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Electrochemical activity of electroless Ni-P coatings in the hydrogen evolution reaction

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Abstract

The purpose of this study was investigation of the electrochemical activity of Ni-P coatings, differing in phosphorus content and structure, in the hydrogen evolution reaction (HER) and the identification of the reasons for their high activity in the reaction being studied.

The coatings were deposited from an electroless nickel plating solution, the phosphorus content in the coatings (from 4.8 to 8.0 wt. %) varied by changing the pH of the solution. It was found that during cathodic polarization in 0.5 M H₂SO₄ additional surface activation occurs as a result of dissolution of the surface layer of the coating, removal of phosphorus from the surface layer, and development of the electrode surface. Of all the coatings studied coatings containing 4.8% phosphorus were most susceptible to cathodic activation. Coatings with a phosphorus content of 8.0% were least susceptible to cathodic activation.

The similar electrochemical activity of the studied coatings (taking into account the roughness factor) in HER indicates that, as a result of cathodic polarization, the composition of the thin surface layer on which the cathodic reaction occurs is approximately the same, regardless of the initial phosphorus content.

Keywords: Electroless Ni-P coating, Electrochemical activity, Hydrogen evolution reaction, Roughness factor, Electrode capacitance

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1. Introduction

The electrochemical activity of Ni-P alloys in the hydrogen evolution reaction (HER) has been studied for quite a long time [1–13]. This is mainly associated with the fact that these alloys have high electrochemical activity in this reaction. At the same time, the reasons for this activity have not yet been clearly established.

A number of studies [3] suggest that high catalytic activity is due to the amorphous structure of coatings; the transition of the amorphous structure of the coatings to a crystalline structure causes a decrease in catalytic activity. In other studies, the high catalytic activity of Ni-P coatings with a crystalline structure is explained by the developed surface of the coatings [2, 4].

A correlation between the catalytic activity of Ni-P alloys and their ability to absorb a sufficiently large amount of hydrogen was discovered [5]. Absorbed hydrogen changes the electronic structure of the alloys, which affects their catalytic activity in HER.

It was stated [6] that Ni-P alloys obtained by electrodeposition are more active in HER compared to alloys obtained by electroless deposition. The catalytic activity of Ni-P alloys is associated with the presence of internal stresses, since the activity of compact coatings was significantly higher than the activity of pressed porous electrodes made from the same compact coatings (there were no stresses in the porous electrodes). The activity of electrodeposited alloys obtained at temperatures above 338 K with fairly low internal stresses was also low. Tafel slopes for coatings obtained at low temperatures were in the range of 0.065–0.100 V, whereas electrodes obtained at temperatures above 338 K had slopes in the range of 0.19–0.27 V.

In [7], the electrocatalytic activity of electroless Ni-P coatings with different phosphorus contents (4–13.8 at. %) in HER in alkaline solutions was investigated. Two Tafel sections were identified on the polarization curves: the first section had a slope of more than 0.15 V, the second section had a slope of more than 0.3 V. The formation of the NiH_x hydride phase was detected using X-ray diffraction analysis at 1 hour of cathodic polarization of coatings. At the same time, the catalytic activity of freshly deposited coatings was somewhat lower than the activity

of polycrystalline nickel. The activity slightly increased after annealing of the coatings at a temperature of 400 °C, as well as after preliminary repeated cycling over a wide potential range. In [8], a higher activity of electroless Ni-P coatings with a lower phosphorus content was observed.

In [9, 10], HER was studied on Ni-P alloys of various compositions obtained by electrodeposition. It has been established that coatings obtained in galvanostatic mode had higher activity compared to coatings obtained in potentiostatic mode. Depending on the composition of the alloys, the nature of the activity was different: alloys containing no more than 6.5 wt. % phosphorus exhibited real activity, while alloys enriched with phosphorus ($\leq 12.6\%$) increased the reaction rate due to surface development. At the same time, the HER mechanism does not depend on the phosphorus content in the coatings, but changes with increasing overvoltage.

Due to the search for effective cathode materials for HER, interest in studying the activity of Ni-P alloys continues unabated [11–14]. Ni-P coatings with chemical composition corresponding to nickel phosphide Ni_2P , which is considered to have high activity in HER were studied [12, 13]. The activity of the resulting amorphous coatings was compared with the activity of the same coatings, but annealed in vacuum at a temperature of 400 °C. It was found that amorphous coatings, compared to crystalline ones, have higher activity in alkaline solutions due to their inherent catalytic activity and greater hydrophilicity. In acidic media, amorphous coatings were less stable and inferior to crystalline (annealed) coatings.

To further increase the activity of Ni-P alloys, which in chemical composition correspond to various nickel phosphides, they were deposited on substrates with a developed surface (nickel foam, carbon fibers, carbon nanotubes). A review of methods for obtaining and properties of such coatings is provided in [12]. The catalytic activity of nickel phosphides is associated with their special electronic structure.

Thus, a review of even some studies shows that the activity of Ni-P alloys in HER depends on a large number of factors. This is partly due to the fact that the studied alloys were produced by

various methods (electrodeposition, electroless deposition, etc.); the alloys differ in composition, structure, methods of additional processing, and size of particles from which the electrode materials were formed. Nevertheless, systematization of information about the electrochemical activity of Ni-P alloys and its relationship with the structure, composition, as well as with changes in the surface of the alloys that can occur during the hydrogen evolution reaction is an urgent task. In this study, the electrochemical activity of Ni-P coatings with different composition and structure, obtained by electroless deposition was studied in 0.5 M H₂SO₄ solution.

2. Experimental

For the deposition of Ni-P coatings, a solution of the following composition, g/l, was used: NiCl₂·6H₂O – 25; NaH₂PO₂·H₂O – 20; CH₃COONa·3H₂O – 15; NH₂CH₂COOH – 20. Thiourea (1 mg/l) was used as a stabilizer. Solutions with different pH – 5.8, 5.3, 5.0 were used; pH was adjusted by adding a 25% ammonia solution.

The coatings were deposited on rectangular samples of nickel foil HO (99.96%) with a thickness of 80 μm. Preliminary preparation of the substrate surface consisted of degreasing with lime paste, washing with distilled water, and pickling in nitric acid (1:1) for 30–90 s. Bath loading was 1.0–1.5 dm²/l. Deposition was carried out under thermostatic conditions at 358 ± 1 K. The phosphorus content in the coatings was determined by energy-dispersive (micro-X-ray) analysis. The thickness of the coatings was calculated using the formula:

$$h = \Delta m / S\rho,$$

where Δm – weight gain, g; S – sample area, cm²; ρ – density, g/cm³. The density of Ni-P deposits was taken equal to 8.0 g/cm³.

The surface structure of the coatings, their composition, as well as changes in the surface composition after cathodic polarization were studied using a Hitachi S3400N scanning electron microscope with an attachment for energy-dispersive analysis.

The microhardness of the coatings was determined by the Vickers method (load – 50 g) using DM-8 Affri digital automatic microhardness tester.

X-ray diffraction analysis of coatings was carried out on cobalt K_α radiation using a Bruker Advanced ECO X-ray diffractometer.

Electrochemical studies of coatings were carried out in a standard YASE-2 electrochemical cell in 0.5 M H₂SO₄ at a temperature of 298 ± 1 K. The reference electrode was a chloridesilver electrode, the auxiliary electrode was a platinum electrode. Cathode curves were obtained using the potentiodynamic method; the potential sweep rate was 2·10⁻⁴ V/s. After establishing a stationary potential (free corrosion potential), the samples were cathodically polarized for 5 min with a current of at least 260 A/m² (shift to the cathode region by 0.2–0.25 V), after which a potential sweep was set with its shift to the anode region. All electrochemical studies were carried out in an argon atmosphere, for which argon was first passed through the solution for 1 h before measurements. The thickness of the studied coatings was not less than 15 μm.

All potentials in the study were recalculated in the scale of a standard hydrogen electrode.

HER on Ni-P coatings was studied by polarization measurements and impedance spectroscopy using a Solartron-1280 device. The measurements included two types of experiments.

The first type included the following stages of measurements. After exposure for 30 min at open-circuit potential, the following procedures were carried out on the studied electrode:

- 1) cathodic polarization at a potential of –0.3 V for 5 min;
- 2) exposure at open-circuit potential for 30 min;
- 3) registration of cyclic voltammograms in the potential range from –0.12 to –0.24 V with a sweep rate of 2·10⁻⁴ V/s (5 cycles);
- 4) exposure at an initial potential of –0.12 V for 20 min;
- 5) registration of the impedance spectrum at a given potential;
- 6) exposure at the next potential (shift to the cathode region by 0.01 V);
- 7) registration of the impedance spectrum at the next potential.

Impedance spectra were measured in the potential range from –0.12 to –0.24 V in the frequency range from 10 kHz to 0.01 Hz with an alternating signal amplitude of 0.01 V.

The second type included the following measurement stages:

- 1) cathodic polarization at a potential of -0.3 V for 5 min;
- 2) exposure at open-circuit potential for 30 min;
- 3) exposure at a potential of -0.14 or -0.15 V for 20 min;
- 4) registration of the impedance spectrum at a given potential;
- 5) cathodic polarization at a potential of -0.3 V for 5 min;
- 6) exposure at a potential of -0.14 or -0.15 V for 20 min;
- 7) registration of the impedance spectrum at the same potential.

Thus, at potentials of -0.14 (or -0.15 V), five cycles of measuring the impedance of the Ni-P electrode were carried out in order to establish the effect of cathodic polarization on the electrochemical behavior of Ni-P coatings in HER.

The analysis of solutions for nickel and phosphorus content in 0.5 M H_2SO_4 solution after cathodic polarization of Ni-P coatings was carried out by inductively coupled plasma atomic emission spectroscopy using a Thermo iCAP 6500 Duo device, measurements were carried out in axial mode, the supplied power was 1150 W.

3. Results and discussion

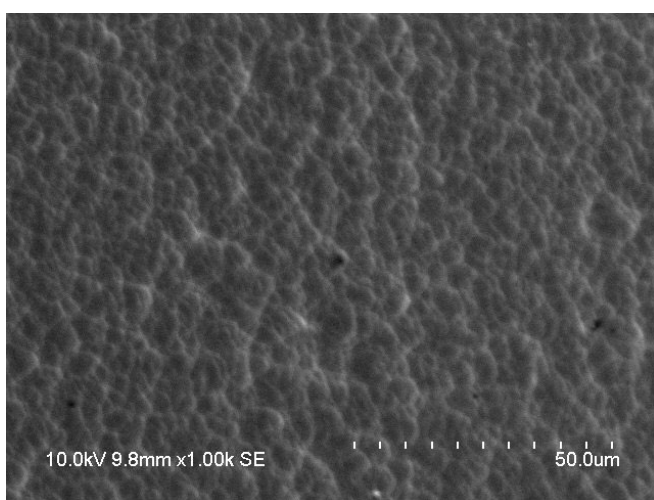
Changing the pH of the solution in the studied range slightly changed the deposition rate of

Ni-P coatings (Table 1). This was due to the fact that the used electroless nickel plating solution has a fairly high buffer capacity. Decrease of the pH of the solution increased the phosphorus content in coatings (Table 1). They had a typical spheroid structure (Fig. 1). Coatings deposited from this solution were characterized by high internal stresses, which caused a cracking of the coatings (Fig. 1b).

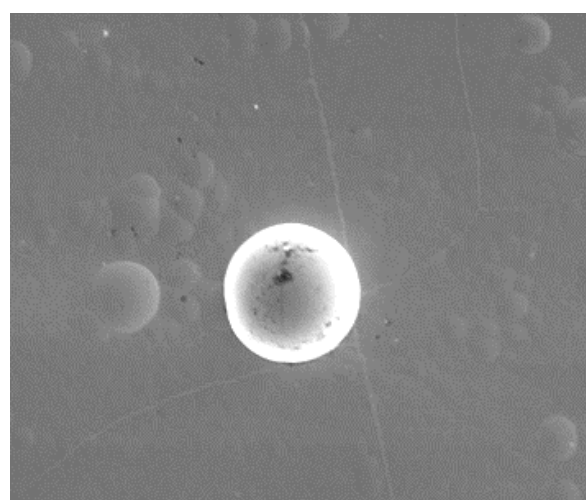
The absence of obvious crystalline faceting of the coatings in micrographs cannot unambiguously indicate the amorphous structure of the coatings; a diffraction pattern of a Ni-P coating with a phosphorus content of 4.8 wt. % is shown in Fig. 2. The most intense lines in the diffraction pattern were lines with indices (111) and (222). This was due to the presence of an axial texture in the coatings with the $\langle 111 \rangle$ direction. Near to the intense line (111) there was a shoulder that corresponds to a fairly wide line with indices (200). The presence of several

Table 1. Parameters of Ni-P coatings obtained from electroless nickel plating solutions with different pH values

Parameters of coatings	pH of electroless nickel plating solution		
	5.0	5.3	5.8
Deposition rate, $\mu\text{m}/\text{h}$	15.3 ± 1.3	15.8 ± 1.9	16.8 ± 0.6
Content of P, wt. %	8.0 ± 0.2	6.9 ± 0.1	4.8 ± 0.1
Hardness, GPa	447 ± 16	454 ± 34	532 ± 37



a



b

Fig. 1. Microphotographs of the surface of Ni-P coatings obtained from a solution with pH 5.0 (a) and 5.3 (b), 358 K. Magnification: a – $\times 1000$, b – $\times 500$

diffraction maxima indicates the crystalline structure of these coatings.

Increasing the phosphorus content in coatings to 6.9 wt. % (Fig. 2) led to a weakening of the (220) and (311) lines. Due to the broadening of the (111) line, instead of a shoulder at the possible location of the (200) line, an asymmetric broadening of the (111) peak was observed, which may be associated with an increase in the dispersion of the crystalline phase and an increase in the proportion of the amorphous phase in the coatings.

At the maximum phosphorus content in the coating, instead of the (111) line, a wide “halo” was observed (Fig. 2). This indicated a significant proportion of the amorphous phase present in the coatings. The intensity of diffraction lines noticeably decreased. It should be noted that, along with the blurred line (222), rather sharp lines (220), and (311) were recorded. Their presence was probably due to the fact that the thickness of the studied coating was only 24 μm . An estimate showed that a Ni-P coating layer of this thickness will absorb only ~75% of the incident X-ray radiation. Radiation transmitted through the coating layer can be reflected from the nickel substrate and produce weak reflections in the diffraction pattern. Coatings with lower phosphorus content (4.8 and 6.9% P) had thicknesses of more than 32 μm , therefore there were no diffraction lines from the substrate.

One of the reasons for the high electrochemical activity of Ni-P coatings in HER in acidic sulphate solutions may be an increase in the electrode surface directly during cathodic polarization. This was indicated by the results of the following performed experiments.

Under cathodic polarization in 0.5 M H_2SO_4 solution the loss of coating mass was determined and a sulfuric acid solution was analyzed to determine the content of nickel and phosphorus. The presence of the latter in the solution

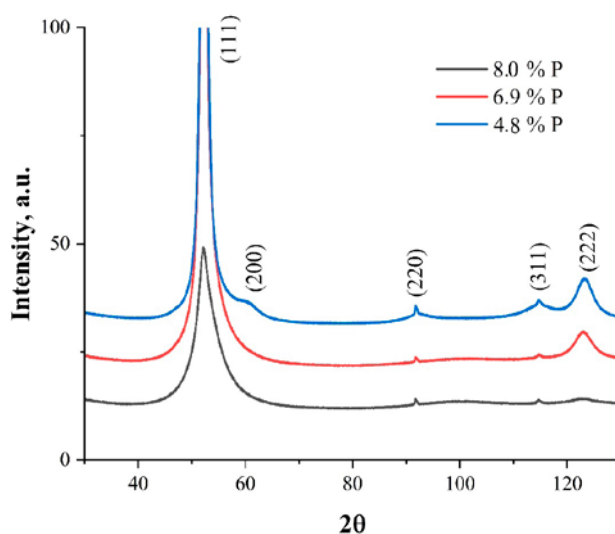


Fig. 2. Diffraction patterns of Ni-P coatings

indicates the dissolution of the coating during cathodic polarization. The dissolution of the coating may be due to the fact that part of the phosphorus was reduced during cathodic polarization and converted into phosphine. The nickel remaining in the thin surface layer was likely to be highly active and can be dissolved in a sulfuric acid solution. Modification of the chemical composition of a thin surface layer will be accompanied by an increase in the true surface of the electrode. The duration of cathodic polarization was 2 h. The results obtained are presented in Table 2.

With increasing phosphorus content, the process of dissolution of Ni-P coatings during cathodic polarization becomes more difficult. It should be noted that in the analyzed sample of sulfuric acid solution the phosphorus content was noticeably lower compared to its content in the coatings (Table 2). Under the condition of uniform dissolution, the ratio of phosphorus and nickel content in the analyzed solution would be equal to its content in the coatings. The lower content of phosphorus in the solution indicates that some

Table 2. Changes in the weight of Ni-P coatings and solution composition during cathodic polarization in a 0.5 M H_2SO_4 solution ($i \sim 300 \text{ A/m}^2$, 2 h)

Phosphorus content in coatings, wt. %	Dissolution rate of coatings, $\text{g}/(\text{m}^2 \text{ h})$	Phosphorus content in solution referred to dissolved part of coating, wt. %
4.8±0.1	0.66±0.15	0.7±0.3
6.9±0,1	0.41±0,11	4.0±1.4
8.0±0,2	0.16±0,05	4.5±1.2

of it could pass into the gas phase in the form of phosphine. This process, as follows from Table 2, was most typical for coatings with a phosphorus content of 4.8 wt. %.

During cathodic polarization, intensive hydrogenation of the coatings occurred, which further increased the internal stresses that arose earlier in the deposition process and caused significant cracking of the coatings (Fig. 3).

During cathodic polarization, the state of the surface of the studied coatings changed. In order to obtain more reproducible results, before impedance measurements, the cycling of Ni-P electrode in the potential range from -0.12 V to -0.3 V with a low sweep rate – $2 \cdot 10^{-4}$ V/s was performed (Fig. 4). After 5 potential sweep cycles,

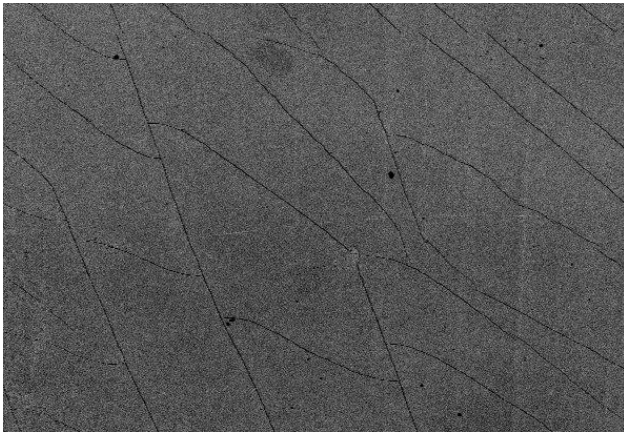


Fig. 3. Microphotograph of the surface of Ni-P coatings after cathodic polarization, $\times 1000$

the cathode current increased more than twice. The increase in current was associated with the surface roughening of the Ni-P electrode during cycling.

The impedance hodographs of the Ni-P electrode were semicircles with a displaced center relative to the abscissa axis (Fig. 4b). With increase in cathodic polarization, the radius of the semicircle decreased. A detailed discussion of the results of impedance spectroscopy will be the subject of the next publication.

Since the real surface area of Ni-P coatings differs markedly from the geometric one and can change during measurements, it is important to have a method for assessing the real surface area for comparison of the activity of the studied coatings, taking into account the roughness factor.

For assessment of the true surface of the electrode, the imaginary part of the impedance Z'' was recorded and the electrode capacitance was calculated using the equation:

$$C = -\frac{1}{(\omega Z'')},$$

where ω is the angular frequency equal to $\omega = 2\pi f$. For these calculations, the frequency $f = 1$ kHz was chosen. When choosing the frequency, the following was taken into account.

On the one hand, the frequency at which the electrode capacitance was determined must be

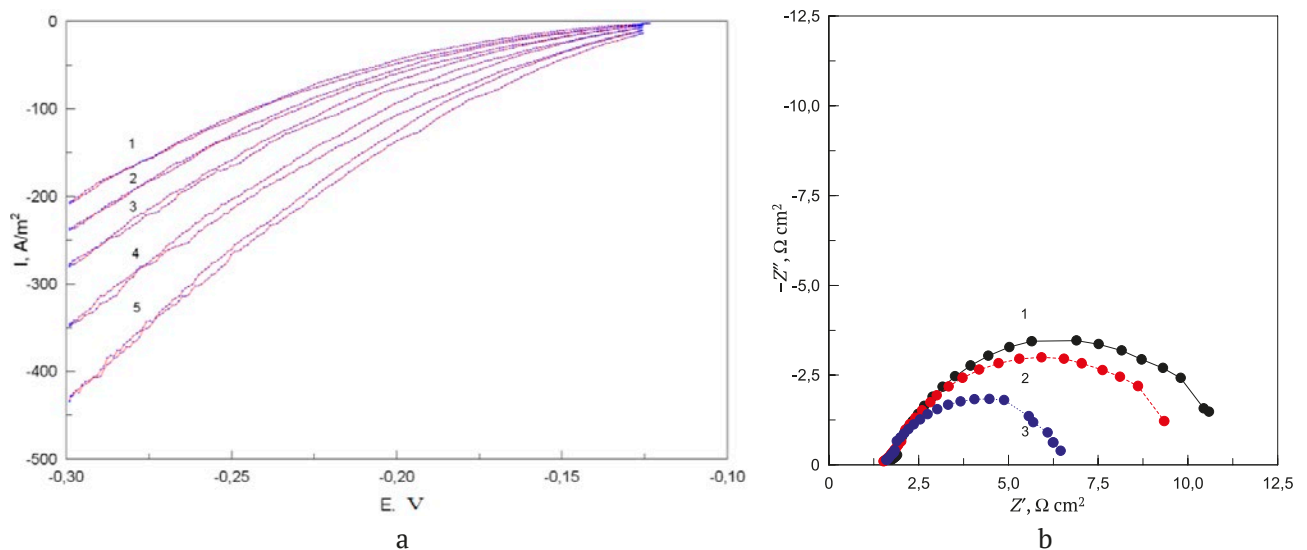


Fig. 4. a – Cyclic voltammograms of Ni-P coating (4.8 wt.% P) in 0.5 M H_2SO_4 solution. Sweep rate of $2 \cdot 10^{-4}$ V/s. b – Impedance hodographs of Ni-P electrode in 0.5 M H_2SO_4 solution at potentials, V: 1: -0.12; 2: -0.13; 3: -0.15. Phosphorus content 4.8 wt.%

sufficiently low in order the alternating current penetrates into the depressions on the rough surface [15] and, thus, the entire electrode surface contributes to the measured capacitance. The frequency range in which roughness-related double-layer capacitance dispersion can be observed was approximately 1–100 kHz for moderately rough surfaces (protrusion heights up to 10 μm) with good electrical conductivity of the electrolyte [16, 17]. The frequency should not be too high also for the reason that capacitance dispersion at high frequencies can be associated not only with the properties of the electrode surface, but also with the measuring equipment [18, 19]. On the other hand, the selected frequency should not be too low; otherwise, a frequency-dependent term due to the Faradaic process will be added to the double layer capacitance. The relatively high capacitance values for the studied coatings (see below) contributed to the fact that the region of significant capacitance dispersion associated with the Faradaic reaction shifts towards lower frequencies. A frequency of 1 kHz can be considered suitable for determining the electrode capacitance for the calculation of the roughness factor of the surface of the electrodes.

After finding the capacity values, we calculated f_r (roughness factor) by dividing the capacitance C by the double-layer capacitance per real surface area ($2 \cdot 10^{-5} \text{ F/cm}^2$) [2].

The calculated values of the capacitance of the Ni-P electrode at various potentials and the values of the roughness factor are shown in Table 3. Values C and f_r slightly change in the potential range shown in the Table 3.

During cathodic polarization, the surface roughening of Ni-P electrodes can occur. For further confirmation, the following experiments were carried out: the studied electrode was subjected to cathodic polarization at a potential of -0.3 V for 5 min, then maintained at a potential of -0.14 V (or -0.15 V , in the case of coatings with a phosphorus content of 6.9 and 8.0%) for 20 min, after impedance measurements were carried out. In each subsequent cycle, the cathode currents increased and the impedance decreased, which could be due to an increase in the electrode surface area.

Impedance measurements (phosphorus content in coatings was 4.8%) were carried out at a potential of -0.14 V , since according to the Table 3, a further increase in polarization did not

Table 3. Capacitance and roughness factor of Ni-P electrodes depending on the electrode potential at different phosphorus contents in the coating

$E, \text{ V}$	4.8 % P		6.9 % P		8.0 % P	
	$C, \text{ mF/cm}^2$	f_r	$C, \text{ mF/cm}^2$	f_r	$C, \text{ mF/cm}^2$	f_r
-0.12	1.26	63	–	–	0.229	12
-0.13	1.6	80	0,54	27	0.261	13
-0.14	1.58	79	0,58	29	0.285	14
-0.15	1.54	77	0,65	32	0.293	15
-0.16	1.68	84	0,66	33	0.316	16
-0.17	–	–	0,62	31	0.303	15
-0.20	–	–	0,59	30	0.303	15

Table 4. Changes in capacitance, roughness factor of Ni-P electrodes and current density at $E = -0.14 \text{ V}$ (phosphorus content 4.8%) or $E = -0.15 \text{ V}$ (phosphorus content 6.9 and 8.0%) during cycling of the potential

Cycle number	4.8 % P				6.9 % P				8.0 % P			
	$C, \text{ mF/cm}^2$	f_r	$i, \text{ A/m}^2$	$i/f_r, \text{ A/m}^2$	$C, \text{ mF/cm}^2$	f_r	$i, \text{ A/m}^2$	$i/f_r, \text{ A/m}^2$	$C, \text{ mF/cm}^2$	f_r	$i, \text{ A/m}^2$	$i/f_r, \text{ A/m}^2$
1	0.715	36	24.8	0.69	0.376	19	6.2	0.33	0.140	7.0	5.4	0.77
2	0.896	45	34.2	0.76	0.439	22	8.2	0.37	0.143	7.2	5.9	0.81
3	1.05	52	44.8	0.85	0.542	27	11.3	0.42	0.148	7.4	6.2	0.84
4	1.27	64	53.6	0.84	0.620	31	14.0	0.45	0.160	8.0	6.8	0.85
5	1.33	66	58.9	0.89	0.708	35	17.0	0.48	0.174	8.7	7.1	0.81

lead to a significant increase in the roughness factor. The roughness factor values based on the electrode capacitance calculated at a frequency of 1 kHz are shown in Table 4.

As can be seen from Table 4, in the process of cathodic polarization the real surface area increased from cycle to cycle, which was accompanied by an almost twofold increase in the roughness factor. This led to an increase in the cathode current recorded in each cycle at a potential of -0.14 V. If the cathode current density is divided by the value f_r , then the normalized current density is obtained. Taking into account the roughness factor, the cathode current increased slightly from cycle to cycle. An increase in the normalized current density indicates that during cathodic polarization not only the surface roughness increased, but also the state of the surface changed: the chemical composition, structure of the surface layer and, consequently, the catalytic activity.

For the performance of measurements on Ni-P coatings with 6.9 and 8.0% P based on the data shown in the Table 3, a potential of -0.15 V was chosen. At this potential, the roughness factor increased from cycle to cycle (Table 4). The normalized current density also increased slightly with cathodic polarization.

Coatings with a phosphorus content of 6.9 wt. % in the process of cathodic polarization increased their activity in the HER, but the effects described above were manifested to a lesser extent. The roughness factor of these coatings was noticeably lower than that of coatings with a phosphorus content of 4.8%. It weakly changed

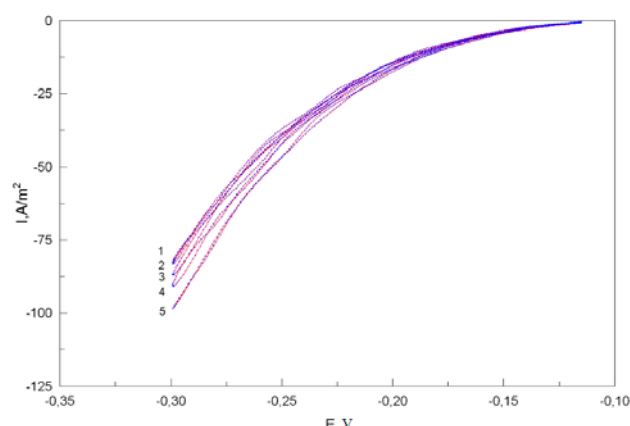


Fig. 5. Cyclic voltammograms of Ni-P coating (8.0 wt. % P) in 0.5 M H_2SO_4 solution. Sweep rate of $2 \cdot 10^{-4}$ V/s

in the indicated potential range (Table 3). This further supports the conclusion that coatings with a phosphorus content of 6.9% were less susceptible to cathodic activation.

Increase in phosphorus content to 8.0 wt. % significantly affected the cathodic behavior of Ni-P coatings. The registration of five successive potential sweep cycles caused a slight increase in the cathodic current density (Fig. 5). This indicates that Ni-P coatings with a given phosphorus content were least susceptible to cathodic activation.

The roughness factors of coatings with a phosphorus content of 8.0% were several times lower than the roughness factors of coatings with a lower phosphorus content and slightly changed with potential (Table 3). Preliminary cathodic polarization at $E = -0.3$ V did not lead to a significant increase in the cathodic current density from cycle to cycle, i.e., the cathodic activation of Ni-P coatings in this case was insignificant. The roughness factor of the surface of Ni-P coatings varied slightly from cycle to cycle of measurements. Changes in the normalized cathode current density from cycle to cycle did not exceed 10% (Table 4).

Based on cathode currents, recorded at various potentials before each impedance measurement (holding for 20 min), stationary polarization curves were obtained. Since quite high values of cathode currents were achieved, a correction was made for the ohmic drop when constructing the cathode curves. Solution resistance R_s between the working electrode and Luggin capillary tip in 0.5 M H_2SO_4 solution was obtained based on impedance measurements. Polarization curves constructed taking into account the correction are presented in Fig. 6a. From the obtained polarization curves, the coefficients of the Tafel equation were calculated (Table 5).

Table 5. Coefficients of the Tafel equation calculated based on stationary polarization curves taking into account correction for ohmic drop

Phosphorus content in coatings, wt. %	Coefficients in Tafel equation			
	a, B	a^*, B	b, B	b^*, B
4.8	0.25	0.39	0.058	0.058
6.9	0.29	0.38	0.060	0.060
8.0	0.32	0.37	0.063	0.063

a^* , b^* are the coefficients in the Tafel equation with regard to the roughness factor

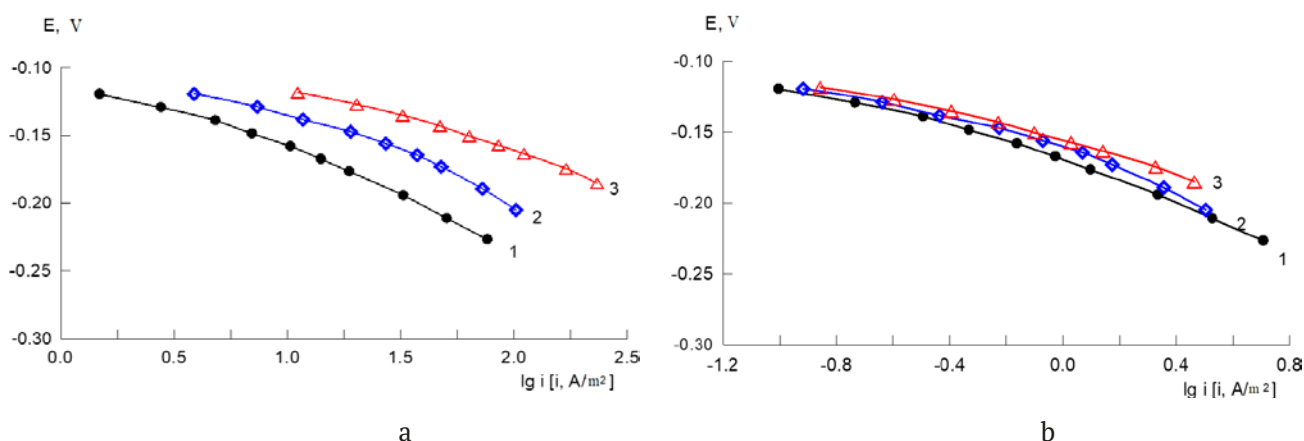


Fig. 6. Polarization curves of Ni-P coatings, plotted taking into account corrections for ohmic losses: a – based on the geometric surface area; b – based on the real surface area. Phosphorus content in coatings, wt.%: 1: 8.0; 2: 6.9; 3: 4.8

Since coatings obtained at different pH values of the electroless nickel plating solution after cathodic polarization were characterized by different roughness factor, their activities were compared taking into account this factor (Fig. 6b). The resulting curves differ slightly by Tafel slopes, but were located close to each other. At the same potentials, the normalized cathode currents for coatings with maximum and minimum phosphorus contents differ by not more than 20%, while without taking into account the roughness factor, the cathode currents differed by more than an order of magnitude (Fig. 6a). When taking into account the roughness factor for all studied phosphorus contents in coatings, close values of the coefficient a of Tafel equation were obtained (Table 5). At the same time, a decrease in phosphorus content in coatings led to a slight decrease in the coefficient b . Some difference in the polarization curves, which persisted even after dividing the current by f_r (Fig. 6b), was probably due to the fact that during cathodic activation of the electrodes, the increase in current was somewhat faster than the increase in the roughness factor, and this effect was more pronounced for coatings with 4.8 and 6.9% phosphorus (Table 3).

4. Conclusions

The high activity of Ni-P coatings in HER is due to the fact that during cathodic polarization, additional activation of the surface occurs as a result of the dissolution of the surface layer of the coating, the removal of phosphorus from

its surface layer and the development of the electrode surface. Out of the studied coatings, coatings containing 4.8% phosphorus were most prone to cathodic activation. Coatings with a phosphorus content of 8.0% were least prone to cathodic activation. The similar electrochemical activity of the studied coatings (taking into account the roughness factor) in HER indicates that, as a result of cathodic polarization, the composition of the thin surface layer on which the cathodic reaction occurs is approximately the same, regardless of the initial phosphorus content. The high activity of Ni-P coatings is also evidenced by the low coefficients of the Tafel equation.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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