square brackets (4) is related to the experimental scattering intensity \( I_e(s) \) using an unknown constant multiplier \( \Lambda \), which is the normalizing factor for the experimental scattering intensity:

\[
\Lambda I_e(s) = I(s) + I_k(s).
\]

The ratio (5) has the form:

\[
i(s) = \frac{\Lambda I_e(s) - I_k(s)}{f^2(s)}.
\]
Since, at \( s \to \infty \), \( i(s) \to 1 \), then it follows the normalizing factor \( \Lambda \) should be chosen in such a way that at large values \( S \) multiplication was approaching \( \Lambda I_e(s) \to f^2(s) + I_k(s) \). This fact is not easy to use, because significant errors are possible during experimental measurements of scattering intensity.

In the case of normalization of the intensity by this method, they act as follows: the ratio of the experimental intensity to the intensity of scattering by one atom is found, that is, the sum of the squares of the atomic factor and Compton scattering. If other errors are introduced into the experimental intensity and there are no systematic errors, then the obtained ratio at large values should oscillate evenly around some constant number, the inverse of which is the normalizing factor. Other methods of finding the normalizing factor are less effective and poorly substantiated.

Scattering intensity normalization in the case of polyatomic objects does not fundamentally differ from those considered above and can be carried out similarly, using summation by the number of components, their quantitative composition and tables of X-ray scattering factors [6].

If the normalizing factor \( \Lambda' \) determined with some error \( \Delta \) from its exact meaning \( \Lambda = \Lambda + \Delta \), is a structural factor \( i(S) = \frac{\Lambda' I(S) - I(S)}{f^2(S)} \), which is included in FRRA can be written as [2]:

\[
i(S)_{exen} = \frac{\Lambda' I(S) - I(S)}{f^2(S)} = \frac{\Lambda' I(S) - I(S)}{f^2(S)} + \frac{\Delta \cdot I(S)}{f^2(S)}. \tag{7}
\]

Then FRRA will have the form:

\[
G'(r) = 4\pi \rho(r)r + \left\{ \frac{\Lambda}{\Delta} \cdot 4\pi \rho(r)r^2 + \frac{2\Lambda}{\pi \Lambda} \int_0^{\infty} \frac{I(S)}{f^2(S)} \cdot \sin(Sr)ds + \frac{2\Delta}{\pi \Lambda} \left[ \sin(S_m r) - S_m r \cdot \sin(S_m r) \right] \right\} = 4\pi \rho(r)r + \{G_1 + G_2 + G_3\}. \tag{8}
\]

Influence \( G_1 \) comes down to the fact that the maxima on the FRRA curve become more blurred, and the addn \( G_2 \) describes oscillations that decay quickly. The main error is introduced by the third term in (8) Error \( \Delta \) in the determination of the structural factor gives maxima at small values when calculating the FRRA \( r \). Using this statement and the results of calculations, it is possible to approach the true value of the structural factor, minimizing all errors, which means to correctly model the structure of alloys and find many physical quantities.

Formulation of the purpose of the research

The purpose of researching the effect of cathodic overvoltage on the structure of electrodeposited Ni-P, Fe-P, and Co-P alloys is to show the possibilities of using a mathematical model of the dependence of the phase state of Ni-P, Co-P, and Fe-P alloys on pulsed current deposition modes.

Presenting main material

Electrolyte solutions with a minimum concentration were used to determine the influence of pulsed current regimes on the close order of Ni-P, Co-P, and Fe-P alloys \( \text{Na}_2\text{HPO}_3 \) in such a way that the structure of the alloys is crystalline during deposition using direct current, and amorphous during pulsed current. The samples were deposited with a pulsed current at a frequency of 30 Hz with a change in pitch from 2 to 32. The magnitude of the overvoltage on the cathode did not change for all deposition modes, but the average current density increased. At the same current density with a decrease in the split ratio from 32 to 2, the maximum value of the cathodes overvoltage dropped more than twice, regardless of the concentration \( \text{Na}_2\text{HPO}_3 \) in the electrolyte solution [7—10].

Depending on the concentration \( \text{Na}_2\text{HPO}_3 \) in the electrolyte solution, the resulting Ni-P, Fe-P, Co-P alloys had a microcrystalline or amorphous state [9—12]. During deposition using a direct current, the amorphous state was fixed at a sodium hypophosphite concentration of at least 10, 12, and
14 kg/m$^3$ (respectively for alloys Ni-P, Co-P and Fe-P). The use of pulsed current made it possible to reduce the concentration of sodium hypophosphite in the electrolyte solution to 8 kg/m$^3$ for Ni-P, and up to 4 kg/m$^3$ for Co-P and Fe-P. Moreover, in alloys deposited using a pulsed current, the amorphous state was fixed at a lower phosphorus content (10, 12, 15 at. %) compared to films obtained using a direct current (12, 12, 17 at. %). This fact is explained by the fact that the yield of metal in the current during deposition with the help of a pulsed current ($f = 30$ Hz, $Q = 32$) was no more than 45—50 %. This mode of deposition contributed to the penetration of about 1,5—2 at. % of hydrogen into the crystal lattice of the metal during the amorphization of alloys based on cobalt, nickels, and iron [13—15].

It was established that the main influence on the formation of close-order amorphous alloys is caused by the amount of cathodes overvoltage [9, 10, 12]. Tabl. 1—3 show the dependences of the phase state of Ni-P, Co-P, and Fe-P alloys on pulsed current deposition modes.

**Table 1.** Dependence of the phase state of Ni-P alloys on deposition modes

<table>
<thead>
<tr>
<th>№</th>
<th>Modes of deposition</th>
<th>P, at. %</th>
<th>Structure</th>
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<tbody>
<tr>
<td>f, Hz</td>
<td>Q</td>
<td>j, A/m$^2$</td>
<td>$\eta_{\text{MAX}}$, V</td>
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<tr>
<td>1</td>
<td>30</td>
<td>32</td>
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<td>2</td>
<td>30</td>
<td>16</td>
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<td>3</td>
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**Table 2.** Dependence of the phase state of Co-P alloys on deposition regimes

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<th>Structure</th>
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<tr>
<td>f, Hz</td>
<td>Q</td>
<td>j, A/m$^2$</td>
<td>$\eta_{\text{MAX}}$, V</td>
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**Table 3.** Dependence of the phase state of Fe-P alloys on deposition regimes

<table>
<thead>
<tr>
<th>№</th>
<th>Modes of deposition</th>
<th>P, at. %</th>
<th>Structure</th>
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<tr>
<td>f, Hz</td>
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<td>j, A/m$^2$</td>
<td>$\eta_{\text{MAX}}$, V</td>
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In the alloy Ni$_{86}$P$_{14}$, despite the same maximum value of the overvoltage on the cathode (0.92 V), the residual value of the overvoltage increases from 0.65 to 0.8 V with a decrease in the gap ratio from 32 to 2, which leads to a decrease in the degree of imbalance of the crystallization process,
the rate of potential increase from 270 to 7.5 V/c, the phosphorus content and to the change in the alloy structure from amorphous to microcrystalline (tabl. 1).

Tabl. 1 — 3 show the following designations: f and Q — frequency and frequency of current pulses; j is the current density; \( \eta_{\text{MAX}} \) and \( \eta_{\text{RES}} \) — maximum and residual value of cathodes overvoltage; \( V_{\text{INC}} \) and \( V_{\text{CPL}} \) — speed of rise and fall of cathodes overvoltage; P is the phosphorus content in the film. Structure: (A) — amorphous, (MC) — microcrystalline.

Similar results are observed for alloys Co\(_{83}\)P\(_{17}\) and Fe\(_{83}\)P\(_{17}\), in which a decrease in sparability from 32 to 2 causes a decrease in the potential rise from 154 to 5.4 V/s and from 260 to 7.3 V/s, respectively, and this changes the structure of the alloys from amorphous to crystalline. Fig. 2.1 shows the diffractograms of the alloys Ni\(_{86}\)P\(_{14}\), Ni\(_{90}\)P\(_{10}\), obtained at different pulse current regimes. As can be seen from Fig. 1 and Tabl. 1, a decrease in the rate of potential growth from 270 to 7.5 V/s leads to a change in the formed structure from amorphous to microcrystalline. Alloy composition Ni\(_{86}\)P\(_{14}\), obtained at a potential growth rate of 270 V/s, has diffuse maxima (Fig. 1, curve 1) [16—19].

![Fig. 1. Diffractograms of Ni-P alloys depending on pulse current regimes: 1 — Ni\(_{86}\)P\(_{14}\) (f= 30 Hz, Q = 32); 2 — Ni\(_{86}\)P\(_{14}\) (f= 30 Hz, Q = 16); 3 — Ni\(_{90}\)P\(_{10}\) (f= 30 Hz, Q = 4); 4 — Ni\(_{90}\)P\(_{10}\) (f= 30 Hz, Q = 2). Cu-K\(_{\alpha}\) radiation](image-url)

Decreasing the pitch to 16 leads to a decrease in the potential growth rate to 120 V/s and, accordingly, to a decrease in the degree of imbalance of the obtained alloys. This contributes to the formation of a microcrystalline structure in the deposited alloys Ni\(_{86}\)P\(_{14}\). On the diffractograms of alloys, diffraction maxima from lattices of crystalline fcc Ni and low-intensity lines from lattices of non-equilibrium phosphides appear against the background of diffuse maxima of the amorphous component Ni\(_3\)P\(_2\) and Ni\(_2\)P\(_{55}\). A further decrease in the sparability to 4 leads to a decrease in the potential growth rate to 20 V/s, a decrease in the disequilibrium of the alloy deposition process and the phosphorus content in the film to 10 at. %, which contributes to the formation of a microcrystalline structure. On the diffractograms (Fig. 1, curves 3, 4) there are lines of microcrystalline Ni and phosphide Ni\(_3\)P. With a gap of 2, a decrease in the rate of potential growth to 7.5 V/s contributes to the formation of a crystal structure Ni\(_{90}\)P\(_{10}\), which is indicated by clearer diffraction lines of the equilibrium phases of Ni and its phosphide Ni\(_3\)P. A similar picture of the dependence of the structure on pulsed current regimes is also characteristic of the Co-P alloy. As can be seen from fig. 2, curves 1—3, a decrease in the rate of potential growth from 154 to 5.4 V/s leads to a change in the formed structure from amorphous to a mixture of equilibrium crystalline phases b–Co and Co\(_2\)P (Fig. 2, curves 2 and 3). In the Fe-P alloy, as the potential growth rate decreases from 260 to 7.3 V/s, the amorphous structure changes to a mixture of crystalline b–Fe and amorphous Fe3P (Fig. 3).
Fig. 2. Diffractograms of Co–P alloys depending on pulse current regimes: 1 — Co$_{83}$P$_{17}$ (f = 30 Hz, Q = 32); 2 — Co$_{83}$P$_{17}$ (f = 30 Hz, Q = 16); 3 — Co$_{90}$P$_{10}$ (f = 30 Hz, Q = 4). Co-K$_b$ radiation

Fig. 3. Diffractograms of Fe–P alloys depending on pulse current regimes: 1 — Fe$_{90}$P$_{10}$ (f = 30 Hz, Q = 32); 2 — Fe$_{90}$P$_{10}$ (f = 30 Hz, Q = 16); 3 — Fe$_{90}$P$_{10}$ (f = 30 Hz, Q = 4); 4 — Fe$_{90}$P$_{10}$ (f = 30 Hz, Q = 2). Co-K$_b$ radiation

To clarify the phase state of the alloys, the microelectronograms of the alloys with the maximum phosphorus content were considered. Thus, in the Ni$_{86}$P$_{14}$ alloy (Fig. 4), the width of the diffuse ring corresponds to the amorphous state with the dimensions of the OVRA up to 2 nm. Structure of alloys Co$_{90}$P$_{17}$ (Fig. 5) and Fe$_{83}$P$_{17}$ (Fig. 6) differs from amorphous because there are no continuous diffuse rings on microelectronograms. The presence of discontinuous rings with separate reflexes indicates that there are OVRA larger than 2 nm in the volume, which can also be classified as amorphous, but with the presence of a more ordered composition [20].
The diffractograms of amorphous Co-P alloys, which were obtained using a pulsed current with a frequency of 30 Hz and a pitch of 32, show that they have three diffuse maxima each, similar to the typical diffractograms of amorphous PM-M alloys and have different degrees of amorphousness, which means that their close order has significant differences. As a result of experimental studies of the influence of deposition modes on the structure of alloys, it is shown that the formation of the amorphous state in Ni-P, Co-P, and Fe-P alloys is significantly influenced by the imbalance of the crystallization process during pulsed electrodeposition, which depends on the rate of increase of over-voltage on the cathode. It was also established that, in order to achieve an amorphous state in Ni-P, Co-P, and Fe-P alloys during pulsed electrodeposition, a 1—2 % lower phosphorus content is required, compared to alloys deposited using direct current.

**Conclusions**

The study of the effect of cathodic overvoltage on the structure of electrodeposited Ni-P, Fe-P, and Co-P alloys was conducted, which showed the possibility of using a mathematical model of the dependence of the phase state of Ni-P, Co-P, and Fe-P alloys on pulsed current deposition modes.

**References**

Розділ 2. Моделювання та оптимізація в технології конструкційних матеріалів


Список використаної літератури


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